

Quantum Mechanics

A New Introduction

Kenichi Konishi & Giampiero Paffuti

QUANTUM MECHANICS



C-6010
0413
K82

Quantum Mechanics

A New Introduction

Kenichi Konishi and Giampiero Paffuti



OXFORD
UNIVERSITY PRESS



3 1996 9668 7

OXFORD

UNIVERSITY PRESS

Great Clarendon Street, Oxford OX2 6DP

Oxford University Press is a department of the University of Oxford.
It furthers the University's objective of excellence in research, scholarship,
and education by publishing worldwide in

Oxford New York

Auckland Cape Town Dar es Salaam Hong Kong Karachi
Kuala Lumpur Madrid Melbourne Mexico City Nairobi
New Delhi Shanghai Taipei Toronto

With offices in

Argentina Austria Brazil Chile Czech Republic France Greece
Guatemala Hungary Italy Japan Poland Portugal Singapore
South Korea Switzerland Thailand Turkey Ukraine Vietnam

Oxford is a registered trade mark of Oxford University Press
in the UK and in certain other countries

Published in the United States
by Oxford University Press Inc., New York

© Kenichi Konishi and Giampiero Paffuti 2009

The moral rights of the authors have been asserted
Database right Oxford University Press (maker)

First published 2009

All rights reserved. No part of this publication may be reproduced,
stored in a retrieval system, or transmitted, in any form or by any means,
without the prior permission in writing of Oxford University Press,
or as expressly permitted by law, or under terms agreed with the appropriate
reprographics rights organization. Enquiries concerning reproduction
outside the scope of the above should be sent to the Rights Department,
Oxford University Press, at the address above

You must not circulate this book in any other binding or cover
and you must impose the same condition on any acquirer

British Library Cataloguing in Publication Data

Data available

Library of Congress Cataloging in Publication Data

Data available

Printed in Great Britain
on acid-free paper by
CPI Antony Rowe, Chippenham, Wiltshire

ISBN 978-0-19-956026-4 (Hbk.)

ISBN 978-0-19-956027-1 (Pbk.)

10 9 8 7 6 5 4 3 2 1

Preface

A student's first encounter with quantum mechanics could be a traumatic one. Instead of the solid differential equation with respect to time (t) which is Newton's classical equation of motion, with its inevitable consequences, she or he learns that the new mechanics predicts as a rule only certain probabilities (!), and that electrons behave like a sort of wave, a bizarre notion—but an empirical fact.¹

When the student makes some progress in her or his study, however, she (he) will realize that, after all, things are not that bad: the fundamental equation of the new mechanics—the Schrödinger equation—is a well-defined, perfectly respectable linear differential equation in t , and when left alone, the microscopic system evolves in a rigorously deterministic fashion. Not only that, but due to the quantization of finite motions, and intimately related to this, to the existence of a new fundamental constant of Nature, the Planck constant, \hbar , quantum mechanics provides a much sharper (and sometimes, far simpler) explanation of the properties of atoms than does classical mechanics. For instance, all atoms of the same kind, in their normal state, have rigorously identical properties. This fact is fundamental, for instance, to the regular structures, and in the working, of the macroscopic world (solids, crystals, biological phenomena, etc). The advantage of the new mechanics over the classical one is, of course, not limited to atoms. There are many phenomena in our daily life, such as electrical conduction, the laser, electronics, quantum optics, and all other related contemporary technologies, which require quantum mechanics for a proper understanding.

Later on in her or his study, the student might find out that physicists today are debating the validity of the standard model predictions sometimes to the *eleventh* digit, for instance concerning the anomalous magnetic moment of the muon (a kind of heavy electron). Of course, here we are comparing a particular model of Nature with experiments; however, the standard model of fundamental interactions—quantum chromodynamics for strong interactions and the Glashow–Weinberg–Salam theory of electroweak interactions—are all based on *relativistic quantum mechanics*. In atomic physics, the agreement between theory and experiment can be equally good and sometimes even more impressive. All this, finally, will convince her (him) that we are indeed dealing with one of the most precise and perhaps most elegant theories ever known in physics.

One day she or he might become a researcher or a teacher, and may start giving a course on quantum mechanics. Perhaps, after many years,

¹The background picture on the front-cover page represents electron wave ripples, formed by 50 kV electron beams going through a collodion thin film with tiny holes. The magnification is such that the full page width corresponds to about 0.6 microns. (Courtesy of Dr. Akira Tonomura, Hitachi Advanced Research Laboratory, Saitama, Japan.)

she (he) will continue to marvel at the simplicity and beauty of quantum mechanics, and at the same time its subtle and far-reaching consequences.

One of the main aims of this book is to try to convey this sense of wonder to young students who are starting to appreciate the beauty of physics.

This book is, in fact, meant to be an introductory textbook on quantum mechanics: it should be adequate for those who are learning it for the first time, as well as for slightly more advanced students. Standard courses on classical physics, including classical mechanics, electromagnetism, statistical mechanics and thermodynamics, plus basic mathematics, should provide a sufficient background.

At the same time, however, we hope that this book, with its many examples of solved problems, and the diverse subjects discussed, will be a useful reference tool for more advanced students, active researchers and teachers alike.

Let us illustrate some of the innovative features of this book. We took great pains to try to present quantum mechanics pedagogically, and at the same time with as much logical clarity and organization as possible. Concepts and methods are introduced gradually, and each of them is elaborated better and more precisely as the pages go on. We start, in fact, from the very basic concepts illustrated by elementary applications, and move on to more structural issues such as symmetry, statistics, and formal aspects of quantum mechanics, and then explore several standard approximation methods. Various applications of physical interest are then discussed, taking full advantage of the artillery we have armed ourselves with.

As far as the content goes, for the most part, it is fairly standard, even though some of the discussions in the main text, e.g. in Chapter 12 (systems with general time-dependent Hamiltonians), in Chapter 13 (metastable states), and in Chapter 15 (atoms), and several topics treated in Supplements (Chapter 20), may often not be found in a standard textbook.

At the end of each chapter, there are a number of problems to be solved analytically, as well as some others to be solved by numerical methods. The solutions to both types of problems are provided in an accompanying CD, in the form of PDF files (analytical problems) or in the form of Mathematica notebooks (there are 88 of these). The latter contain self-explanatory expositions of the solutions proposed, as well as an elementary guide to the Mathematica commands used, so that they should be easily usable even by those who are seeing a Mathematica program for the first time. The reader is encouraged to run the program, enjoy observing how the wave functions evolve, for example, modify and extend the problems as she (he) pleases, try to improve the precision of the calculation, etc. (Here are practical tips for the beginner: first, carefully read the *ReadmeFirst* file before starting; second, make a copy of each *nb* file before proceeding, and keep the original intact. Use a copy, when actually running the program, and making modifications

and extensions.)

In some cases the analysis is pushed a little deeper into the heart of the problem than is ordinarily done in a quantum mechanics textbook (such as the problem of the divergences of perturbation series and resummation; the study of metastable systems; concrete determination of atomic spectra for general elements, etc.), but always in a concrete, physical fashion, never going too much into mathematics.

All in all, this is meant to be a contemporary, but at the same time relatively self-contained and comprehensive, textbook on quantum mechanics.

The book is organized as follows. Part I is an elementary introduction to the basics of quantum mechanics. Together with some initial sections on perturbation theory and variational methods in Part II, Part I could correspond to standard material for an introductory semester course on quantum mechanics in most universities. Part II is dedicated to the three standard methods of approximation, perturbation theory, the variational method, and the semiclassical approximation, through which the concepts in the theory are further developed and the range of applicability vastly increased. In Part III the formalism and methods of analyses developed are applied to various physical situations, from general time-dependent Hamiltonians, general discussions of metastable systems, the motion of electrically charged particles in electromagnetic fields, atoms, the scattering problem, atomic nuclei, and elementary particles.

Part IV is dedicated to two fundamental issues of a conceptual nature: quantum entanglement and the measurement problems.

Part V—the Supplements—is a collection of discussions of various natures, ranging from a review of useful formulas and tables, to some advanced topics, technical issues, and mathematical appendices. They are independent of each other, there is no ordering among them, and many are even independent of the main text, so that each of them can be read at leisure in a convenient moment for each reader.

The accompanying CD, as already anticipated, contains the Mathematica notebooks and PDF files in which the problems proposed at the end of each chapter are solved and discussed. The subfiles for each chapter contain all the notebooks of that chapter, accompanied by a file called Guide-to-NB.nb. In this file a list of all the Mathematica notebooks of that chapter is given, as well as a brief description of each notebook. All analyses have been done by using **Mathematica 6**, Wolfram Research, and tested with **Mathematica 7**, which has just come out.

For updates and corrections, consult our webpages:

<http://www.df.unipi.it/~konishi>
<http://www.df.unipi.it/~paffuti>

We are grateful to Mark Seymour of OUP for his brave attempt at polishing our English and for his invaluable help in improving the look of the whole book. Of course, the responsibility for any errors in the text or formulas, or for any misleading expressions, which may undoubtedly still remain or might have been introduced during the course of corrections,

is ours and ours only. Thanks are also due to Charlotte Green of OUP for her crisp approach to editorial help, and to Sonke Adlung, the senior physics editor, for his admirable patience during this book's long period of gestation.

Our hearty gratitude goes to our friends and colleagues who helped us at various moments and in various—small and big—ways. A short list includes: A. Bonaccorso, D. M. Brink, P. Calabrese, P. Cecchi, R. Collina, E. D'Emilio, A. Di Giacomo, G. Dunne, T. Elze, M. Fukugita, C. Giannessi, V. Gracco, R. Guida, R. Jackiw, F. Maccarrone, G. Marchesini, M. Matone, P. Menotti, M. Mintchev, F. M. Miranda, G. Morchio, E. Onofri, L. Picasso, M. Rocca, S. Shore, A. Toncelli, M. Tonelli, A. Tonomura, P. Truini, A. Vainshtein, and G. Veneziano.

A final message to all of you (especially to the young):

Read and Enjoy!

Pisa, February 2009

K. Konishi and G. Paffuti

Contents

I Basic quantum mechanics	1
1 Introduction	5
1.1 The quantum behavior of the electron	5
1.1.1 Diffraction and interference—visualizing the quantum world	5
1.1.2 The stability and identity of atoms	6
1.1.3 Tunnel effects	8
1.2 The birth of quantum mechanics	9
1.2.1 From the theory of specific heat to Planck's formula	9
1.2.2 The photoelectric effect	14
1.2.3 Bohr's atomic model	15
1.2.4 The Bohr–Sommerfeld quantization condition; de Broglie's wave	17
Further reading	18
Guide to the Supplements	18
Problems	19
Numerical analyses	19
2 Quantum mechanical laws	21
2.1 Quantum states	21
2.1.1 Composite systems	24
2.1.2 Photon polarization and the statistical nature of quantum mechanics	24
2.2 The uncertainty principle	26
2.3 The fundamental postulate	29
2.3.1 The projection operator and state vector reduction	31
2.3.2 Hermitian operators	32
2.3.3 Products of operators, commutators, and compatible observables	33
2.3.4 The position operator, the momentum operator, fundamental commutators, and Heisenberg's relation	35
2.3.5 Heisenberg's relations	36
2.4 The Schrödinger equation	37
2.4.1 More about the Schrödinger equations	38
2.4.2 The Heisenberg picture	40
2.5 The continuous spectrum	40
2.5.1 The delta function	41
2.5.2 Orthogonality	43

2.5.3	The position and momentum eigenstates; momentum as a translation operator	43
2.6	Completeness	45
	Problems	47
	Numerical analyses	48
3	The Schrödinger equation	49
3.1	General properties	49
3.1.1	Boundary conditions	49
3.1.2	Ehrenfest's theorem	50
3.1.3	Current density and conservation of probability	51
3.1.4	The virial and Feynman–Hellman theorems	52
3.2	One-dimensional systems	53
3.2.1	The free particle	54
3.2.2	Topologically nontrivial space	55
3.2.3	Special properties of one-dimensional Schrödinger equations	56
3.3	Potential wells	58
3.3.1	Infinitely deep wells (walls)	58
3.3.2	The finite square well	59
3.3.3	An application	61
3.4	The harmonic oscillator	63
3.4.1	The wave function and Hermite polynomials	63
3.4.2	Creation and annihilation operators	67
3.5	Scattering problems and the tunnel effect	71
3.5.1	The potential barrier and the tunnel effect	71
3.5.2	The delta function potential	74
3.5.3	General aspects of the scattering problem	78
3.6	Periodic potentials	80
3.6.1	The band structure of the energy spectrum	80
3.6.2	Analysis	82
	Guide to the Supplements	84
	Problems	85
	Numerical analyses	87
4	Angular momentum	89
4.1	Commutation relations	89
4.2	Space rotations	91
4.3	Quantization	92
4.4	The Stern–Gerlach experiment	95
4.5	Spherical harmonics	96
4.6	Matrix elements of \mathbf{J}	98
4.6.1	Spin- $\frac{1}{2}$ and Pauli matrices	100
4.7	The composition rule	101
4.7.1	The Clebsch–Gordan coefficients	104
4.8	Spin	105
4.8.1	Rotation matrices for spin $\frac{1}{2}$	107
	Guide to the Supplements	108

Problems	109
5 Symmetry and statistics	111
5.1 Symmetries in Nature	111
5.2 Symmetries in quantum mechanics	113
5.2.1 The ground state and symmetry	116
5.2.2 Parity (\mathcal{P})	117
5.2.3 Time reversal	121
5.2.4 The Galilean transformation	123
5.2.5 The Wigner–Eckart theorem	125
5.3 Identical particles: Bose–Einstein and Fermi–Dirac statistics	127
5.3.1 Identical bosons	130
5.3.2 Identical fermions and Pauli's exclusion principle	132
Guide to the Supplements	133
Problems	134
6 Three-dimensional problems	135
6.1 Simple three-dimensional systems	135
6.1.1 Reduced mass	135
6.1.2 Motion in a spherically symmetric potential	136
6.1.3 Spherical waves	137
6.2 Bound states in potential wells	140
6.3 The three-dimensional oscillator	141
6.4 The hydrogen atom	143
Guide to the Supplements	148
Problems	149
Numerical analyses	150
7 Some finer points of quantum mechanics	151
7.1 Representations	151
7.1.1 Coordinate and momentum representations	152
7.2 States and operators	155
7.2.1 Bra and ket; abstract Hilbert space	155
7.3 Unbounded operators	158
7.3.1 Self-adjoint operators	160
7.4 Unitary transformations	167
7.5 The Heisenberg picture	169
7.5.1 The harmonic oscillator in the Heisenberg picture	171
7.6 The uncertainty principle	172
7.7 Mixed states and the density matrix	173
7.7.1 Photon polarization	176
7.8 Quantization in general coordinates	178
Further reading	182
Guide to the Supplements	182
Problems	182
8 Path integrals	183
8.1 Green functions	183

8.2 Path integrals	186
8.2.1 Derivation	186
8.2.2 Mode expansion	190
8.2.3 Feynman graphs	192
8.2.4 Back to ordinary (Minkowski) time	197
8.2.5 Tunnel effects and instantons	198
Further reading	201
Numerical analyses	202
II Approximation methods	203
9 Perturbation theory	207
9.1 Time-independent perturbations	207
9.1.1 Degenerate levels	212
9.1.2 The Stark effect on the $n = 2$ level of the hydrogen atom	214
9.1.3 Dipole interactions and polarizability	217
9.2 Quantum transitions	219
9.2.1 Perturbation lasting for a finite interval	221
9.2.2 Periodic perturbation	223
9.2.3 Transitions in a discrete spectrum	223
9.2.4 Resonant oscillation between two levels	225
9.3 Transitions in the continuum	226
9.3.1 State density	228
9.4 Decays	228
9.5 Electromagnetic transitions	233
9.5.1 The dipole approximation	234
9.5.2 Absorption of radiation	237
9.5.3 Induced (or stimulated) emission	238
9.5.4 Spontaneous emission	239
9.6 The Einstein coefficients	240
Guide to the Supplements	242
Problems	242
Numerical analyses	244
10 Variational methods	245
10.1 The variational principle	245
10.1.1 Lower limits	247
10.1.2 Truncated Hilbert space	249
10.2 Simple applications	250
10.2.1 The harmonic oscillator	250
10.2.2 Helium: an elementary variational calculation	252
10.2.3 The virial theorem	254
10.3 The ground state of the helium	255
Guide to the Supplements	261
Problems	261
Numerical analyses	262

11 The semi-classical approximation	265
11.1 The WKB approximation	265
11.1.1 Connection formulas	268
11.2 The Bohr-Sommerfeld quantization condition	271
11.2.1 Counting the quantum states	273
11.2.2 Potentials defined for $x > 0$ only	275
11.2.3 On the meaning of the limit $\hbar \rightarrow 0$	276
11.2.4 Angular variables	276
11.2.5 Radial equations	279
11.2.6 Examples	282
11.3 The tunnel effect	283
11.3.1 The double well	285
11.3.2 The semi-classical treatment of decay processes	289
11.3.3 The Gamow-Siegert theory	292
11.4 Phase shift	295
Further reading	300
Guide to the Supplements	300
Problems	301
Numerical analyses	302
 III Applications	 303
12 Time evolution	307
12.1 General features of time evolution	307
12.2 Time-dependent unitary transformations	309
12.3 Adiabatic processes	311
12.3.1 The Landau-Zener transition	313
12.3.2 The impulse approximation	315
12.3.3 The Berry phase	316
12.3.4 Examples	318
12.4 Some nontrivial systems	320
12.4.1 A particle within moving walls	320
12.4.2 Resonant oscillations	324
12.4.3 A particle encircling a solenoid	327
12.4.4 A ring with a defect	328
12.5 The cyclic harmonic oscillator: a theorem	331
12.5.1 Inverse linear variation of the frequency	335
12.5.2 The Planck distribution inside an oscillating cavity	336
12.5.3 General power-dependent frequencies	338
12.5.4 Exponential dependence	339
12.5.5 Creation and annihilation operators; coupled oscillators	340
Guide to the Supplements	341
Problems	341
Numerical analyses	342
 13 Metastable states	 343

13.1	Green functions	343
13.1.1	Analytic properties of the resolvent	345
13.1.2	Free particles	349
13.1.3	The free Green function in general dimensions	351
13.1.4	Expansion in powers of H_I	352
13.2	Metastable states	356
13.2.1	Formulation of the problem	356
13.2.2	The width of a metastable state; the mean half-lifetime	358
13.2.3	Formal treatment	361
13.3	Examples	368
13.3.1	Discrete–continuum coupling	368
13.4	Complex scale transformations	370
13.4.1	Analytic continuation	372
13.5	Applications and examples	374
13.5.1	Resonances in helium	375
13.5.2	The potential $V_0 r^2 e^{-r}$	375
13.5.3	The unbounded potential; the Lo Surdo–Stark effect	376
	Further reading	379
	Problems	379
	Numerical analyses	379
14	Electromagnetic interactions	381
14.1	The charged particle in an electromagnetic field	381
14.1.1	Classical particles	381
14.1.2	Quantum particles in electromagnetic fields	383
14.1.3	Dipole and quadrupole interactions	385
14.1.4	Magnetic interactions	388
14.1.5	Relativistic corrections: LS coupling	388
14.1.6	Hyperfine interactions	390
14.2	The Aharonov–Bohm effect	392
14.2.1	Superconductors	395
14.3	The Landau levels	397
14.3.1	The quantum Hall effect	399
14.4	Magnetic monopoles	401
	Guide to the Supplements	404
	Problems	404
	Numerical analyses	404
15	Atoms	405
15.1	Electronic configurations	405
15.1.1	The ionization potential	408
15.1.2	The spectrum of alkali metals	410
15.1.3	X rays	410
15.2	The Hartree approximation	412
15.2.1	Self-consistent fields and the variational principle	415
15.2.2	Some results	417
15.3	Multiplets	418

15.3.1 Structure of the multiplets	419
15.4 Slater determinants	424
15.5 The Hartree–Fock approximation	427
15.5.1 Examples	430
15.6 Spin-orbit interactions	433
15.6.1 The hydrogen atom	436
15.7 Atoms in external electric fields	438
15.7.1 Dipole interaction and polarizability	438
15.7.2 Quadrupole interactions	442
15.8 The Zeeman effect	443
15.8.1 The Zeeman effect in quantum mechanics	444
Further reading	450
Guide to the Supplements	451
Problems	451
Numerical analyses	452
16 Elastic scattering theory	453
16.1 The cross section	453
16.2 Partial wave expansion	457
16.2.1 The semi-classical limit	459
16.3 The Lippman–Schwinger equation	460
16.4 The Born approximation	461
16.5 The eikonal approximation	463
16.6 Low-energy scattering	465
16.7 Coulomb scattering: Rutherford's formula	468
16.7.1 Scattering of identical particles	473
Further reading	474
Guide to the Supplements	475
Problems	476
Numerical analyses	476
17 Atomic nuclei and elementary particles	477
17.1 Atomic nuclei	477
17.1.1 General features	477
17.1.2 Isospin	478
17.1.3 Nuclear forces, pion exchange, and the Yukawa potential	480
17.1.4 Radioactivity	482
17.1.5 The deuteron and two-nucleon forces	483
17.2 Elementary particles: the need for relativistic quantum field theories	485
17.2.1 The Klein–Gordon and Dirac equations	487
17.2.2 Quantization of the free Klein–Gordon fields	490
17.2.3 Quantization of the free Dirac fields and the spin–statistics connection	491
17.2.4 Causality and locality	492
17.2.5 Self-interacting scalar fields	494
17.2.6 Non-Abelian gauge theories: the Standard Model	495

Further reading	496
IV Entanglement and Measurement	499
18 Quantum entanglement	503
18.1 The EPRB <i>Gedankenexperiment</i> and quantum entanglement	503
18.2 Aspect's experiment	508
18.3 Entanglement with more than two particles	511
18.4 Factorization versus entanglement	512
18.5 A measure of entanglement: entropy	514
Further reading	516
19 Probability and measurement	517
19.1 The probabilistic nature of quantum mechanics	517
19.2 Measurement and state preparation: from PVM to POVM	519
19.3 Measurement “problems”	521
19.3.1 The EPR “paradox”	522
19.3.2 Measurement as a physical process: decoherence and the classical limit	525
19.3.3 Schrödinger’s cat	527
19.3.4 The fundamental postulate versus Schrödinger’s equation	529
19.3.5 Is quantum mechanics exact?	530
19.3.6 Cosmology and quantum mechanics	531
19.4 Hidden-variable theories	532
19.4.1 Bell’s inequalities	532
19.4.2 The Kochen–Specker theorem	535
19.4.3 “Quantum non-locality” versus “locally causal theories” or “local realism”	538
Further reading	539
Guide to the Supplements	539
V Supplements	541
20 Supplements for Part I	545
20.1 Classical mechanics	545
20.1.1 The Lagrangian formalism	545
20.1.2 The Hamiltonian (canonical) formalism	547
20.1.3 Poisson brackets	549
20.1.4 Canonical transformations	550
20.1.5 The Hamilton–Jacobi equation	552
20.1.6 Adiabatic invariants	552
20.1.7 The virial theorem	554
20.2 The Hamiltonian of electromagnetic radiation field in the vacuum	554

20.3 Orthogonality and completeness in a system with a one-dimensional delta function potential	556
20.3.1 Orthogonality	557
20.3.2 Completeness	558
20.4 The S matrix; the wave packet description of scattering	560
20.4.1 The wave packet description	560
20.5 Legendre polynomials	564
20.6 Groups and representations	566
20.6.1 Group axioms; some examples	566
20.6.2 Group representations	568
20.6.3 Lie groups and Lie algebras	570
20.6.4 The $U(N)$ group and the quarks	573
20.7 Formulas for angular momentum	575
20.8 Young tableaux	581
20.9 N -particle matrix elements	584
20.10 The Fock representation	586
20.10.1 Bosons	586
20.10.2 Fermions	588
20.11 Second quantization	589
20.12 Supersymmetry in quantum mechanics	590
20.13 Two- and three-dimensional delta function potentials	595
20.13.1 Bound states	597
20.13.2 Self-adjoint extensions	598
20.13.3 The two-dimensional delta-function potential: a quantum anomaly	599
20.14 Superselection rules	601
20.15 Quantum representations	604
20.15.1 Weyl's commutation relations	605
20.15.2 Von Neumann's theorem	605
20.15.3 Angular variables	606
20.15.4 Canonical transformations	608
20.15.5 Self-adjoint extensions	610
20.16 Gaussian integrals and Feynman graphs	611
21 Supplements for Part II	615
21.1 Supplements on perturbation theory	615
21.1.1 Change of boundary conditions	615
21.1.2 Two-level systems	616
21.1.3 Van der Waals interactions	618
21.1.4 The Dalgarno-Lewis method	619
21.2 The fine structure of the hydrogen atom	621
21.2.1 A semi-classical model for the Lamb shift	626
21.3 Hydrogen hyperfine interactions	630
21.4 Divergences of perturbative series	633
21.4.1 Perturbative series at large orders: the anharmonic oscillator	633
21.4.2 The origin of the divergence	635
21.4.3 The analyticity domain	636

21.4.4 Asymptotic series	638
21.4.5 The dispersion relation	642
21.4.6 The perturbative–variational approach	645
21.5 The semi-classical approximation in general systems	648
21.5.1 Introduction	648
21.5.2 Keller quantization	650
21.5.3 Integrable systems	653
21.5.4 Examples	654
21.5.5 Caustics	655
21.5.6 The KAM theorem and quantization	655
22 Supplements for Part III	657
22.1 The $K^0-\bar{K}^0$ system and CP violation	657
22.2 Level density	661
22.2.1 The free particle	665
22.2.2 $g(E)$ and the partition function	666
22.2.3 $g(E)$ and short-distance behavior	669
22.2.4 Level density and scattering	671
22.2.5 The stabilization method	673
22.3 Thomas precession	674
22.4 Relativistic corrections in an external field	676
22.5 The Hamiltonian for interacting charged particles	678
22.5.1 The interaction potentials	679
22.5.2 Spin-dependent interactions	681
22.5.3 The quantum Hamiltonian	682
22.5.4 Electron–electron interactions	682
22.5.5 Electron–nucleus interactions	683
22.5.6 The $1/M$ corrections	686
22.6 Quantization of electromagnetic fields	687
22.6.1 Matrix elements	689
22.7 Atoms	692
22.7.1 The Thomas–Fermi approximation	693
22.7.2 The Hartree approximation	700
22.7.3 Slater determinants and matrix elements	703
22.7.4 Hamiltonians for closed shells	707
22.7.5 Mean energy	712
22.7.6 Hamiltonians for incomplete shells	712
22.7.7 Eigenvalues of H	716
22.7.8 The elementary theory of multiplets	717
22.7.9 The Hartree–Fock equations	719
22.7.10 The role of Lagrange multipliers	721
22.7.11 Koopman’s theorem	723
22.8 H_2^+	726
22.9 The Gross–Pitaevski equation	729
22.10 The semi-classical scattering amplitude	731
22.10.1 Caustics and rainbows	732
23 Supplements for Part IV	735

23.1 Speakable and unspeakable in quantum mechanics	735
23.1.1 Bell's toy model for hidden variables	735
23.1.2 Bohm's pilot waves	736
23.1.3 The many-worlds interpretation	739
23.1.4 Spontaneous wave function collapse	740
24 Mathematical appendices and tables	743
24.1 Mathematical appendices	743
24.1.1 Laplace's method	743
24.1.2 The saddle-point method	744
24.1.3 Airy functions	748
References	765
Index	775

Part I

Basic quantum mechanics

Part I of this book introduces the basic concepts of quantum mechanics, from the fundamental laws and the main postulates of quantum mechanics, simple applications in one-dimensional systems, and angular momentum, to simple three-dimensional systems and some finer points of the quantum mechanical laws. Feynman's path-integral formulation of quantum mechanics is introduced.

1

Introduction

Physical phenomena in the microscopic world are extraordinary and often appear even paradoxical from the viewpoint of our daily experiences. A closer look, however, shows that they possess a simple and elegant logic of their own. By way of introduction to this entire volume on quantum mechanics, let us discuss a few such features, taking the example of the electron. We then briefly review the historical development which led to the discovery of quantum mechanics.

1.1 The quantum behavior of the electron

The examples chosen are the diffraction and interference, the stability and identity of atoms (of the same kind), and the tunneling phenomenon.

1.1.1 Diffraction and interference—visualizing the quantum world

Two of the most interesting, “non-classical”, behaviors of the electron are diffraction and interference, both of which are typical features of a wave. As is well known, light is a wave, a propagating wave of electromagnetic fields, and as such, exhibits all phenomena typical of waves, such as interference and diffraction. Consider as an example the famous double-slit experiment à la Young (1801). The typical interference fringes between the light beams which go through two different slits look like Fig. 1.1. If the distance between the two slits, the distance between the double slits and the screen, and the vertical position on the screen are d , L , and x , respectively (see Fig. 1.2), the diffraction angle is approximately given by $\theta \sim x/L$ (assuming $d \ll L; x \ll L$), so the difference in the path lengths of the two rays is

$$\Delta d \simeq d \sin \theta \simeq d\theta \simeq \frac{dx}{L}.$$

Thus for light of wavelength λ , the condition for constructive or destructive interference is

$$\frac{\Delta d}{\lambda} = n, \quad \text{or} \quad n + \frac{1}{2}, \quad n = 0, 1, 2, \dots,$$

respectively.

In the experiment of Fig. 1.1, $L/d \sim 10^3$; $\lambda \sim 10^3 \text{ \AA} = 10^{-5} \text{ cm}$, so the inter-fringe gap is of the order of 0.1 mm.

1.1 The quantum behavior of the electron	5
1.2 The birth of quantum mechanics	9
Further reading	18
Guide to the Supplements	18
Problems	19
Numerical analyses	19



Fig. 1.1 A typical interference fringe in Young's experiment

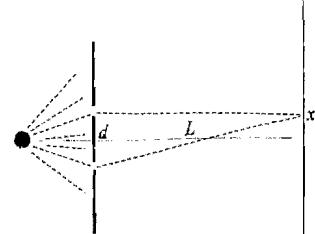


Fig. 1.2 A schematic view of Young's experiment.

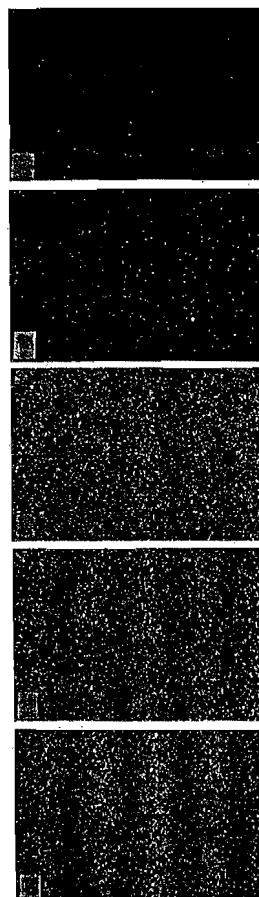


Fig. 1.3 Interference with single electrons

¹In fact, such an experiment was performed already in [Taylor (1909)].

An analogous experiment using an *electron beam* was performed for the first time only recently, in 1989! Note that this kind of experiments used to be called a “Gedankenexperiment”, that is, a “thought” or “hypothetical” experiment. They no longer are. The figures taken from an article by Tonomura, et al. [Tonomura (1989)] display an extraordinary resemblance to the preceding Fig. 1.1 of Young’s experiment. It is true that there *are* some differences. The first is in the scale. In the case of visible light, the spacing between the interference fringes is of the order of millimeters, while it is of the order of 10^{-4} mm in the experiment with the electron beam. But such a difference, a quantitative and not qualitative one, is not conceptually important, although it reflects considerable technical difficulties for preparing such experiments.

An apparently more important difference is the fact that the electrons are particles (while light is “obviously” a wave) with a definite mass and charge: in fact, the images due to individual electrons are clearly visible in Fig. 1.3. Furthermore, in this experiment, a very weak flux of electrons, $\sim 10^3 \text{ s}^{-1}$ is used. Together with the known average electron velocity, $\sim 0.4c$, this implies that the mean distance between the electrons is about ~ 150 km. On the other hand, the whole experimental apparatus has a size of ~ 1.5 m. Under such circumstances, it is reasonable to assume that the electrons arrive “one by one”, without appreciable interactions among them. The five images refer, respectively, to exposures to 10, 100, 3000, 20 000 and 70 000 electrons.

We arrive at an apparently paradoxical conclusion: an individual electron, clearly an indivisible particle, somehow “sees” both slits and behaves as if it were a wave, and the two wavefronts of a single electron interfere! This property is known as “wave–particle duality”. *It is of fundamental importance that such a duality concerns the properties of an individual electron, and not some mysterious collective behavior of the electrons in the beam.* It is just the way a quantum mechanical particle behaves.

With the technology available today Young’s experiment can be repeated with light of a very reduced intensity, so that the quanta of light—photons—arrive one by one.¹ With hindsight, then, we realize that actually there is no essential difference between Young’s experiment and that of Tonomura, et al. (1989).

It turns out (de Broglie in 1925) that *all* particles in the atomic world (elementary particles, nuclei, atoms, molecules) possess wave–particle duality. More quantitatively, a particle with momentum p behaves in a sense as a wave with wavelength λ , where $\lambda = h/p$. Vice versa, a quantum of light (with wavelength λ) behaves as a particle with momentum $p = h/\lambda$.

1.1.2 The stability and identity of atoms

The second feature concerns the stability and the absolute identity of atoms (of the same kind). Consider for example the hydrogen atom, a bound state of an electron and a proton. The motion of the electron

around the nucleus is described, in classical mechanics, by the equation

$$m\ddot{r} = -\frac{e^2}{r^2} + m r \dot{\theta}^2; \quad r^2 \dot{\theta} = \text{const.}, \quad (1.1)$$

where for simplicity we have assumed a circular motion with radius r . The static Coulomb force is, however, just one of the manifestations of the electromagnetic interactions: a charged particle in an accelerated motion would, according to Maxwell's theory, radiate and lose its energy gradually. An orbit with constant r would not be stable. For an electron with acceleration $\ddot{\mathbf{v}}$, the energy loss per unit interval of time is

$$S = \frac{2 e^2}{3 c^3} (\dot{\mathbf{v}})^2 \quad (\text{erg/s}) \quad (1.2)$$

(see [Landau and Lifshitz (1976 b)]). Let us assume also that the energy loss is so small that the orbit can be assumed to be circular for many cycles. From eqn (1.1) one finds that

$$|\dot{\mathbf{v}}| = \frac{e^2}{mr^2}.$$

Substitution of this into eqn (1.2) yields

$$S = -\frac{dE}{dt} = \frac{2 e^6}{3 m^2 c^3 r^4}$$

for the energy loss per unit time interval. But for circular motion, the virial theorem tells us that

$$E = \frac{1}{2} m v^2 - \frac{e^2}{r} = -\frac{e^2}{2r},$$

so that

$$r^2 \dot{r} = -\frac{4 e^4}{3 m^2 c^3}.$$

Let t_c be the time needed for the complete collapse, $r(t_c) = 0$, assuming that at the beginning the system had the radius of a typical atom, $a \sim 10^{-8}$ cm. Integrating the equation, one gets

$$t_c = \frac{m^2 c^3}{4 e^4} a^3 \simeq 10^{-10} \text{ s},$$

namely, a hydrogen atom would collapse in 10^{-10} s! This is (fortunately) not what happens in Nature.

Even if we allow for the possibility that there could be some unknown reason for which eqn (1.2) does not apply to the atomic world—after all, Maxwell's theory was discovered in the macroscopic world—and ignoring the aforementioned difficulty, there is another, very serious, problem with the “planetary” model of atoms. It lies in the fact that each atom will have a different, quite random radius, depending on how it has been formed (i.e., depending on the initial conditions).

As we shall see below, all periodic motions are actually “quantized”: only a certain discrete set of orbits is allowed. As a consequence, all

the atoms of the same kind, in the normal state (i.e., with the lowest possible energy), have *rigorously identical* properties. Quantization also naturally solves the problem of instability: there is a quantum orbit with minimal possible energy: the electron in such an orbit cannot further irradiate and lose energy, having no lower states to go to.

It is easy to see the reason why eqn (1.1) cannot have a solution with a well-defined, or characteristic, radius, independent of the initial conditions. With only dimensional parameters m and e at our disposal, with dimensions

$$m = [\text{g}]; \quad e = [\text{g}^{1/2} \text{cm}^{3/2} \text{s}^{-1}],$$

it is not possible to form any quantity with the dimension of length. In contrast, in quantum mechanics, there is another constant \hbar , Planck's constant, with a dimension,

$$\text{g} \cdot \text{cm}^2/\text{s} = \text{erg} \cdot \text{s},$$

which will enter dynamical equations. Its numerical value is given by

$$\hbar = 6.626\,068\,96(33) \times 10^{-27} \text{ (erg} \cdot \text{s}).$$

Having three constants m , e , and \hbar at our disposal, it is now possible to form a quantity

$$r_B = \frac{\hbar^2}{4\pi^2 m e^2},$$

which has the dimension of a length, called the Bohr radius. Its numerical value is

$$r_B \simeq 5 \times 10^{-9} \text{ cm}, \quad (1.3)$$

which is quite reasonable as the dimension of an atom.

The absolutely identical intrinsic properties of elementary particles, atoms, or molecules, of the same type, are at the basis of the regularity and stability of macroscopic world (crystals, stars and planets, biological systems, etc.) Without such regularity, biological phenomena which require an exceedingly high precision in the structures at the microscopic level, would not be possible. The simplicity in the microscopic world is in clear contrast, and at the same time in harmony, with the infinite variety of the macroscopic world we live in.

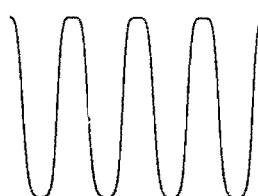


Fig. 1.4 A periodic potential

1.1.3 Tunnel effects

The third example is related to the familiar phenomenon of electrical conduction. In a simplified model, the electrons move in a periodic potential like Fig. 1.4, which is a one-dimensional representation of a metallic crystal lattice. A classical particle with energy less than the barrier height would not be able to pass from one potential well to another, unless the external field were not strong enough to overcome the potential barrier. The electron, a quantum mechanical particle/wave, is able to move freely between the barriers (if its energy lies in certain

"bands" of allowed values), allowing electrical conduction. This is an example of the so-called tunnel effect and is closely related to the wave-particle duality mentioned earlier.

Quantum mechanics describes these and many other phenomena of the microscopic world in a consistent and elegant mathematical formalism.

1.2 The birth of quantum mechanics

Before presenting quantum mechanics itself, however, let us discuss the developments which took place in the years 1900–1925. The efforts involved in trying to solve the difficulties of the classical theory of specific heat and of the so-called black-body radiation, as well as in trying to understand the mysteries of atomic spectral lines, which all eventually led to the formulation of quantum mechanics, make for an extraordinary story of scientific discovery.

1.2.1 From the theory of specific heat to Planck's formula

Let us consider a macroscopic system described by the canonical variables $\{p_i, q_i\}$, $i = 1, \dots, s$. The number of degrees of freedom is large, typically of the order of the Avogadro number, $N_A \simeq 6 \times 10^{23}$. Suppose that such a system is in thermal equilibrium with a heat bath, kept at temperature T . Let $E(q_1, p_1, \dots, q_s, p_s)$ be the energy of the system. According to Boltzmann's theory, the probability that the system is found in the micro states lying in the range $(q_1, q_1 + dq_1)$, $(p_1, p_1 + dp_1)$, \dots , $(p_s, p_s + dp_s)$ is given by the formula

$$P(q_1, \dots, p_s) dq_1 \cdots dp_s = \frac{1}{N} e^{-E(q_1, p_1, \dots, p_s)/kT}, \quad (1.4)$$

where N is the normalization factor. $k = 1.380\,658 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$ is the Boltzmann conversion constant.

The "equipartition law" follows from Boltzmann's law immediately. Namely, for a system described by a Hamiltonian of the form

$$H = \sum_{i=1}^s (\alpha_i p_i^2 + \beta_i q_i^2), \quad (1.5)$$

the mean values of each term of the Hamiltonian turn out to be equal:

$$\langle \alpha_n p_n^2 \rangle = \langle \beta_n q_n^2 \rangle = \frac{1}{2} kT, \quad (\text{indep. of } n),$$

i.e., loosely we can say that each degree of freedom gets an equal share $\frac{1}{2} kT$ of the energy. The classical theory of specific heats is a simple consequence of the equipartition law. Indeed, for ideal monoatomic gas such as the noble gases, $\alpha_i = \frac{1}{2m}$, $\beta_i = 0$, while for diatomic gases such as H_2 , O_2 , etc., the expression for the energy is

$$E = \sum_j E_j; \quad E_j = \frac{(p_{jx}^2 + p_{jy}^2 + p_{jz}^2)}{2m} + \frac{p_\theta^2 + p_\phi^2 / \sin \theta^2}{2I},$$

where the last two terms represent the rotational degrees of freedom (we neglect here the vibrational modes between the two atoms). The total energy for a mole is then

$$U = \frac{3}{2}kTN_A = \frac{3}{2}RT; \quad \text{and} \quad U = \frac{5}{2}kTN_A = \frac{5}{2}RT,$$

respectively, for the monoatomic and diatomic gases, N_A is the Avogadro number, and

$$R = N_A k \simeq 8.31441 \times 10^7 \text{ erg mol}^{-1}\text{K}^{-1} = 1.987 \text{ cal mol}^{-1}\text{K}^{-1}$$

is the gas constant. The specific heat is then given in the two cases by

$$C_V = \frac{\partial U}{\partial T} = \begin{cases} \frac{3}{2}R \simeq 2.98, & \text{monoatomic gases,} \\ \frac{5}{2}R \simeq 4.97, & \text{diatomic gases} \end{cases}$$

(in units of $\text{cal mol}^{-1}\text{K}^{-1}$).

These results are in good agreement with experimental values at room temperature; as the temperature lowers, C_V decreases below the predicted values. For diatomic gases the observed C_V decreases and approaches the value $\frac{3}{2}R$ at around 50 K. Analogous results were found for the specific heat of the solid, which is consistent with the value $C_V = 3R \simeq 5.9 \text{ cal mol}^{-1}\text{K}^{-1}$ (known as the Dulong-Petit law) at room temperature, and tends to zero as the temperature approaches zero.

In all cases, then, it seems that at any given temperature not all of the degrees of freedom get the share $\frac{1}{2}kT$ expected from the equipartition law. As the temperature lowers, more degrees of freedom get frozen and eventually all of the degrees of freedom die out.

In the last decade of the 19th century, the failure of classical physics became more widely acknowledged owing to the problem of *black-body radiation*.

Consider an empty cavity kept at a fixed temperature T . Its interior is filled with electromagnetic radiation, in thermal equilibrium with the heat bath (the wall of the cavity). Now what is the color of the light inside? What is the wavelength and relative intensity of light there? How much heat is needed to increase the temperature of the interior of the cavity by one degree ("the specific heat of the vacuum")?

Classical physics' answer to this problem is as follows. The energy of electromagnetic fields in the vacuum is (see [Landau and Lifshitz (1976 b)]):

$$H = \frac{1}{8\pi} \int_V (\mathbf{E}^2 + \mathbf{H}^2) dv.$$

By introducing the vector potential and imposing an appropriate boundary condition for perfectly reflecting boundary for simplicity of calculation, we find that the above Hamiltonian can be cast in the form

$$H = \sum_{\mathbf{k}} \left(\frac{c^2}{4} \mathbf{p}_{(1)}^2 + \mathbf{k}^2 \mathbf{q}_{(1)}^2 \right) + \sum_{\mathbf{k}} \left(\frac{c^2}{4} \mathbf{p}_{(2)}^2 + \mathbf{k}^2 \mathbf{q}_{(2)}^2 \right),$$

the system is equivalent to two infinite sets of independent harmonic oscillators. By taking the cavity to be of cubic form, each side of length L , the wave numbers k are found to have the discrete values

$$k_x = \frac{\pi n_x}{L}; \quad k_y = \frac{\pi n_y}{L}; \quad k_z = \frac{\pi n_z}{L}; \quad n_x, n_y, n_z = 0, 1, 2, 3, \dots, \infty$$

(see Supplement 20.2). Since this Hamiltonian has the standard form, (1.5), we can apply the equipartition law to compute the total energy: the answer is simply

$$U = f k T, \quad f (= \text{the number of degrees of freedom}) = \infty,$$

and thus

$$U = \infty; \quad C = \frac{\partial U}{\partial T} = \infty.$$

In other words, the energy of electromagnetic radiation inside a cavity kept at a given temperature is predicted to be infinite according to Maxwell's theory. In order to increase the temperature of the interior of the cavity by one degree an infinite amount of heat would be needed. These conclusions are clearly absurd and are in clear contrast to the experience—think of an oven at home which eats up an infinite amount of electricity to warm up by just one degree! Empirically the energy of black-body radiation is known to be given, per unit volume, by

$$U = \sigma T^4; \quad \sigma = 7.64 \times 10^{-15} \text{ erg cm}^{-3} \text{ K}^{-4}, \quad (1.6)$$

a result known as the Stefan-Boltzmann law.

This is the *problem of black-body radiation*.

The cause for this disastrous result is easy to identify: there are an infinite number of high frequency modes—corresponding to arbitrarily large values of n_x, n_y, n_z —each of which claims their “share” of energy kT . The experimental fact indicates that in fact far fewer degrees of freedom are effectively active at any given temperature.

Not all is lost, however. Let us consider the contribution from the modes having a restricted range of frequencies, $(\nu, \nu + \delta\nu)$, instead of computing the total energy

$$U = \int_0^\infty d\nu u(\nu),$$

directly. As $\nu_{(n)} = \frac{|n|c}{2L}$, it follows that

$$dn = \frac{2 L d\nu}{c}.$$

Each oscillation mode corresponds to the set of positive integers $\mathbf{n} = (n_x, n_y, n_z)$: the number of modes having frequencies between ν and $\nu + d\nu$ is given by

$$N(\nu) d\nu = 2 \frac{1}{8} (4 \pi n^2) dn = \frac{8 \pi L^3}{c^3} \nu^2 d\nu.$$

The factor 2 takes into account the two possible polarizations. Applying the equipartition law, one gets for a unit volume and for a unit range of frequency

$$u(\nu)d\nu = kTN(\nu)d\nu = \frac{8\pi kT}{c^3} \nu^2 d\nu. \quad (1.7)$$

This is the classical formula for $u(\nu)$ (the *Rayleigh-Jeans formula*). Experiments show that:

- (1) At any given temperature T , the Rayleigh-Jeans formula agrees well with the experimental data at sufficiently low frequencies.
- (2) The frequency range in which the Rayleigh-Jeans formula is valid widens towards the higher frequencies as T increases (Figure 1.5).
- (3) For any fixed frequency the classical formula is good at sufficiently high T but fails at lower T : we see clearly that the problem is of the same nature as the one which plagued the classical theory of specific heats. As the temperature is lowered, more degrees of freedom get frozen and cease to get the full share of energy.

The first step towards the solution of the problem was taken by Wien in 1893, who observed that the experimental data satisfy the “displacement law” (or “scaling law”)

$$u(\nu) d\nu = \frac{8\pi}{c^3} F\left(\frac{\nu}{T}\right) \nu^3 d\nu, \quad (1.8)$$

with a function F to be determined empirically. Namely, if $u(\nu)$ is known at a temperature, by (1.8) we get the distribution at any other temperature. Formula (1.8) is also consistent with the Stefan-Boltzmann law. In fact the displacement law (1.8) can be theoretically derived from thermodynamics [Tomonaga (1968)].

Even if Wien was not able to determine the functional form of $F(x)$, he was able to find the empirical behavior of $F(x)$, valid at large x ,

$$F(x) \simeq k\beta e^{-\beta x}; \quad \beta = \text{const.},$$

or, by substitution in (1.8), the formula (“Wien’s formula”)

$$u(\nu) d\nu = \frac{8\pi k\beta}{c^3} e^{-\beta\nu/T} \nu^3 d\nu = \frac{8\pi h\nu}{c^3} e^{-h\nu/kT} \nu^2 d\nu, \quad (1.9)$$

where

$$\hbar \equiv k\beta = 6.626 \times 10^{-27} \text{ erg} \cdot \text{s}. \quad (1.10)$$

We then had the classical formula (1.7) good at low frequencies, and Wien’s formula (1.9) valid at high frequencies. It was Planck in 1900 who found the celebrated formula (*the Planck distribution*)

$$u(\nu) d\nu = \frac{8\pi}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1} \nu^2 d\nu, \quad (1.11)$$

which interpolated correctly between the two formulas and which was in agreement with all known experimental data.²

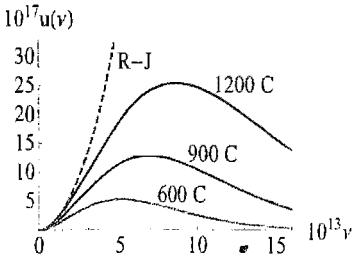


Fig. 1.5 Black-body spectrum. The Rayleigh-Jeans formula for $T = 1200$ C is plotted for comparison.

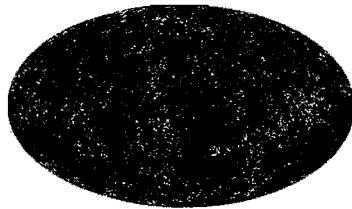


Fig. 1.6 The anisotropy of the CMB taken by the WMAP Science Team (we thank the WMAP Science Team for this image).

²Our universe itself is a “black-body”, filled with the fossil radiation from the initial epoch of expansion of the universe, at a temperature 2.725 K today (*cosmic microwave background radiation*, or CMB). An anisotropy of the order of 0.0002 K has been observed (2003), showing the original temperature fluctuations at the time of matter decoupling, which might have been responsible for galaxy formation (see Figure 1.6).

The reader should verify that this formula reduces to eqn (1.7) or to eqn (1.9), respectively, in the region $h\nu/kT \ll 1$ or $h\nu/kT \gg 1$. The moral of the story is that the Planck distribution follows if the replacement

$$\langle E \rangle = kT \implies \frac{h\nu}{e^{h\nu/kT} - 1} \quad (1.12)$$

is made in the classical equipartition law for the *energy share* of the oscillator of frequency ν , at temperature T . But what is the meaning of eqn (1.12)?

Planck's fundamental contribution to physics, which signaled the birth of quantum physics, was the realization that the above substitution meant the "energy quantum". Let us briefly review how the hypothesis of the energy quantum gives the energy share (1.12) instead of the equipartition law. For each frequency and for each of the polarizations, the Hamiltonian of the electromagnetic fluctuations is a simple oscillator of the form

$$H = aq^2 + bp^2.$$

In polar coordinates $E \equiv x^2 + y^2$; $\theta \equiv \tan^{-1} y/x$, where $x = \sqrt{a}q$; $y = \sqrt{b}p$, the mean energy is

$$\langle E \rangle = \frac{\partial}{\partial(-1/kT)} \log \mathcal{N}', \quad \mathcal{N}' = \int dE e^{-E/kT},$$

where the trivial angular integration has been cancelled between the denominator and numerator. If we perform the integration over E the result is, of course, the equipartition law, kT .

Let us instead assume that the energy comes in (for some reason) multiples of a unit quantum, ϵ ,

$$E_n = n\epsilon, \quad n = 0, 1, 2, 3, \dots$$

The integration must then be replaced by a *summation*

$$\int dE \rightarrow \epsilon \sum_n, \quad (1.13)$$

and we get

$$\langle E \rangle = \frac{\partial}{\partial(-1/kT)} \log \mathcal{N}'', \quad \mathcal{N}'' = \epsilon \sum_n e^{-n\epsilon/kT} = \frac{\epsilon}{1 - e^{-\epsilon/kT}},$$

that is

$$\langle E \rangle = \frac{\epsilon}{e^{\epsilon/kT} - 1}.$$

If the energy unit is chosen as

$$\epsilon = h\nu,$$

this gives precisely what was needed (eqn (1.12)) to get Planck's formula!

The meaning of Planck's formula is thus the *quantization* of electromagnetic energy: light of wavelength $\lambda = c/\nu$ is made up of quanta each

of which has energy $h\nu$. The equipartition law fails for oscillation modes with high frequencies (in the sense $h\nu \gg kT$). A quantum theory of the specific heat of matter, which takes into account the quantization of matter oscillation modes, was subsequently given independently by Debye and Einstein.

1.2.2 The photoelectric effect

The solution of the problem of black-body radiation and the discovery of the energy quantum by Planck, signaled the birth of quantum physics. These ideas had to wait for several more years, however, before they were accepted generally by the scientific community. More direct evidence for the light quantum was needed. Exactly such evidence was provided by Einstein's explanation in 1905 of the so-called photoelectric effect (discovered by Hertz in 1887). In these experiments, an X ray (an electromagnetic ray of very high frequency) illuminates the surface of an alkali metal, such as Li. Electrons shoot out of the surface of the metal, and can be collected and measured in the form of the photoelectric current (see Fig. (1.7)). The most salient features are:

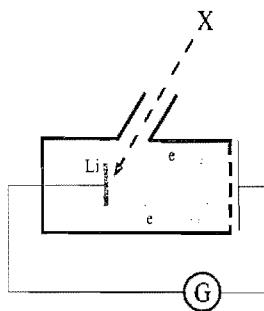


Fig. 1.7 A schematic view of the photoelectric effect

- (i) The energy of the individual electrons is independent of the intensity of the incident X ray.
- (ii) As the intensity of the X ray is increased, the number of electrons (the photoelectric current) increases.
- (iii) The energy of individual electrons depends instead on the frequency (wavelength) of the incident light: the shorter the wavelength of the incident ray, the bigger the electron energy.
- (iv) The photoelectric current starts flowing at once, at the moment the surface is illuminated.

It turns out that it is exceedingly difficult to understand these phenomena by using Maxwell's theory [Tomonaga (1968)]. It was Einstein who noted that all of these features were nothing but direct evidence of Planck's light quantum. Indeed suppose that the X ray is made up of a flux of photons carrying the energy $h\nu$ each (for a monochromatic ray). Assume furthermore that an electron that is initially bound in an atom in the metal surface absorbs all of the photon energy when hit. If the energy gained is sufficient to overcome the binding energy, the electron will be released. The theory predicts a very simple relation between the light frequency and the maximum energy of the outgoing electron (Einstein's relation):

$$E = h\nu - A, \quad (1.14)$$

where the constant A depends on the metal element used. The experimental data (Fig. 1.8) indeed show the linear behavior predicted by Einstein's relation: from the slope of the line interpolating the points (in this experiment five spectral lines are used) one finds the value for h :

$$h \simeq 6.65 \cdot 10^{-27} \text{ erg} \cdot \text{s},$$

which is in good agreement with the value found by Planck, eqn (1.10), from the analysis of black-body radiation.

The *Compton effect* (Problem 1.2) is another phenomenon which shows clearly the particle nature of light.

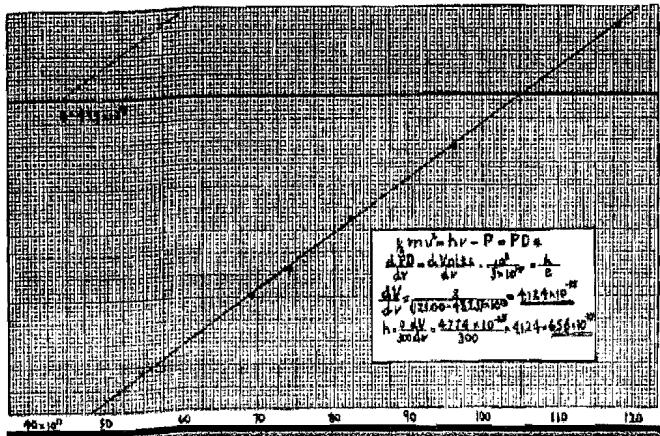


Fig. 1.8 Millikan's experimental result, reproduced with permission from the article [Millikan (1916)]. Copyright 1916 by the American Physical Society.

1.2.3 Bohr's atomic model

The crucial step towards the discovery of quantum mechanics was taken by Bohr in 1913. At the time of Bohr it was known that a gas heated to high temperatures emitted light with a characteristic spectrum. (For example, the sodium lamp makes light with a characteristic orange color.) For hydrogen, a series of spectral lines included the wavelengths 6 562.8, 4 861.3, 4 340.5, 4 101.7, ... (Å). Balmer had discovered in 1885 that these lines could be summarized by an empirical formula,

$$\lambda = \frac{n^2}{n^2 - 4} \lambda_0, \quad \lambda_0 = 3645.6 \text{ Å}, \quad n = 3, 4, 5, \dots$$

Later, Rydberg discovered that the law looked simpler if the frequency, and not the wavelength, was considered, which obeyed the law

$$\nu(n_2, n_1) = T_2(n_2) - T_1(n_1) \quad (1.15)$$

where the $T(n)$ was called the spectral term characterizing a series. In particular, the spectral lines of various alkali elements can be expressed in a very simple form,

$$\frac{\nu}{c} = \frac{1}{\lambda} = \frac{R}{(m+a)^2} - \frac{R}{(m+b)^2}, \quad (1.16)$$

where R is a universal constant (i.e., independent of the element),

$$R = 109 678 \text{ cm}^{-1},$$

(called the *Rydberg's constant*) and a, b are some constants depending on the element. Formula (1.16) or (1.15) represent the line spectra of various elements well, and in particular satisfy the algebraic relations

$$\nu(n_3, n_1) = \nu(n_3, n_2) + \nu(n_2, n_1)$$

(*Ritz's combination rule*). It remained to explain Rydberg's formulas.

Bohr's idea was that the energy of the bound electrons could take only some quantized values, just like the energy of the electromagnetic fields in a cavity. More precisely, Bohr formulated the following set of hypothesis about the atoms (the ensemble of these hypotheses came to be known as *Bohr's atomic model*):

- (1) The possible values of the bound electrons in an atom are quantized, E_1, E_2, \dots (*energy levels*). As long as an electron is in one of these allowed states (*stationary states*) it does not irradiate.
- (2) The atom emits light when an electron makes a transition from one state (n) to another (m); the light emitted or absorbed in such transitions has a frequency such that

$$h\nu = E_n - E_m : \quad (1.17)$$

it is equal to the energy of the photon created or destroyed.

- (3) An electron that is in a stationary state moves according to classical mechanics³.
- (4) For very high orbits ($n \gg 1$) the result of the new mechanics must be consistent with that of classical physics. This hypothesis is known as *Bohr's correspondence principle*.

Note that Bohr's hypotheses eliminate the difficulties of the “planetary model” of atoms, discussed in Section 1.1.2. The first two lead to a natural explanation of Rydberg's formulas, attributing to the spectral term (or to the energy levels E_n) the fundamental significance, rather than their differences. With great ingenuity, combining the empirical formula $E_n \propto -\frac{1}{n^2}$ and the classical formula (1.1), with the help of the correspondence principle, Bohr was able to obtain the energy levels for the hydrogen atom:

$$E_n = -\frac{Rhc}{n^2}; \quad n = 1, 2, \dots$$

(known as *Bohr's levels*) as well as to determine the Rydberg constant in terms of the known constants, m, e, c e h :

$$R = \frac{2\pi^2 m e^4}{c h^3} \simeq 1.09 \times 10^5 \text{ cm}^{-1},$$

in agreement with its empirical value (see [Tomonaga (1968)]). Moreover, Bohr managed to find the size of the hydrogen atom

$$r_B = \frac{\hbar^2}{m e^2} \simeq 0.529 177 \cdot 10^{-8} \text{ cm}$$

(known as the *Bohr radius*) where a constant \hbar related to h ,

$$\hbar \equiv \frac{h}{2\pi} \simeq 1.05 \times 10^{-27} \text{ erg} \cdot \text{sec},$$

(pronounced “ h – bar”) is also known as the Planck constant.

The existence of the stationary states in atoms was demonstrated in a series of elegant experiments by Franck and Hertz in 1913.

³This hypothesis will be substantially corrected by the proper formulation of quantum mechanics.

1.2.4 The Bohr–Sommerfeld quantization condition; de Broglie's wave

Quantization was thus shown to hold for electromagnetic field energy (Planck), for atomic (or molecular) oscillation energy in matter (Debye–Einstein), and for atomic binding energies (Bohr), but a proper formulation of quantum mechanics had to wait for the work of Heisenberg (1925), Schrödinger (1926), and others. It is of historical and pedagogical importance to take note of two more key ideas, before we talk about quantum mechanics itself.

Bohr and Sommerfeld attempted to formulate the idea of quantization in a universal way, so that the rule can be applied to any classically finite motion. Their proposal, known as the Bohr–Sommerfeld quantization rule, states that among possible classical motions only those satisfying the condition (writing the rule for one-dimensional motion, for simplicity),

$$\oint p dq = n \hbar \quad (n = 0, 1, 2, \dots) \quad (1.18)$$

where q and p refer to a pair of canonical variables and the integration is over a full period of classical motion, are allowed.

Remarks

- The limitation to quasi-periodic motions is important. Further development by Einstein covered the case of systems which are classically integrable. Some much more recent developments on eqn (1.18) deals with general systems. See Supplement 21.5.
- For harmonic oscillators, (1.18) gives, in agreement with Planck's hypothesis, $E_n = n \omega \hbar = n \hbar \nu$, which, to be rigorous, differs from the correct quantum mechanical result by an additive constant (see Section 3.4).
- For the hydrogen atom, eqn (1.18) leads correctly to Bohr's energy levels.
- It is important for the consistency of the formalism that the integral appearing in eqn (1.18) is an *adiabatic invariant*. Namely, when a parameter appearing in the Hamiltonian is varied slowly, the integral taken over an approximate period remains invariant.
- The Bohr–Sommerfeld quantization condition turns out not to be exact: in quantum mechanics it is approximately valid in the semi-classical limit.

The last missing piece of the puzzle, which was needed to complete the formulation of quantum mechanics, was the realization that wave-particle duality, discovered first for light and then for the electron, was

actually valid for *any* atomic particles (by de Broglie in 1925). Quantitatively, to each particle with momentum p a sort of wave with wavelength

$$\lambda = \frac{h}{p} \quad (1.19)$$

is to be associated (*de Broglie's wave*). Vice versa, the quantum of monochromatic light (with wavelength λ) behaves like a particle with momentum $p = h/\lambda$.

More precisely, a particle is to be described by a wave packet, whose momentum components are related through de Broglie's formula to various Fourier components. The velocity of the particle is identified with the group velocity of the superposed waves, and not with the phase velocity [Born (1989)]. De Broglie argued that, furthermore, the Bohr-Sommerfeld condition followed from eqn (1.19).

The simple relation (1.19) is of fundamental importance. It provided the first key to quantitatively interpret the unusual concept of wave-particle duality.

Further reading

For more on the historical development, see *Atomic Physics* by Max Born [Born (1989)]. The book by Tomonaga [Tomonaga (1968)] is a unique textbook, written with the aim of explaining *how* quantum physics has been discovered and how quantum mechanics has subsequently been formulated in the present form.

English translations of many of the original papers on quantum mechanics (by Heisenberg, Born, Jordan, and Schrödinger [Heisenberg (1925), Born, Heisenberg, and

Jordan (1926), Schrödinger (1926)]) can be found in two books: *Sources of Quantum Mechanics* [van der Waerden (1968)] and *Wave Mechanics* [Ludwig (1968)], together with other important contributions by Bohr, de Broglie, Dirac, Einstein, van Vleck, Pauli and others. Unfortunately the fundamental series of papers by Schrödinger [Schrödinger (1926)] (in German) are only partially reproduced in the latter.

Guide to the Supplements

Supplement 20.1 reviews the most salient features of the Lagrangian and Hamiltonian formalisms of classical mechanics. In Supplement 20.2 we show how the energy of

electromagnetic fields in vacuum can be expressed as an infinite number of independent harmonic oscillators.

Problems

- (1.1) Form all possible quantities having the dimension of length, by using m_e , h , and e^2 . Try the same but also allowing the velocity of light, c .
- (1.2) Consider the scattering of an X-ray on an electron at rest. An X ray with wavelength λ is regarded as a flux of photons, each with energy $h\nu$ and momentum $p = h\nu/c$, where $\nu = c/\lambda$. Let p and E be the momentum and energy of the electron in the final state and let ϕ and θ be the angles between the directions of the final photon momentum and electron momentum, with respect to the incident photon momentum. The final state photon has energy and momentum $h\nu'$ and $h\nu'/c$. Use energy and momentum conservation to derive the Compton formula

$$\lambda' - \lambda = \frac{2h}{mc} \sin^2\left(\frac{\phi}{2}\right)$$

- (1.3) Consider a hydrogen atom (composed of an proton and an electron; $m_p \simeq 1836 m_e$). Calculate the reduced mass μ and compare it with m_e . Solve the classical equation of motion assuming a circular orbit of radius r and write the solution for the angular variable θ in the form $\theta(t) = 2\pi\nu t + \delta$. Compute ν for $r = 5 \times 10^{-9}$ cm. Compute $h\nu$ and compare this energy with a thermal energy kT for $T = 290$ K. k

is the Boltzmann constant, $k = 1.38 \times 10^{-16}$ erg K $^{-1}$.

- (1.4) Verify that the Hamiltonian of a charged particle moving in an external electromagnetic field,

$$H = \frac{(\mathbf{p} - \frac{q}{c}\mathbf{A})^2}{2m} + q\phi,$$

follows from the Lagrangian

$$L = m \frac{\dot{\mathbf{r}}^2}{2} + \frac{q}{c} \dot{\mathbf{r}} \cdot \mathbf{A} - q\phi(\mathbf{r}).$$

Compare the Euler-Lagrange equations and Hamilton's equations for such a particle.

- (1.5) Show that in classical mechanics the volume in phase space occupied by the states between (q_i, p_i) and $(q_i + \delta q_i, p_i + \delta p_i)$ remains invariant as the system evolves in time (Liouville's theorem).
- (1.6) Compute the Planck distribution for an observer moving with velocity V .
- (1.7) A plain mirror, approximated by a plane perpendicular to the z axis, is moving with velocity V in the z direction, in a cavity filled with radiation at temperature T . Compute the frictional force on the mirror.

Numerical analyses

- (1.1) Study the temperature dependence of the Planck distribution.

2

Quantum mechanical laws

In this chapter, the main concepts of quantum mechanics are introduced.

2.1 Quantum states

The experiment by Tonomura et al., discussed in Chapter 1 directly confirms the de Broglie relation (1.19). This leads us to define the state of a system, not in terms of simultaneous values of all canonical variables $\{p, q\}$ as in classical mechanics, but as a sort of a wave. According to

the fundamental law of quantum mechanics

the quantum state of a given system is described by a complex function, $\psi(\{q\}, t)$, called the *wave function*:

$$\boxed{\text{quantum state} \sim \psi(\{q\}, t)} . \quad (2.1)$$

It depends on the canonical coordinates and on time but not on the conjugate momenta.¹

Knowledge of the wave function amounts to complete knowledge of a state. It allows one to determine the *probability* of getting various results in any measurement made in that state.

In spite of some formal similarity, there is an essential difference between the meaning of the wave function and that of a classical wave. The function ψ should not be thought of as something representing the space-time propagation of matter or of energy, as is the case with classical waves. The interpretation of ψ is of a probabilistic nature.

For instance, the quantum mechanical probability of finding the system in the coordinate interval $[q, q + dq]$ is given by

$$\boxed{dP = |\psi(\{q\}, t)|^2 dq} \quad (2.2)$$

($dq \equiv dq_1 dq_2 \dots dq_s$). For a particle moving in ordinary three-dimensional space, the probability of observing it in the vicinity of the point \mathbf{r} is

$$|\psi(\mathbf{r}, t)|^2 d^3 \mathbf{r} . \quad (2.3)$$

In a three-dimensional system with s degrees of freedom, $\psi(\{q_s\})$ is a function of s variables (e.g., $s = 6$ for a system of two particles):

2.1 Quantum states	21
2.2 The uncertainty principle	26
2.3 The fundamental postulate	29
2.4 The Schrödinger equation	37
2.5 The continuous spectrum	40
2.6 Completeness	45
Chapter summary	48
Problems	47
Numerical analyses	48

¹Such a description appears to introduce the loss of an elegant symmetry under the exchange of canonical coordinates and momenta, present in the Hamiltonian formulation of classical mechanics. Actually, the quantum mechanical laws do have an analogous symmetry for $q \leftrightarrow p$: its apparent loss is due to the choice of a particular language, *a representation*, as will be explained later on (Section 7.1).

this illustrates the fact that ψ cannot be directly associated with any property of matter in three dimensions.

As the total probability must be unity, we must impose

$$\|\psi\|^2 \equiv \int |\psi(\{q\}, t)|^2 dq = 1.$$

²For instance, $\psi(\mathbf{r}, t) = e^{+i\mathbf{r}^2}$ is not normalizable; such a function does not represent any physical state.

This is known as the *normalization condition*. Any wave function for which the integral $\int |\psi(\{q\}, t)|^2 dq$ is finite can be normalized by multiplying it by an appropriate constant: it is said to be *normalizable*². It follows that wave functions ψ and $c\psi$, where c is an arbitrary complex number different from zero, represent the same physical state, i.e.,

$$\psi \sim c\psi, \quad c \neq 0.$$

³More precisely, ψ belongs to a Hilbert space; see Section 7.2.

In other words, the quantum state is described by the ray of a normalizable function ψ in the space \mathcal{H} .³

Physical states expressed by wave functions possess a property of fundamental importance: they obey

the superposition principle.

The superposition principle asserts that if ψ_1 and ψ_2 are two possible (quantum) states, then so is any linear combination

$$\psi = c_1\psi_1 + c_2\psi_2,$$

⁴There are important exceptions to this rule (see Section 20.14) even though in most of the book this will not bother us.

where $c_{1,2}$ are two arbitrary complex numbers, $|c_1|^2 + |c_2|^2 \neq 0$.⁴ This can be summarized mathematically by saying that the ensemble of the allowed states forms a *linear space* \mathcal{H} of wave functions.

For consistency, the superposition principle requires that the time evolution of the wave function is described by an equation of the form

$$\mathcal{L}\psi = 0,$$

where \mathcal{L} is a *linear operator*, i.e., an operator such that

$$\mathcal{L}(c_1\psi_1 + c_2\psi_2) = c_1\mathcal{L}\psi_1 + c_2\mathcal{L}\psi_2.$$

The explicit form of \mathcal{L} will be given below.

As has been noted above, the probability interpretation of quantum mechanics imposes what types of functions are allowed in \mathcal{H} : they must satisfy

$$\int |\psi|^2 dq < \infty,$$

namely, they must be square integrable (space \mathbb{L}^2). In a finite dimensional vector space, it is often useful to have the concept of *scalar product*. For instance, in \mathbb{R}^3 we define

$$\mathbf{a} \cdot \mathbf{b} \equiv a_1 b_1 + a_2 b_2 + a_3 b_3;$$

this allows us to define the *norm* of a vector by $\|\mathbf{a}\| = \sqrt{\mathbf{a} \cdot \mathbf{a}}$. Analogously, the scalar product between two state vectors ψ_1, ψ_2 can be introduced in our space of wave functions as

$$\langle \psi_1 | \psi_2 \rangle = \int \psi_1^* \psi_2 dq ; \quad (2.4)$$

the *norm* of a state vector is then defined naturally by

$$\|\psi\| = \sqrt{\langle \psi | \psi \rangle} .$$

A vector space in which a scalar product between any pair of the elements is defined is known as a *Hilbert space*. Clearly the space \mathbb{L}^2 is a Hilbert space, with respect to the scalar product, eqn (2.4).

We have introduced above a notation due to Dirac for the state vectors: $|\psi\rangle$ and $\langle\psi|$ are called “ket” and “bra” vectors, respectively (these terms come from the word “bracket”). A more abstract significance of these vectors will be discussed later.

Remarks

The description of the quantum state by a wave function introduces a certain similarity to classical wave dynamics, and for this reason, the term “wave mechanics” was used in the past to indicate the quantum mechanical (Schrödinger) equations. However, there are essential differences between classical wave dynamics and quantum dynamics. The distinction in meaning of the wave function itself, compared to any classical wave amplitude, has already been pointed out.

For example, in quantum mechanics, the wave functions ψ and $c\psi$ ($c \neq 0$) describe one and the same state, while two classical waves differing by a factor in the amplitude represent physically distinct phenomena, with different energies.

The very concept of superposition requires in quantum mechanics an interpretation that differs considerably from its classical counterpart. Let us consider, for instance, two states A and B of a given system. Suppose that A and B are such that the measurement of a variable O gives the result a (in state A) or b (in state B), with certainty. Now, according to the superposition principle, another state C , described by the state vector,

$$|C\rangle = c_A |A\rangle + c_B |B\rangle, \quad |c_A|^2 + |c_B|^2 \neq 0 ,$$

with some arbitrary complex numbers c_A and c_B , is also a possible physical state. The physical properties of the new state C will be somewhere between those of state A and those of state B , but *in what sense?* In particular, what result is expected if measurement of the variable O is made in state C ?

According to the quantum mechanical laws, to be expounded below, such a measurement always gives a result of either a or b , with respective probabilities

$$\mathcal{P}_a = \frac{|c_A|^2}{|c_A|^2 + |c_B|^2}; \quad \mathcal{P}_b = \frac{|c_B|^2}{|c_A|^2 + |c_B|^2} ;$$

no other results are possible, even if the variable O may *a priori* take other possible values. The intermediate character of state C thus expresses itself through the probability of a particular result for an observation being intermediate between the corresponding probabilities for the original states, not through the result itself being intermediate between the corresponding results for the original states (a passage quoted verbatim from §4 of Dirac's book [Dirac (1958)]).

2.1.1 Composite systems

In a system composed of two (or more) non-interacting and uncorrelated subsystems A and B , the wave function takes a factorized form,

$$\psi_{A,B} = \psi_A \psi_B, \quad (2.5)$$

where ψ_A and ψ_B describe the respective states of the two subsystems. This leads to the factorized probabilities, reflecting the independence of the two subsystems. Such is, of course, a very reasonable assumption to make in any sensible theory. The success of quantum mechanics in many practical applications indicates that the **factorization** property, (2.5), generally holds with very high precision.

On the other hand, in quantum mechanics, the wave function for systems involving identical particles (many electrons, many protons, etc.) must obey certain symmetry properties with respect to the exchange of identical particles. Such a requirement—called Bose–Einstein (BE) or Fermi–Dirac (FD) **statistics**—introduces a characteristic correlation among the particles of the same kind, even when the interactions among them are negligibly weak. Bose–Einstein or Fermi–Dirac statistics have far-reaching consequences in all applications of quantum mechanics from elementary particle, nuclear, atomic, and molecular physics, to condensed matter physics and astrophysics. See Section 5.3.

More generally, even when the statistics are not relevant, two (or more) parts which interacted in the past usually exhibit definite correlations in quantum mechanics. In certain circumstances, these characteristic correlations, called **quantum entanglement**, manifest themselves even when the separate parts cannot causally interact in the present or future times. The correlations occur in an apparently non-local and non-causal fashion, in glaring contrast to the fact that fundamental interactions—strong and electroweak interactions—are described by a local and causal theory to an impressively high precision.⁵ These extraordinary aspects of quantum mechanical correlations will be discussed in Part IV of this book.

⁵The standard theory of the fundamental interactions—quantum chromodynamics for the strong forces and the Glashow–Salam–Weinberg electroweak theory—is a theory of point-like particles, which is rigorously *local* and *causal*; it is known to describe Nature very precisely, at least down to distance scales of the order of $\sim 10^{-16}$ cm.

2.1.2 Photon polarization and the statistical nature of quantum mechanics

The polarization of light is described, in classical physics, by the polarization vector $\epsilon^\lambda(\mathbf{k})$ which characterizes the vector potential

$$\mathbf{A} = A^\lambda(\mathbf{k}) \epsilon^\lambda(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}-i\omega t} + \text{c.c.}$$

For simplicity we have assumed that light is monochromatic. In the radiation gauge,

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}, \quad \boldsymbol{\epsilon} \cdot \mathbf{k} = 0.$$

The last condition implies that there are two independent possible polarizations. For instance, a linear polarization in the x direction corresponds to $\boldsymbol{\epsilon}^1 = (1, 0, 0)$, $\mathbf{k} = (0, 0, k)$, so that

$$E_x = \frac{A^1}{c} \omega \cos(\mathbf{k} \cdot \mathbf{r} - \omega t), \quad E_y = 0;$$

or analogously, to $\boldsymbol{\epsilon}^2 = (0, 1, 0)$, if the polarization is in the y direction. Linearly polarized light in an intermediate direction $(\cos \theta, \sin \theta, 0)$ is described by the polarization vector $\boldsymbol{\epsilon} = (\cos \theta, \sin \theta, 0)$. Light with a “circular” polarization is instead described by, for instance, $\boldsymbol{\epsilon}^1 = \frac{1}{\sqrt{2}}(1, i, 0)$, so that the electric field components are

$$E_x = \frac{A^+}{\sqrt{2}c} \omega \cos(\mathbf{k} \cdot \mathbf{r} - \omega t), \quad E_y = \frac{A^-}{\sqrt{2}c} \omega \sin(\mathbf{k} \cdot \mathbf{r} - \omega t);$$

light with an elliptic polarization by $\boldsymbol{\epsilon} = \frac{1}{\sqrt{5}}(2, i, 0)$, etc. A general state of polarization can be expressed as

$$\boldsymbol{\epsilon} = c_1 \boldsymbol{\epsilon}^1 + c_2 \boldsymbol{\epsilon}^2, \quad |c_1|^2 + |c_2|^2 = 1. \quad (2.6)$$

In quantum mechanics a light beam is a flux of photons, and the origin of the polarization must be sought in the characteristics of individual photons: it should be regarded as being due to two possible quantum states of a photon of given momentum (i.e., of given wavelength and direction of propagation). If these other physical attributes are disregarded, the state of a single photon is described by the state vector⁶

$$|\psi\rangle = c_1 |1\rangle + c_2 |2\rangle, \quad (2.7)$$

$|c_1|^2 + |c_2|^2 = 1$, where for instance $|1\rangle$, $|2\rangle$ can be taken to represent the two linear polarizations in the x and y directions, and

$$\langle 1|1\rangle = \langle 2|2\rangle = 1, \quad \langle 1|2\rangle = 0.$$

These states correspond to the classical polarization vectors, (2.6). A photon linearly polarized in the direction $(\cos \theta, \sin \theta)$ in the plane perpendicular to the photon propagation can be naturally described by the state vector (2.7) with $c_1 = \cos \theta$, $c_2 = \sin \theta$.

Now certain crystals have the property of letting light pass through only when it is polarized along the crystal's characteristic axis, known as the polarization axis. Or simply consider the plastic materials known as *Polaroid*. When the incident light is polarized along the polarization axis, all the light is transmitted. Light with an orthogonal polarization cannot pass. When light enters, with a linear polarization along the

⁶The polarization state of a photon is a typical example of quantum mechanical “two-state systems” or “two-level systems.” In quantum information theory such a system is called a quantum bit, or simply, a *qubit*.

direction which makes angle θ with respect to the polarization axis of the crystal, the intensity of the transmitted light obeys an empirical rule,

$$I(\theta) = I(0) \cos^2 \theta, \quad (2.8)$$

known as Malus' law.

Consider now the physics of this beautiful empirical law, from the quantum mechanical point of view. If the incident photon has the appropriate polarization (say, $|1\rangle$), it passes. If it has the wrong polarization (i.e., $|2\rangle$), it does not. What happens to an incident photon that is polarized in the direction $(\cos \theta, \sin \theta)$, described by the state vector

$$|\psi\rangle = \cos \theta |1\rangle + \sin \theta |2\rangle ?$$

A photon, with a definite energy $h\nu$, cannot split. There are no other options left: it must either pass or not pass. The only sensible answer to the above question is that such a photon has some *probability* of passing and some *probability* of not passing. If we assign the probabilities $P_+ = |c_1|^2 = \cos^2 \theta$ (of passing) and $P_- = |c_2|^2 = \sin^2 \theta$ (of not passing) then for light beam consisting of many photons with the same polarization, the number of photons which have passed through the crystal will be $I(0) \cdot \cos^2 \theta$ if $I(0)$ is the number of incoming photons. We have thus *derived* Malus' law for the intensity of transmitted light (which is obviously proportional to the number of photons which have passed through the crystal) from quantum mechanics!

We see clearly that the probabilistic interpretation of quantum mechanics is a direct consequence of certain empirical facts about light. Put even more strongly, *it is the only logical formulation of these facts*.

2.2 The uncertainty principle

The fact that the electron is described as a kind of wave means that the classical concept of particle trajectory no longer makes sense. An electron cannot simultaneously have a definite position and momentum. It is not claimed that the concept itself of either particle position or particle momentum loses meaning. Rather the description of the physical state in quantum mechanics is no longer equivalent to the collection of definite values of canonical coordinates and momenta, q_i, p_i .

At the same time, however, the laws of quantum mechanics must reduce to those of classical mechanics in the limit where the Planck constant h can be considered to be negligibly small. The constant h must somehow signal the borderline between the domains of validity for the classical and quantum formulas.

Mathematical expressions for this limitation were derived by Heisenberg. Let us suppose that we are going to measure the position and momentum of a particle. The measurement will be done with a certain resolution, Δx_i and Δp_i , for each component. *Heisenberg's uncertainty*

principle states that these obey the inequalities

$$\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2}; \quad \Delta y \cdot \Delta p_y \geq \frac{\hbar}{2}; \quad \Delta z \cdot \Delta p_z \geq \frac{\hbar}{2}. \quad (2.9)$$

These *uncertainty relations* follow from the description of the particle state in terms of a wave function. For example, consider a wave packet of Gaussian form which at $t = 0$ is given by

$$\psi(x, 0) = \text{const } e^{-x^2/d^2}.$$

The distribution is centered around $x = 0$ but has a dispersion

$$\Delta x = \sqrt{\langle (x - \langle x \rangle)^2 \rangle} \sim d, \quad (2.10)$$

which can be interpreted as representing an uncertainty of its position. As already anticipated in the preceding section, the expectation value of e.g., x^2 , is to be calculated with the probability density $|\psi(x)|^2$.

The wave function $\psi(x)$ can be seen as a superposition of plane waves. Indeed, its Fourier decomposition is:

$$\psi(x) = \int_0^\infty d\lambda \left(a(\lambda) e^{2\pi i x/\lambda} + a^*(\lambda) e^{-2\pi i x/\lambda} \right) = \int_{-\infty}^\infty d\lambda a(\lambda) e^{2\pi i x/\lambda}.$$

According to de Broglie's relation $p = \frac{\hbar}{\lambda}$ we must re-interpret this as a decomposition into different momentum components of the Gaussian wave packet:

$$\psi(x) = \int_{-\infty}^\infty dp \tilde{\psi}(p) e^{ipx/\hbar},$$

where we have introduced $\hbar \equiv h/2\pi$. The Fourier component $\tilde{\psi}(p)$ is easily calculated for a Gaussian wave:

$$\tilde{\psi}(p) = \int_{-\infty}^\infty \frac{dx}{2\pi\hbar} e^{-ipx/\hbar} e^{-x^2/d^2} = \text{const. } e^{-p^2 d^2 / 4\hbar^2}.$$

Such a result can naturally be interpreted as implying an uncertainty of the momentum of the order of

$$\Delta p \sim \frac{\hbar}{d}. \quad (2.11)$$

Heisenberg's relation follows from eqns (2.10) and (2.11).

The uncertainty relations imply that if the position of a particle is exactly known, the knowledge of its momentum is completely lost, or vice versa, and in general, the product of their uncertainties cannot be less than $\hbar/2$.

One might wonder what such a constraint really means in physical terms. For instance, can't one prepare a particle beam (e.g., in the x direction) so well collimated that its momentum component p_z can be thought to be perfectly known ($p_z = 0$), and make a measurement of the vertical position z with an arbitrarily high precision, to produce a

state in which both p_z and z are simultaneously exactly known? Or at least, a state arbitrarily close to such a state?

These questions were analyzed by Heisenberg, through a series of “Gedankenexperiments” (hypothetical, thought experiments) [Heisenberg (1930)]. We shall consider here just two examples. The first concerns the measurement of the horizontal position of an electron by an optical microscope (Fig. 2.1). Light comes from the left, scattered by the electron, and enters the objective lens. As is well known from optics, the resolution in such an apparatus is limited by the formula,

$$\Delta x \sim \frac{\lambda}{\sin \epsilon},$$

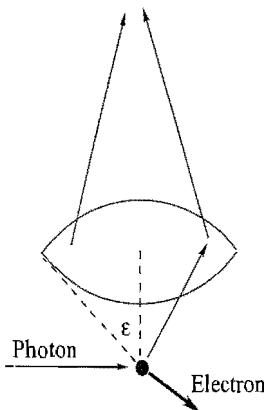


Fig. 2.1 Measurement of the horizontal position of an electron by a microscope

where λ is the wavelength of the light used, and ϵ is the angular aperture of the lens. During the measurement process, the electron receives a recoil of the order of $h\nu/c$, as a result of Compton scattering (see Problem 1.2). Because the direction of the photon is known only within the angular aperture ϵ , the horizontal component of the electron momentum will also be affected, by momentum conservation, by an amount

$$\Delta p_x \sim \frac{h\nu}{c} \sin \epsilon \sim \frac{h}{\lambda} \sin \epsilon$$

from which the uncertainty relation

$$\Delta x \Delta p_x \sim h$$

follows. The duality of light is essential in this argument.

Another possible Gedankenexperiment is the measurement of the vertical position (z) of the electron which enters horizontally into a wall with a slit (Fig. 2.2). Suppose that the beam is so well collimated that the vertical component of the momentum can be considered to be exactly zero, before hitting the wall. The width (aperture) of the slit d introduces an uncertainty in the position determination

$$\Delta z \sim d,$$

of the electron that has passed through it. Now, according to de Broglie, an electron of momentum p behaves like a wave with wavelength $\lambda = h/p$: as such, it will suffer diffraction during its passage through the narrow slit, with a diffraction angle α ,

$$\sin \alpha \sim \frac{\lambda}{d},$$

where another well-known result from optics has been used. Thus, upon its passage through the slit, the electron will acquire a momentum uncertainty of the order of

$$\Delta p_z \sim |p| \sin \alpha = \frac{h}{\lambda} \frac{\lambda}{d} = \frac{h}{d}.$$

For the product of the position and momentum uncertainties we again find that

$$\Delta z \Delta p_z \sim h.$$

In this derivation the wave-particle duality of the electron has been the key.

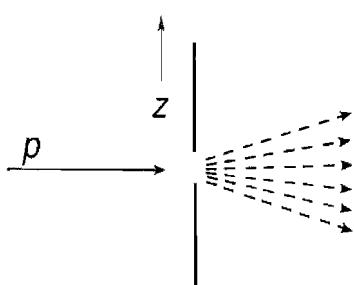


Fig. 2.2 Determination of the vertical position of an electron passing through a slit

Remarks

- These inequalities tell us something about *simultaneous* measurement of conjugate variables. It is important that the simultaneity is understood in an appropriate, physical sense. In contrast, the product of the uncertainty of p_z just before, and the uncertainty of z immediately after, the electron passes through the slit, for instance, could be made arbitrarily small. However, such a product has only a philosophical meaning: it cannot be used as initial data for studying and predicting successive events.⁷
- Heisenberg's inequalities reflect an objective, physical limitation, independent of the external conditions (the techniques used, the expertise of the experimentalist, the quality of the apparatus used, etc.); they arise from the very dynamical properties of the physical processes involved in the measurement.
- These discussions highlight an essential aspect of quantum mechanical measurement: in experiments involving atomic or subatomic systems, the disturbance caused by the process of measurement on the microscopic system under examination cannot be controlled beyond certain limit.
- The probabilistic nature of quantum mechanical prediction for the results of measurement is an inevitable consequence of Heisenberg's uncertainty principle.

As a consequence of Heisenberg's uncertainty relations, determinism in the classic sense is in general lost during the measurement. In contrast, systems left unperturbed evolve in time in a perfectly deterministic manner, according to the Schrödinger equation (see below), which is a linear differential equation with respect to time.

All this is in clear contrast with what happens in classical mechanics. In macroscopic processes, the disturbance caused by the process of measurement on the system being observed is usually assumed to be negligible. The classical concept of determinism hinges upon such a tacit assumption.⁸

2.3 The fundamental postulate

We have seen above that the quantum state is described by a complex function, the wave function, $\psi(\{q\}, t)$. How are the dynamical variables treated in such a formalism? What are the possible outcome of a measurement? What does the new mechanics predict?

In quantum mechanics, a *linear operator* \hat{f} is associated with each dynamical variable f , and acts in the space \mathcal{H} of wave functions. By definition a linear operator satisfies

$$\hat{f}(c_1\psi_1 + c_2\psi_2) = c_1\hat{f}\psi_1 + c_2\hat{f}\psi_2,$$

where c_1, c_2 are arbitrary complex numbers⁹.

⁷ There is, of course, no problem in defining such a concept *mathematically*, but it would not be of much use: it is normally impossible to attain such rigourous contemporaneity in real experiments. Worse, it is a frame-dependent concept in special relativity.

⁸ We should bear in mind, of course, that traditional, absolute determinism has suffered a serious blow in the last couple of decades, even in the realm of classical mechanics. It suffices to recall the physics of non-linear phenomena, such as chaos, butterfly effects, the impossibility of long-term weather forecasting, etc.

⁹ Examples: the wave function of a particle moving in three dimensions has the form, $\psi(\mathbf{r}, t)$; differential operators $\frac{\partial}{\partial t}, \frac{\partial}{\partial x}, \frac{\partial}{\partial z}, \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ are all linear operators; so is the operator $\psi \rightarrow U(\mathbf{r})\psi$, while the operator $\hat{Q}\psi = \psi^2$ is not.

For instance, consider the position of a particle. In accordance with the interpretation of $|\psi(q)|^2$ as the probability density, we must assert that the measurement of q in the state ψ gives a mean value

$$\langle q \rangle_\psi = \int dq q |\psi(q)|^2 = \int dq \psi^*(q) q \psi(q).$$

That one can predict (in general) only the mean value of q is compatible with Heisenberg's principle: having a probability distribution, we shall have a non-vanishing dispersion of q from its mean value, $\langle (q - \langle q \rangle)^2 \rangle$, which then should be quantitatively related by Heisenberg's uncertainty relations to the analogous dispersion for the momentum p . This will be discussed below.

For any function $f(q)$ of the position variable, we shall analogously assign a linear operator, \hat{f} , defined as follows:

$$\hat{q} \psi(q) = q \psi(q); \quad \hat{f} \psi(q) = f(\hat{q}) \psi(q) = f(q) \psi(q);$$

its expectation value is accordingly given by

$$\langle \psi | \hat{f} | \psi \rangle = \int dq \psi^*(q) \hat{f} \psi(q).$$

We shall see that these rules are naturally extended to an operator representing more general dynamical variables below.

Now in what sense are these expectation values related to an experimental observation? When a particular quantity is measured repeatedly under identical conditions, the results could be f_1, \dots, f_n . The expectation (or mean) value is by definition $\sum f_i/n$ in the limit of large n . In quantum mechanics, the possible outcome of experiments on the dynamical variable f are the eigenvalues $\{f_n\}$ of the associated operator \hat{f} ,

$$\hat{f} \psi_n = f_n \psi_n, \quad ||\psi_n|| = 1, \quad (2.12)$$

where the function ψ_n (called the *eigenfunction*, or *eigenvector*, of \hat{f}) represents a quantum state in which the measurement of the quantity f gives the result f_n with certainty. The corresponding state is known as the *eigenstate* of f . In such a state there is indeed no dispersion

$$\langle \psi_n | \hat{f}^2 | \psi_n \rangle - \langle \psi_n | \hat{f} | \psi_n \rangle^2 = 0.$$

A generic state is described by a superposition of eigenfunctions $\{\psi_n\}$ of any chosen operator \hat{f} :

$$\psi(q) = \sum_n c_n \psi_n(q), \quad ||\psi_n|| = 1. \quad (2.13)$$

What happens if the quantity f is measured, in this quantum state?

The fundamental postulate of quantum mechanics

asserts that the probability of finding a result f_n in the measurement of a quantity f made in the state $\psi(q) = \sum_n c_n \psi_n(q)$ is given by

$$P_n = |c_n|^2. \quad (2.14)$$

If we make use of the orthogonality of the eigenstates (to be proven below)

$$\langle \psi_n | \psi_m \rangle = \int dq \psi_n^*(q) \psi_m(q) = \delta_{n,m}, \quad (2.15)$$

the normalization condition of the state ψ ,

$$\|\psi\| = 1.$$

implies that

$$\sum_n P_n = \sum_n |c_n|^2 = 1,$$

a result to be expected for the total probability. The expectation value of the operator \hat{f} is then

$$\langle \psi | \hat{f} | \psi \rangle = \int dq \psi^*(q) \hat{f} \psi(q) = \sum_n |c_n|^2 f_n = \sum_n P_n f_n, \quad (2.16)$$

where the linearity of the operator has been used. Equation (2.16) is justifiably the quantity to be compared to the average of the measured values for f .

An alternative formula for the probability, (2.14), is

$$P_n = |\langle \psi_n | \psi \rangle|^2, \quad (2.17)$$

where we have used an orthonormality relation among $\{\psi_n\}$ to get

$$\langle \psi_n | \psi \rangle \equiv \int dq \psi_n^*(q) \psi(q) = c_n.$$

In other words, the probability of finding a result f_n in the measurement of f is the square of the absolute value of the projection of the wave function ψ on the relative eigenfunction ψ_n .

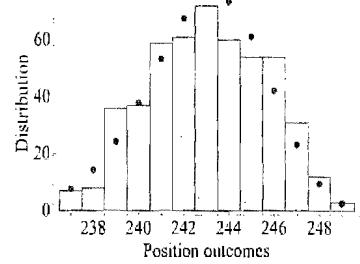


Fig. 2.3 Experimentally, as usual, probabilities are defined as a limit of frequencies for the positive outcomes. For a finite number of measurements we have a distribution of values. In this figure a quantum mechanical simulated experiment predicts about 243 as positive outcomes of a test. With a finite number of repetitions we have a (binomial) distribution for the results. For the details see notebook NB-2.1.nb.

2.3.1 The projection operator and state vector reduction

The fundamental postulate of quantum mechanics (2.14), (2.17) must actually be complemented by another, almost implicit, postulate: the system, immediately after the measurement which gave a result, f_n , is in the state,

$$|\psi\rangle = |n\rangle :$$

the system has been projected onto the corresponding eigenstate,

$$|\psi\rangle \Rightarrow \mathcal{P}_n |\psi\rangle = |n\rangle \langle n|\psi\rangle = c_n |n\rangle \sim |n\rangle , \quad (2.18)$$

where

$$\mathcal{P}_n \equiv |n\rangle \langle n|$$

is a projection operator satisfying

$$\mathcal{P}_n^2 = \mathcal{P}_n, \quad \mathcal{P}_n \mathcal{P}_m = 0, \quad m \neq n.$$

The probability for this particular outcome, eqns (2.14) and (2.17), can be written in still another form, i.e., as the expectation value of the projection operator \mathcal{P}_n in the state $|\psi\rangle$:

$$P_n = \langle \psi | \mathcal{P}_n | \psi \rangle .$$

Requirement (2.18) means that the same experiment, repeated immediately after the first measurement, gives the same result, f_n . This rule, confirmed by experimental observations, is indeed necessary for the theory to make sense at all. The result of a measurement must be utilizable as a *preparation of the state*, or as an *initial condition*, for predicting the successive evolution and for further studying the system.

2.3.2 Hermitian operators

A question arises naturally: which among all possible linear operators are candidates for describing a dynamical variable (an observable)? The fact that the result of a measurement in physics is a real number imposes a particular condition on the possible operators. Clearly all the eigenvalues of the operator \hat{f} , f_n , must be real as they represent the possible experimental outcome of the measurement, and, as a consequence, so must its expectation value be also.

Let us define the transpose \hat{f}^T of an operator. Given a state vector ψ , if there exists a function $\chi \in \mathcal{H}$ such that for any $\phi \in \mathcal{H}$ the relation

$$\int dq (\hat{f}\phi^*) \psi = \int dq \phi^* \chi ,$$

holds, then

$$\chi \equiv \hat{f}^T \psi .$$

A Hermitian conjugate of an operator is then defined as

$$\hat{f}^\dagger \equiv (\hat{f}^T)^* = (\hat{f}^*)^T .$$

An operator is Hermitian (or symmetric) if $\hat{f}^\dagger = \hat{f}$, i.e., if

$$\langle \phi | \hat{f} \psi \rangle = \langle \psi | \hat{f} \phi \rangle^* \equiv \langle \hat{f} \phi | \psi \rangle , \quad \forall \psi, \phi \in \mathcal{D}(\hat{f})$$

$$(2.19)$$

where $\mathcal{D}(\hat{f})$ is the domain of the operator \hat{f} , i.e., $\psi \in \mathcal{D}(\hat{f})$ if $\hat{f}\psi \in \mathcal{H}$. We thus find that *a dynamical variable is represented by a Hermitian operator*. For a Hermitian operator, one indeed finds (by choosing $\psi = \phi$ in eqn (2.19)) that the expectation value in any state is real: $\langle \hat{f} \rangle = \langle \hat{f} \rangle^*$. A particular choice for the state, $\psi = \psi_n$, further gives the required result $f_n^* = f_n$ for each eigenvalue. The Hermitian property of \hat{f} is also necessary. Let us indeed suppose that the relation $\langle \psi | \hat{f} | \psi \rangle = \langle \psi | \hat{f} | \psi \rangle^*$ holds for any ψ . Setting $\psi = \chi + e^{i\alpha} \phi$, we find that

$$e^{i\alpha} \langle \chi | \hat{f} | \phi \rangle + e^{-i\alpha} \langle \phi | \hat{f} | \chi \rangle \in \mathbb{R},$$

(real) for any real constant α . It follows that

$$\langle \phi | \hat{f} | \chi \rangle = \langle \chi | \hat{f} | \phi \rangle^*,$$

for any choice of χ, ϕ , that is, \hat{f} is Hermitian, by definition (eqn (2.19)). We thus conclude that *to each dynamical variable there is associated a linear, Hermitian operator*.¹⁰

Theorem 2.1 *The eigenstates of a Hermitian operator, associated with distinct eigenvalues, are mutually orthogonal.*

¹⁰ Examples: the operators $x, y, x^2, i\partial/\partial x, i\partial/\partial t$ etc., are Hermitian; $\partial/\partial x$ is not.

Proof From eqn (2.12) follows a relation

$$\int dq \psi_m^* \hat{f} \psi_n = f_n \int dq \psi_m^* \psi_n \quad (2.20)$$

and an analogous one in which n and m are interchanged,

$$\int dq \psi_n^* \hat{f} \psi_m = f_m \int dq \psi_n^* \psi_m. \quad (2.21)$$

Taking the combination (2.20)–(2.21), one finds that

$$(f_n - f_m) \int dq \psi_m^* \psi_n = \int dq \psi_m^* (\hat{f} - \hat{f}^\dagger) \psi_n = 0, \quad (2.22)$$

where use was made of the fact that $\{f_n\}$ are real and that $\hat{f}^\dagger = \hat{f}$. It then follows that

$$\int dq \psi_m^* \psi_n = 0, \quad \text{if } f_n \neq f_m.$$

□

2.3.3 Products of operators, commutators, and compatible observables

The product of two operators f and g is defined as¹¹

$$f g \psi \equiv f(g \psi).$$

¹¹ The ^ mark in front of an operator symbol will henceforth often be omitted for notational simplicity.

In general, $f g$ and $g f$ are distinct. The *commutator* between f and g is defined by

$$[f, g] \equiv f g - g f.$$

If $[f, g] = 0$, the two operators are said to *commute*. The commutators satisfy the Jacobi identity

$$[f, [g, h]] + [g, [h, f]] + [h, [f, g]] = 0.$$

In the interpretation of quantum mechanics, and in particular in the formulation of the concept of the maximum set of compatible observables, the following theorem plays an important role.

Theorem 2.2 *If two operators f and g commute, there exists an orthonormal set of states $\{\psi_n^i\}$ such that*

$$f \psi_n^i = f^i \psi_n^i; \quad g \psi_n^i = g_n \psi_n^i, \quad (2.23)$$

i.e., one can choose the simultaneous eigenstates of f and g as the base states. In other words, f and g correspond to two observables which can have definite values simultaneously, i.e., can be measured simultaneously, with an arbitrary precision.

Proof Consider an eigenstate of g , ψ_n , with eigenvalue g_n . That is, $g \psi_n = g_n \psi_n$ with a normalizable wave function ψ_n . As f and g commute, one finds that

$$g(f \psi_n) = f g \psi_n = g_n f \psi_n;$$

that is, the state $f \psi_n$, if normalizable, is again an eigenstate of g with the same eigenvalue, g_n . If $f \psi_n \propto \psi_n$, the assertion is proven, so we can assume that $f \psi_n \neq \text{const.} \psi_n$. If either $f \psi_n = 0$ or $f \psi_n \notin \mathcal{H}$ (the function $f \psi_n$ is non-normalizable), then no new eigenstates of g can be found this way. In general, however, there will be a finite number of states¹² which belong to the subspace of the eigenstates of g , with a given eigenvalue g_n ,

$$g \psi_n^i = g_n \psi_n^i : \quad i = 1, 2, \dots, s.$$

In this subspace g acts trivially as a unit operator, while f acts as

$$f \psi_n^i = F_{ij} \psi_n^j.$$

From the fact that f is Hermitian, it follows that (suppressing the index n)

$$F_{ij} = \int dq \psi^{j*} f \psi^i = \int dq (f^* \psi^{j*}) \psi^i = (\int dq \psi^{i*} f \psi^j)^* = F_{ji}^*;$$

that is, F is a Hermitian matrix. Any Hermitian matrix can be diagonalized by a unitary transformation,

$$\psi^i = U_{ij} \phi^j, \quad \phi^i = (U^{-1})_{ij} \psi^j = U_{ij}^\dagger \psi^j, \quad U^\dagger U = U U^\dagger = \mathbf{1},$$

$$U^\dagger \mathbf{F} U = \tilde{\mathbf{F}} = \begin{pmatrix} f_1 & 0 & \cdots \\ 0 & f_2 & \cdots \\ \vdots & \vdots & \ddots \\ 0 & 0 & \cdots \end{pmatrix}.$$

¹²There are systems with infinite degeneracy of the levels, a well-known example being the Landau levels of an electron moving in a plane, under the influence of a magnetic field perpendicular to the plane (Section 14.3). For simplicity, we limit ourselves here to cases with finite degrees of degeneracy.

In the new base, the operator f acts as

$$f \phi^i = f (\mathbf{U}^\dagger \psi)_i = \mathbf{U}^\dagger \mathbf{F} \mathbf{U} \phi = f_i \phi_i : \quad (2.24)$$

ϕ^i is an eigenstate of f with the eigenvalue f_i . As G_{ij} , being proportional to a unit matrix, is invariant under any unitary transformation, ϕ_n^i thus constructed are simultaneous eigenstates of f and g . In brief, we simply diagonalized the operator f in the degenerate subspace of eigenstates of the operator g , or vice versa. \square

The above discussion can be generalized to any number of operators which commute with each other. Starting from a variable, one then arrives at the maximum set of *compatible observables*, which are represented by the maximum set of mutually commuting operators, \hat{f}^I . The eigenvalues of these operators are those quantities which can be simultaneously measured with an arbitrary precision, i.e., there exists a quantum state in which all of the dynamical quantities f^I have definite values. Note that in a given system the choice of the maximum set of observables is not unique. The set of simultaneous eigenvalues \hat{f}_i^I of the maximal observables (often called simply “quantum numbers”) determine the quantum state completely.

Vice versa, Heisenberg’s uncertainty relation refers to a pair of non-commuting operators, such as two canonically conjugate variables. There are no quantum states in which these non-commuting variables simultaneously have definite values. It is not possible, independently of the technical or experimental details, to “prepare” such a state.

2.3.4 The position operator, the momentum operator, fundamental commutators, and Heisenberg’s relation

The position operator acts simply as

$$\hat{q} \psi(q, t) = q \psi(q, t),$$

i.e., by multiplication. The momentum is instead described by a differential operator

$$\hat{p} = -i\hbar \frac{\partial}{\partial q}$$

(2.25)

or, for a particle moving in three dimensions, by

$$\mathbf{p} = -i\hbar \nabla,$$

acting on the wave function.

It is an empirical fact—perhaps with a deep significance—that these fundamental rules of quantum mechanics are valid for variables in *Cartesian coordinate systems*.¹³

¹³The quantization rule in general curvilinear coordinate systems will be discussed in Section 7.8.

It follows that the canonically conjugate variables satisfy the commutation relation

$$[\hat{q}_i, \hat{p}_j] = i\hbar\delta_{ij}, \quad (2.26)$$

known as the *canonical commutation relation*. For a particle moving in three dimensions the commutation relation is

$$[x_i, p_j] = i\hbar\delta_{ij}.$$

The components of the position operator commute among each other; so do the components of \hat{p} : $[x_i, x_j] = [p_i, p_j] = 0$.

The rule (2.25) can be interpreted as a realization of de Broglie's hypothesis. In fact, according to de Broglie, to each particle of momentum p one associates a wavelength \hbar/p , where \hbar is the Planck constant. A wave with a fixed wavelength is a plane wave,

$$\psi_p(x) = e^{i2\pi x/\lambda} = e^{ipx/\hbar},$$

upon which the operator (2.25) gives a definite (numerical) value, p . A generic function can be written as a Fourier transform

$$\psi(x) = \int \frac{dp}{2\pi} c(p) e^{ipx/\hbar},$$

or as a linear combination of plane waves, and the action (2.25) can be naturally interpreted as the momentum operator, because of its linear character.

A more abstract motivation for (2.25), which in many senses is more satisfactory, will be given by studying the effects of translation on quantum states.

The operator \mathbf{p} is *Hermitian*. In fact,

$$\int d^3x \varphi^*(\mathbf{x}) [\frac{\hbar}{i} \nabla \psi(\mathbf{x})] = \int d^3x [\frac{\hbar}{i} \nabla \varphi(\mathbf{x})]^* \psi(\mathbf{x})$$

¹⁴Normalizable functions—integrable in \mathbb{R}^3 —vanish at infinity. as can be easily verified by making use of partial integration.¹⁴

2.3.5 Heisenberg's relations

With the position and momentum operators defined as above, the uncertainty relations derived in Section 2.2 by a physical argument can now be derived rigorously by using the quantum mechanical rules. Let us, in fact, demonstrate for any pair of Hermitian operators Q, P satisfying

$$[Q, P] = i\hbar,$$

the uncertainty relation (2.27) below.

We define the uncertainty of Q or of P as its dispersions

$$\Delta Q \equiv \sqrt{\langle(Q - Q_0)^2\rangle}, \quad \Delta P \equiv \sqrt{\langle(P - P_0)^2\rangle},$$

where

$$Q_0 = \langle Q \rangle = \langle \psi | Q | \psi \rangle, \quad P_0 = \langle P \rangle = \langle \psi | P | \psi \rangle$$

are their mean values in the state ψ . Define an operator

$$A = Q - Q_0 + i\alpha(P - P_0),$$

where α is any real number. By using the fact that $\langle \psi | A^\dagger A | \psi \rangle \geq 0$ for any operator A and for any state, we find an inequality

$$\langle (Q - Q_0)^2 \rangle - \alpha \hbar + \alpha^2 \langle (P - P_0)^2 \rangle \geq 0,$$

valid for any α . A quadratic form is semi-positive definite when its discriminant is semi-negative definite

$$\hbar^2 - 4(\Delta Q)^2 \cdot (\Delta P)^2 \leq 0;$$

therefore one finds that

$$\boxed{\Delta Q \cdot \Delta P \geq \frac{\hbar}{2}.} \quad (2.27)$$

2.4 The Schrödinger equation

The superposition principle implies that the time evolution of quantum systems be described by a linear equation. The fundamental equation of quantum mechanics is in fact the Schrödinger equation

$$\boxed{i\hbar \frac{\partial}{\partial t} \psi(q, t) = \hat{H}(\hat{q}, \hat{p}; t) \psi(q, t).} \quad (2.28)$$

The operator H is called the Hamiltonian. Equation (2.28) replaces the Newtonian equation of classical mechanics.

The Hamiltonian H is the quantum operator corresponding to the classical Hamiltonian, and being the operator representing the energy of the system, is Hermitian. In most cases discussed in this book, there is a simple correspondence,

$$\boxed{\hat{H}(\hat{q}, \hat{p}; t) = H(q, p; t)|_{q \rightarrow \hat{q}; p \rightarrow \hat{p} = -i\hbar \frac{\partial}{\partial q}}} \quad (2.29)$$

where $H(q, p; t)$ is the classical Hamiltonian. This rule holds for variables in Cartesian coordinates. For quantization in general curvilinear coordinates, see Section 7.8.

Note that just as the momentum operator acts as a generator of space translations, the Hamiltonian (energy operator) produces time shifts,¹⁵

$$\boxed{H \rightarrow i\hbar \frac{\partial}{\partial t}; \quad p_i \rightarrow -i\hbar \frac{\partial}{\partial x_i}.} \quad (2.30)$$

¹⁵This rule can be written as a four-vector relation $p_\mu \rightarrow i\hbar \frac{\partial}{\partial x^\mu}$. It is truly remarkable that quantum mechanics “knows” about special relativity! This fact is at the base of the successful construction of relativistic quantum mechanics and relativistic quantum field theories. Of course, the highly successful standard model of fundamental interactions—the Glashow–Weinberg–Salam theory of electro-weak interactions and quantum chromodynamics for strong interactions—is based on such a framework.

Plane waves: It is possible to give a heuristic motivation for these rule of quantum mechanics. Consider a plane wave

$$\psi_0 = \text{const. } e^{-i(\omega t - kx)},$$

representing monocromatic light with a given polarization. By applying $i\hbar \frac{\partial}{\partial t}$ to ψ_0 one gets

$$i\hbar \frac{\partial}{\partial t} \psi_0 = \hbar \omega \psi_0 = \hbar \nu \psi_0 \quad (\omega = 2\pi\nu),$$

which is just the energy of the photon, so

$$i\hbar \frac{\partial}{\partial t} \psi_0 = E \psi_0.$$

On the other hand, according to de Broglie's relation $k = \frac{2\pi}{\lambda} = \frac{p}{\hbar}$, the action of $-i\hbar \frac{\partial}{\partial x}$ gives the answer

$$-i\hbar \frac{\partial}{\partial x} \psi_0 = p \psi_0.$$

showing that it is indeed the operator representing the momentum. Moreover, the energy eigenvalue $E = h\nu$ and the momentum eigenvalue $p = \hbar/\lambda$ satisfy the relation $E = pc$, which is the correct relativistic relation between the energy and momentum of a free massless particle (photon). The equation

$$\left(\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \Delta \right) \psi = 0,$$

is, of course, the Maxwell equation in vacuum (for the vector potential in the radiation gauge), which can be re-interpreted as a relativistic Schrödinger equation.

2.4.1 More about the Schrödinger equations

Let us now consider a system with a time-independent Hamiltonian,

$$H = H(\hat{q}, \hat{p}).$$

The eigenvalue equation for the energy is

$$H\psi_n = E_n \psi_n. \quad (2.31)$$

Equation 2.31 is also known as the *Schrödinger equation*, or to distinguish from eqn (2.28), which describes the time evolution of the system, as the *time-independent Schrödinger equation*. The energy eigenvalues E_n in such systems are obviously constant. Let us all the same prove this result as follows:

$$\begin{aligned} \frac{d}{dt} \langle H \rangle_{\psi_n} &= \frac{d}{dt} E_n = \frac{d}{dt} \int dq \psi_n^* E_n \psi_n \\ &= \frac{d}{dt} \int dq \psi_n^* H \psi_n = \frac{1}{i\hbar} \int dq \psi_n^* [H, H] \psi_n = 0. \end{aligned}$$

By an entirely analogous argument, one can prove that the expectation value of any (time-independent) operator f which commutes with the Hamiltonian, in any state, is a constant

$$\frac{d}{dt}\langle f \rangle = \frac{1}{i\hbar} \langle [f, H] \rangle = 0.$$

The time dependence of an energy eigenstate—known as a stationary state—is particularly simple. By integrating the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \psi_n = H \psi_n(t) = E_n \psi_n(t),$$

one finds that

$$\psi_n(t) = e^{-iE_n t/\hbar} \psi_n(0).$$

The solution of the Schrödinger equation for a generic (not necessarily a stationary) state $|\psi\rangle$ is given by

$$|\psi(t)\rangle = e^{-iHt/\hbar} |\psi(0)\rangle;$$

the operator $U(t) = e^{-iHt/\hbar}$ describes the time evolution of a state vector. Note that this is a *formal* solution of the Schrödinger equation: it is a highly symbolic formula as in general the evolution operator $e^{-iHt/\hbar}$ might be a horribly complicated operator (it is not a simple phase!).

If, however, the expansion of the initial wave function in energy eigenstates is known:

$$\psi(0) = \sum_n a_n \psi_n, \quad a_n = \langle \psi_n | \psi(0) \rangle,$$

then the solution can be cast in an explicit form,

$$\psi(t) = e^{-iHt/\hbar} \sum_n a_n \psi_n = \sum_n a_n e^{-iE_n t/\hbar} \psi_n(0).$$

During the evolution of the system, the expectation value of various observables

$$\langle O \rangle_\psi \equiv \langle \psi(t) | O | \psi(t) \rangle \equiv \int dq \psi^*(t) O \psi(t)$$

will in general change with time. In fact¹⁶

$$\frac{d}{dt} \langle O \rangle_\psi = \langle \psi | \left(\frac{\partial}{\partial t} O + \frac{1}{i\hbar} [O, H] \right) | \psi \rangle. \quad (2.32)$$

The observable satisfying

$$\frac{d}{dt} \langle O \rangle_\psi = 0 \quad (2.33)$$

for any state is said to be *conserved*. A time-independent ($(\partial/\partial t)O = 0$) and conserved operator necessarily commutes with the Hamiltonian.

It is also interesting to note that a time-independent observable, even if not conserved, always satisfies

$$\frac{d}{dt} \langle O \rangle_{\psi_n} = 0,$$

where ψ_n is a stationary state.

¹⁶Note the resemblance between eqn (2.32) and the equation for dO/dt in classical mechanics, written in terms of Poisson brackets: $dO/dt = \partial O/\partial t + \{O, H\}$.

2.4.2 The Heisenberg picture

It is possible to describe the time evolution in quantum mechanics in a way more closely related to classical evolution, where one speaks about evolution of the dynamical quantities, rather than of the states. Dynamical quantities are represented by self-adjoint operators (see Section 7.3.1), defined through their matrix elements. At a generic time t , the matrix elements of a dynamical quantity A are given by

$$\langle \varphi(t) | A | \psi(t) \rangle = \langle \varphi(0) | e^{iHt/\hbar} A e^{-iHt/\hbar} | \psi(0) \rangle.$$

This suggests an alternative description of the evolution: the states are fixed in time and the dynamical quantities vary, with

$$A_H(t) = e^{iHt/\hbar} A(0) e^{-iHt/\hbar}. \quad (2.34)$$

Such a representation is called the *Heisenberg picture* and will be studied in more detail in Section 7.5. Here we note that from definition (2.34), it follows that

$$i\hbar \frac{dA_H}{dt} = i\hbar \frac{\partial A_H}{\partial t} + [A_H, H], \quad (2.35)$$

where a possible parametric dependence on t has been added (the partial derivative in eqn (2.35)). The similarity with eqn (2.32) is obvious, even if the meaning of each term is different.

The Schrödinger and Heisenberg pictures coincide at $t = 0$. An observable which depends explicitly on t is understood as an operator $A_S(t)$ in the Schrödinger representation, as for example $q t^2$. In this case relation (2.34) reads

$$A_H(t) = e^{iHt/\hbar} A_S(t) e^{-iHt/\hbar},$$

and its derivative reproduces eqn (2.35), as can be easily checked.

2.5 The continuous spectrum

Up to now the eigenvalues have been assumed to be discrete, for simplicity. Certain operators (for instance, the position operator, or the energy of an unbound electron, etc.) possess a continuous spectrum of eigenvalues. Postponing a more careful discussion to Section 7.3, let us generalize the forgoing discussion to include these more general cases.

The eigenvalue equation takes the form

$$\hat{f} \psi_f(q) = f \psi_f(q),$$

where now f can take a continuous range of values. A generic function can be expanded in the base of such eigenfunctions as

$$\psi(q) = \int df c(f) \psi_f(q) \quad (2.36)$$

(cf. eqn (2.13)). The fundamental postulate of quantum mechanics, eqn (2.14), can be generalized to the statement that the probability of

finding a result between f and $f + df$ is given by

$$dP = |c(f)|^2 df . \quad (2.37)$$

As the total probability must be unity, we must require that

$$\int df |c(f)|^2 = 1 ,$$

while the normalization condition for $\psi(q)$ is

$$\int dq \psi(q)^* \psi(q) = 1 .$$

The orthonormality relation is subtler for the case of the continuous spectrum. Following the same steps as in eqn (2.22), we find that

$$(f - f') \langle f' | f \rangle = (f - f') \int dq \psi_{f'}(q)^* \psi_f(q) = 0 ,$$

and therefore

$$\langle f' | f \rangle = 0, \quad f' \neq f .$$

Considered as a function of f' , $\langle f' | f \rangle$ must have a peculiar property: it is zero everywhere except at $f' = f$. If $\langle f | f \rangle$ were a finite number, however, we would conclude that

$$\langle \psi | \psi \rangle = \int df \int df' c(f)^* c(f') \langle f' | f \rangle = \int |c(f)|^2 \int df' \langle f' | f \rangle = 0 ,$$

which does not make sense. We must therefore require $\langle f | f \rangle = \infty$, so that

$$\int df' \langle f' | f \rangle = 1 ,$$

where the normalization is chosen for convenience.

2.5.1 The delta function

The “generalized function” or “distribution” $\delta(x)$ having precisely these properties was introduced by Dirac. The delta function is defined by

$$\delta(x) = 0 ; \quad x \neq 0; \quad \delta(0) = \infty ;$$

and

$$\int_a^b dx \delta(x) g(x) = \begin{cases} g(0), & \text{if } a < 0 < b; \\ 0, & \text{otherwise,} \end{cases}$$

for any function $g(x)$ continuous at $x = 0$.

It follows from the definition that

$$\int_a^b dx \delta(x - c) g(x) = \begin{cases} g(c), & \text{if } a < c < b; \\ 0, & \text{otherwise.} \end{cases}$$

Some of the most useful properties are:

$$\begin{aligned}
 \delta(-x) &= \delta(x); & \delta(ax) &= \frac{1}{|a|} \delta(x); \\
 g(x)\delta(x-y) &= g(y)\delta(x-y); & x\delta(x) &= 0; \\
 \frac{d}{dx}\theta(x) &= \delta(x); & \theta(x) &= \begin{cases} 1, & \text{if } x \geq 0; \\ 0, & \text{if } x < 0; \end{cases} \\
 \delta(g(x)) &= \sum_{i=1}^r \frac{1}{|g'(x_i)|} \delta(x - x_i), & g(x_i) &= 0, i = 1, 2, \dots, r.
 \end{aligned} \tag{2.38}$$

The delta function is an even function of its argument, and thus

$$\int_0^\infty dx \delta(x) g(x) = \frac{1}{2} g(0).$$

The delta function can be defined as a limit of ordinary functions. Some examples are (bearing in mind that the limit is taken outside the integration):

$$\delta(x) \equiv \lim_{\epsilon \rightarrow 0} \frac{1}{\sqrt{\pi\epsilon}} e^{-x^2/\epsilon^2}; \quad \delta(x) \equiv \lim_{L \rightarrow \infty} \frac{\sin(Lx)}{\pi x}; \tag{2.39}$$

$$\delta(x) \equiv \lim_{L \rightarrow \infty} \frac{\sin^2(Lx)}{\pi L x^2}; \quad \delta(x) = \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \frac{\epsilon}{\epsilon^2 + x^2}; \tag{2.40}$$

$$\frac{1}{x - i\epsilon} = \frac{\mathcal{P}}{x} + \pi i \delta(x),$$

where \mathcal{P} is Cauchy's principal value. In the last formula, the limit $\lim_{\epsilon \rightarrow 0^+}$ is understood.

Let us prove the second of eqns (2.39). Suppose $a < 0 < b$, then

$$\begin{aligned}
 \lim_{L \rightarrow \infty} \int_a^b dx \frac{\sin(Lx)}{\pi x} f(x) &= \lim_{L \rightarrow \infty} [f(0) \int_a^b dx \frac{\sin(Lx)}{\pi x} + O(\frac{1}{L})] \\
 &= \frac{f(0)}{\pi} \int_{-\infty}^{\infty} dz \frac{\sin z}{z} = f(0).
 \end{aligned}$$

The last integral can be done by the method of integration in the complex plane. The proof of the first of eqns (2.40) is analogous.

A very useful formula is the following representation of the delta function

$$\int_{-\infty}^{\infty} dx e^{ix(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} = 2\pi \delta(\mathbf{k} - \mathbf{k}'), \tag{2.41}$$

and its three-dimensional analogue,

$$\int d\mathbf{r} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} = (2\pi)^3 \delta^3(\mathbf{k} - \mathbf{k}').$$

(2.42)

These can be easily proven by using the second of eqns (2.39). An important application of eqn (2.41) is the proof of the formula for the inverse Fourier transform. If

$$F(x) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{ikx} \tilde{F}(k),$$

then the *Fourier transform* of $F(x)$, $\tilde{F}(k)$, is given by

$$\tilde{F}(k) = \int_{-\infty}^{\infty} dx e^{-ikx} F(x).$$

This can be proven easily by using eqn (2.41).

2.5.2 Orthogonality

The orthogonality condition in the case of continuous eigenvalues thus takes the form

$$\int dq \psi_f^*(q) \psi_{f'}(q) = \delta(f - f')$$

(2.43)

(cf. eqn (2.15)). The expansion coefficient $c(f)$ in eqn (2.36) can be found, as in the case of discrete spectra, by projecting the wave function onto one of the eigenstates,

$$c(f) = \int df \psi_f(q)^* \psi(q), \quad (2.44)$$

as can be checked immediately by using eqn (2.43).

2.5.3 The position and momentum eigenstates; momentum as a translation operator

A *position eigenstate* is given by

$$\psi_{\mathbf{r}_0}(x) = \delta^3(\mathbf{r} - \mathbf{r}_0) = \delta(x - x_0) \delta(y - y_0) \delta(z - z_0) :$$

it represents a particle positioned at \mathbf{r}_0 , as $x \psi_{\mathbf{r}_0}(x) = x_0 \psi_{\mathbf{r}_0}(x)$, etc., thanks to the property of the delta function. Clearly the ensemble of such states satisfies both the orthonormality and completeness relations.

The eigenstates of the momentum operator

$$\hat{\mathbf{p}} = -i\hbar \nabla$$

are given by

$$\psi_{\mathbf{p}_0}(\mathbf{r}) = \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i\mathbf{p}_0 \cdot \mathbf{r}}{\hbar}}, \quad (2.45)$$

where \mathbf{p}_0 is the eigenvalue (i.e., numerical vector). $\psi_{\mathbf{p}_0}$ satisfies the eigenvalue equation

$$\hat{\mathbf{p}} \psi_{\mathbf{p}_0} = \mathbf{p}_0 \psi_{\mathbf{p}_0}.$$

In general, the momentum eigenvalue is continuous: the orthonormality relation reads

$$\int d\mathbf{r} \psi_{\mathbf{p}}^*(\mathbf{r}) \psi_{\mathbf{p}'}(\mathbf{r}) = \delta^3(\mathbf{p} - \mathbf{p}') ;$$

(with a convenient normalization), while the completeness of the states $\{\psi_{\mathbf{p}}\}$ is expressed as

$$\int d\mathbf{p} \psi_{\mathbf{p}}(\mathbf{r}) \psi_{\mathbf{p}}^*(\mathbf{r}') = \delta^3(\mathbf{r} - \mathbf{r}') . \quad (2.46)$$

Just as in classical mechanics momentum acts as the generator of the canonical transformation for space translations, the momentum operator in quantum mechanics is the generator of spatial translations. In fact, it is easy to prove that for any operator H , the relation

$$H(\mathbf{r} + \mathbf{r}_0, \mathbf{p}) = e^{i\mathbf{p}\cdot\mathbf{r}_0/\hbar} H(\mathbf{r}, \mathbf{p}) e^{-i\mathbf{p}\cdot\mathbf{r}_0/\hbar} \quad (2.47)$$

holds.

Proof To prove eqn (2.47), it is sufficient to consider the following one-dimensional problem: let us compute

$$G(x, \alpha) \equiv e^{\frac{i p \alpha}{\hbar}} F(x) e^{\frac{-i p \alpha}{\hbar}} ; \quad p \equiv -i\hbar \frac{d}{dx} .$$

Taylor-expand $G(x, \alpha)$ around $\alpha = 0$. $G(x, 0) = F(x)$ obviously. The first derivative with respect to α is

$$\frac{d}{d\alpha} G(x, \alpha)|_{\alpha=0} = e^{\frac{i p \alpha}{\hbar}} \left[\frac{ip}{\hbar}, F(x) \right] e^{\frac{-i p \alpha}{\hbar}}|_{\alpha=0} = F'(x) ,$$

where we have used the commutation relation

$$\left[\frac{ip}{\hbar}, F(x) \right] = \left[\frac{d}{dx}, F(x) \right] = \frac{d}{dx} \cdot F(x) - F(x) \frac{d}{dx} = F'(x) .$$

Analogously

$$\frac{d^2}{d\alpha^2} G(x, \alpha)|_{\alpha=0} = F''(x) ,$$

and so on. One thus finds that

$$G(x, \alpha) = \sum_n \frac{\alpha^n}{n!} \frac{d^n}{d\alpha^n} G(x, \alpha)|_{\alpha=0} = \sum_n \frac{\alpha^n}{n!} \frac{d^n}{dx^n} F(x) = F(x + \alpha) .$$

Let us apply eqn (2.47) to a Hamiltonian which is invariant under spatial translations. It then follows that

$$H(\mathbf{r} + \mathbf{r}_0, \mathbf{p}) = H(\mathbf{r}, \mathbf{p}) ,$$

$$H(\mathbf{r}, \mathbf{p}) = e^{i\mathbf{p}\cdot\mathbf{r}_0/\hbar} H(\mathbf{r}, \mathbf{p}) e^{-i\mathbf{p}\cdot\mathbf{r}_0/\hbar} .$$

Expanding the right-hand side in \mathbf{r}_0 to first order, one finds that

$$[p_i, H] = 0 ;$$

that is, if the system is invariant under spatial translations the momentum operator commutes with the Hamiltonian, and vice versa. It is a conserved operator (eqn (2.33)). This generalizes naturally the well known result from classical mechanics.

Finally, let us note that the momentum and position eigenstates found here are consistent with Heisenberg's uncertainty relation. Indeed, in the state $\psi_{\mathbf{p}_0}$ (eqn (2.45)) the momentum is well-defined, but the position of the particle is indefinite, as $|\psi_{\mathbf{p}_0}|^2 = \text{const}$. Vice versa, in the position eigenstate $\psi_{\mathbf{r}_0}(x) = \delta^3(\mathbf{r} - \mathbf{r}_0)$, the particle position is perfectly known, but its momentum distribution is flat:

$$\delta^3(\mathbf{r} - \mathbf{r}_0) = \frac{1}{(2\pi\hbar)^3} \int d^3\mathbf{p} e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}_0)/\hbar} a(\mathbf{p}); \quad a(\mathbf{p}) = 1 :$$

it contains no information about the momentum.

2.6 Completeness

By re-substituting eqn (2.44) into eqn (2.36), one finds that

$$\psi(q) = \int dq' \psi(q') \left[\int df \psi_f^*(q') \psi_f(q) \right] ;$$

the consistency requires that

$$\int df \psi_f(q) \psi_f^*(q') = \delta(q - q'). \quad (2.48)$$

Note that the right-hand side of this relation is somewhat symbolic: for instance for a particle in three dimensions it must be replaced by a three-dimensional delta function

$$\delta(q - q') \rightarrow \delta^3(\mathbf{r} - \mathbf{r}') \equiv \delta(x - x') \delta(y - y') \delta(z - z') .$$

Equation (2.48) is known as the *completeness relation* and states that any state ψ can be expressed as a linear combination of the eigenstates $\{\psi_f\}$; in other words, the eigenfunctions $\{\psi_f\}$ form a complete set. If the operator under consideration has both discrete and continuous spectra, only the sum of the eigenfunctions $\{\psi_n, \psi_f\}$ form such a complete set, and the completeness relation must be understood as

$$\psi(q) = \sum_n c_n \psi_n(q) + \int df c(f) \psi_f(q)$$

or

$$|\psi\rangle = \sum_n |n\rangle \langle n|\psi\rangle + \int df |f\rangle \langle f|\psi\rangle$$

for any $|\psi\rangle$. These relations are known also as *Parseval's relation*. It is often symbolically expressed as

$$\sum_n |n\rangle \langle n| = \sum_n \mathcal{P}_n = \mathbf{1} ,$$

where \mathcal{P}_n is the projection operator onto the eigenstate $|n\rangle$.

The completeness relation is an indispensable part of the logic of the quantum mechanical laws. For any variable f , the corresponding Hermitian operator \hat{f} has a *spectral decomposition*,

$$\hat{f} = \sum_n \hat{f} |n\rangle \langle n| = \sum_n f_n \mathcal{P}_n .$$

A measurement made of f in any state (completeness)

$$|\psi\rangle = \sum_n c_n |n\rangle$$

gives one of its eigenvalues, f_n , with probability

$$P_n = |c_n|^2 = |\langle n|\psi\rangle|^2 = \langle \mathcal{P}_n \rangle_\psi ,$$

leaving the system in the projected state,

$$\mathcal{P}_n |\psi\rangle = c_n |n\rangle \sim |n\rangle .$$

The total probability for different outcomes is given, by virtue of the completeness relation, by

$$\sum_n P_n = \sum_n \langle \psi | n \rangle \langle n | \psi \rangle = ||\psi|| = 1 .$$

Chapter summary

- The quantization rule is given by

$$H \rightarrow \hat{H}(\{\hat{q}_i\}, \{\hat{p}_i\}; t) = H(\{q_i\}, \{p_i\}; t)|_{q_i \rightarrow \hat{q}_i = q_i; p_i \rightarrow \hat{p}_i = -i\hbar \frac{\partial}{\partial q_i}} ;$$

$$p_i \rightarrow -i\hbar \frac{\partial}{\partial x_i} .$$

- Time evolution of an undisturbed quantum system is described by the Schrödinger equation, $i\hbar \frac{\partial}{\partial t} \psi = H \psi$;
- An experiment for finding out the value of an observable f in a state $|\psi\rangle = \sum_n c_n |\psi_n\rangle$, where $|\psi_n\rangle$ is the n th eigenstate of the corresponding Hermitian operator \hat{f} , yields one of its eigenvalues f_n , with probability

$$P_n = |c_n|^2 = |\langle \psi_n | \psi \rangle|^2 ,$$

leaving the system in the projected state ($\mathcal{P}_n = |\psi_n\rangle \langle \psi_n|$)

$$\mathcal{P}_n |\psi\rangle = c_n |\psi_n\rangle \sim |\psi_n\rangle .$$

Problems

- (2.1) (a) Prove the following relations:

$$(f^\dagger)^\dagger = f; \quad (fg)^\dagger = g^\dagger f^\dagger;$$

$$[f, gh] = g[f, h] + [f, g]h,$$

$$[fg, h] = f[g, h] + [f, h]g.$$

- (b) Prove that if f and g are Hermitian so are $fg + gf$ and $i[f, g]$.
- (c) Verify the properties of the delta function (2.38).
- (d) Verify that the three-dimensional delta function can be written as
- $$\delta^3(\mathbf{r} - \mathbf{r}_0) = \frac{1}{r^2} \delta(r - r_0) \delta(\cos \theta - \cos \theta_0) \delta(\phi - \phi_0)$$
- in spherical coordinates.
- (e) Show that for any operator A , the operator $A A^\dagger$ has a positive semi-definite expectation value in any state,

$$\langle AA^\dagger \rangle \geq 0.$$

- (f) Show that if $[A, B] = c$ is a c -number, then

$$e^{\zeta A} B e^{-\zeta A} = B + c \zeta.$$

- (2.2) Consider a two-state system

$$H = \begin{pmatrix} E_0 & -\eta \\ -\eta & E_0 \end{pmatrix}.$$

- (a) Can η be a complex number? ;
 (b) Determine the eigenvalues of H ;
 (c) At $t = 0$, the system is in the state

$$|\psi(0)\rangle = \frac{|1\rangle + i|2\rangle}{\sqrt{2}}.$$

Determine the probabilities $P_1(t)$ or $P_2(t)$, that at time t the system can be found in the state $|1\rangle$ or $|2\rangle$. Make a sketch of $P_1(t)$ e $P_2(t)$ as functions of t .

- (2.3) A two-level system (a qubit) is described by the Hamiltonian

$$H = E_0 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Consider the measurement of two variables described by the operators A and B ,

$$A = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad B = \begin{pmatrix} 2 & -\sqrt{2}i \\ \sqrt{2}i & 1 \end{pmatrix}$$

in this system.

- (a) Verify that the eigenvalues of A are ± 1 and find its eigenvectors. Find the eigenvalues and eigenvectors for B .

- (b) Are the observables A and B compatible? Are they conserved?

- (c) Suppose that the observation of A has resulted in $A = 1$. What would be the results for B , and what would be the relative probabilities, if such a measurement is made immediately after that of A ?

- (d) The system is subjected to a second measurement of A . What would be the probability of finding the result $A = 1$, in the following different cases? (See Fig. 2.4.)

- (i) The observation on B is *not* made, and the second measurement of A is made immediately after the first measurement of (c).

- (ii) The observation on B is *not* made, and the second measurement of A is made after a time interval t .

- (iii) The observation on B is made, and the result is known to have been b_1 (the larger eigenvalue of B).

- (iv) The observation on B is made, but the person who measures A immediately after that of B is unaware of the result on B .

- (2.4) A three-state system is described by a Hamiltonian

$$H = E_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} - \frac{\varepsilon}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}.$$

- (a) Compute the eigenvalues of H and the eigenstates $|a\rangle, |b\rangle, |c\rangle$ corresponding to the ground state, and the first and the second excited states, expressing the result in terms of

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}; \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}; \quad |3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix};$$

- (b) Verify that the Hamiltonian H commutes with the operator

$$\Pi = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}; \quad \Pi^2 = 1.$$

Discuss the relevance of this for the results of (a).

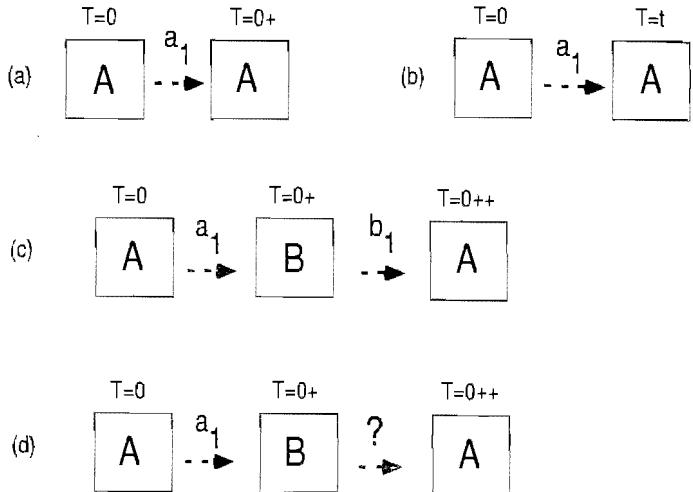


Fig. 2.4 Four different situations in Problem 2.3 (d)

- (c) Write the states $|1\rangle, |2\rangle, |3\rangle$ in terms of the energy eigenstates.
 (d) The system is in the state $|1\rangle$ at time $t = 0$. Find the state $|\psi(t)\rangle$ at time t , in terms of the states $|1\rangle, |2\rangle, |3\rangle$. Find the probability $P_2(t)$ of finding the state in $|2\rangle$ at time t and make a sketch of $P_2(t)$ as a function of t .
- (2.5) Consider a three-state system. Suppose that the Hamiltonian has non-degenerate eigenvalues. In the base of Hamiltonian eigenstates two Hermitian operators A and B are given by

$$A = \begin{pmatrix} 0 & 0 & -ia \\ 0 & 0 & 0 \\ ia & 0 & 0 \end{pmatrix}; \quad B = \begin{pmatrix} b & 0 & 0 \\ 0 & 0 & b \\ b & 0 & 0 \end{pmatrix};$$

with a, b real and positive.

- (a) Compute the eigenvalues and the eigenvectors of A .
 (b) Compute the eigenvalues and the eigenvectors of B .
 (c) At time $t = 0$ the measurement of A has given its maximum eigenvalue. What is the probability of finding the maximum possible result for B if the measurement of B is performed immediately after that of A ? Discuss the relevance of this on the results of (a).
 (d) Would the probability of finding the same maximum eigenvalue of B would be the same as in (c), if the measurement of B were made at a generic time $t > 0$?

Numerical analyses

- (2.1) Solve Problem 2.3 using Mathematica. Write a simulation program for the proposed set of measurements. In a finite number of measurements,

the outcomes will be distributed with a binomial distribution: compare the results of the simulation with the expected distribution.

Roughly speaking, the wave packet thus moves according to the classical equations of motion.

This is a very reasonable and comfortable result: after all, we believe that classical mechanics must somehow be recovered in an appropriate limit, and Ehrenfest's theorem can be thought of as one of those results in quantum mechanics which reflect the Newtonian physics incorporated within it.

It might even be tempting to think of the wave packet as representing a classical particle, with the position and momentum somewhat blurred at the atomic level by quantum fluctuations. Or one could take an even bolder step and suggest that $|\psi|^2$ represents a sort of matter distribution (Schrödinger)?

Any kind of “matter” interpretation of wave packets such as these *is incorrect*. A wave function represents the probability amplitude. A wave packet diffuses and easily splits, for example, passing through a potential barrier. On the other hand, it is an experimental fact that an electron never splits into fragments passing through “a double slit”; neither does a photon having an intermediate polarization direction split: it *either* chooses to pass *or* not pass through a polarizer. The probabilistic interpretation of the split wave packet is forced upon us by observational facts.

3.1.3 Current density and conservation of probability

$|\psi(\mathbf{r})|^2 \equiv \rho$ represents the (probability) density of the particle. A quantity closely related to it is the (probability) current density, which is the measure of the flux. In fact, the Schrödinger equation tells us that

$$\begin{aligned} \frac{\partial}{\partial t} |\psi|^2 &= \psi^* \frac{\partial}{\partial t} \psi + \left(\frac{\partial}{\partial t} \psi^* \right) \psi = \frac{1}{i\hbar} [\psi^* H \psi - (H^* \psi^*) \psi] \\ &= \frac{1}{i\hbar} \left[\psi^* \left(-\frac{\hbar^2 \nabla^2}{2m} \psi \right) - \left(-\frac{\hbar^2 \nabla^2}{2m} \psi^* \right) \psi \right] \\ &= \frac{1}{i\hbar} \left\{ \nabla \cdot \left[\psi^* \left(-\frac{\hbar^2 \nabla}{2m} \psi \right) \right] + \nabla \cdot \left[\left(\frac{\hbar^2 \nabla}{2m} \psi^* \right) \psi \right] \right\} = -\nabla \cdot \mathbf{j} \end{aligned}$$

where

$$\mathbf{j} = \frac{i\hbar}{2m} \{ (\nabla \psi^*) \psi - \psi^* \nabla \psi \},$$

i.e.,

$$\frac{\partial}{\partial t} \rho + \nabla \cdot \mathbf{j} = 0 : \quad (3.3)$$

the continuity equation. If the above equation is integrated over a finite volume, V , a relation

$$\frac{\partial}{\partial t} \int_V d^3 \mathbf{r} |\psi|^2 = - \oint_{\partial V} dS \mathbf{n} \cdot \mathbf{j}, \quad (3.4)$$

(Gauss' theorem) follows, which allows us to interpret \mathbf{j} as the probability flux into or out of the volume. Equations (3.3) and (3.4) thus represent the conservation of the total probability (known as *unitarity*).

For a plane wave (a momentum eigenstate)

$$\psi_{\mathbf{p}} = e^{-\frac{i}{\hbar}(Et - \mathbf{p} \cdot \mathbf{r})},$$

the current density is

$$\mathbf{j} = \frac{\mathbf{p}}{m} = \mathbf{v} :$$

equal to the classical velocity.

3.1.4 The virial and Feynman–Hellman theorems

Theorem 3.2 The virial theorem

The expectation values of the kinetic and potential energy terms in a stationary state satisfy the relation

$$2 \left\langle \psi_n \left| \frac{\mathbf{p}^2}{2m} \right| \psi_n \right\rangle = \langle \psi_n | \mathbf{r} \cdot \nabla V | \psi_n \rangle. \quad (3.5)$$

(cf. eqn (20.23)).

Proof The virial theorem in classical mechanics (20.23) is about the time average over many periods of the kinetic and potential terms of the Hamiltonian. The theorem here, eqn (3.5), concerns the *quantum average* of the corresponding operators. To prove it, consider the expectation value of the commutator (writing things in one dimension for simplicity)

$$[xp, H] = \left[xp, \frac{p^2}{2m} + V(x) \right] = i\hbar \left(2 \frac{p^2}{2m} - x V' \right)$$

in a stationary state ψ_n . The first term vanishes because

$$\langle \psi_n | [xp, H] | \psi_n \rangle = \langle \psi_n | xp | \psi_n \rangle E_n - E_n \langle \psi_n | xp | \psi_n \rangle = 0.$$

The theorem,

$$2 \left\langle \psi_n \left| \frac{p^2}{2m} \right| \psi_n \right\rangle = \langle \psi_n | x V' | \psi_n \rangle$$

follows. □

Theorem 3.3 The Feynman–Hellman theorem

The dependence of an energy eigenvalue on a parameter g which appears in the potential $V(g)$ is given by

$$\frac{\partial E_n}{\partial g} = \left\langle \frac{\partial V}{\partial g} \right\rangle_n, \quad (3.6)$$

namely, by the expectation value of $\frac{\partial V}{\partial g}$ in the corresponding eigenstate.

3

The Schrödinger equation

In quantum mechanics the dynamics is described by the Schrödinger equation. We first discuss the general properties of the Schrödinger equation and then proceed to illustrate how the quantum mechanical laws introduced in the previous chapter work in concrete physical situations. Both the bound-state problems and scattering processes are analyzed, mainly through various examples of one-dimensional systems.

3.1 General properties

Let us define the general boundary conditions for solving the Schrödinger equation, discuss a number of important theorems involving the expectation values of some operators, and introduce the key concept of quantum mechanics: (probability-) density and current density, and probability conservation.

3.1.1 Boundary conditions

The three-dimensional time-independent Schrödinger equation reads

$$H\psi = E\psi,$$

where

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) = -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}). \quad (3.1)$$

It is a second-order differential equation and requires for its solution two boundary conditions, which are determined by the physical requirements for each problem. In agreement with the interpretation of $|\psi|^2$ as the probability density, we shall require ψ to be continuous everywhere. The continuity of the first derivative of ψ follows from the Schrödinger equation itself. For simplicity, consider a one-dimensional case,

$$-\frac{\hbar^2}{2m}\psi''(x) = (E - V(x))\psi(x).$$

Integrating both sides over the interval $[x_0 - \epsilon, x_0 + \epsilon]$, one has

$$\psi'(x_0 + \epsilon) - \psi'(x_0 - \epsilon) \simeq 2\epsilon \frac{2m}{\hbar^2} (E - V(x_0)) \psi(x_0) \rightarrow 0,$$

if the potential is finite at $x = x_0$. It follows that ψ' together with ψ must be continuous everywhere, as long as the potential remains finite.

3.1 General properties	49
3.2 One-dimensional systems	53
3.3 Potential wells	58
3.4 The harmonic oscillator	63
3.5 Scattering problems and the tunnel effect	71
3.6 Periodic potentials	80
Guide to the Supplements	84
Problems	85
Numerical analyses	87

There are exceptions to this general rule, when the potential has some singular behaviors. See Section 3.5.2 for the condition on the first derivative of the wave function in the presence of a delta function potential.

From the fact that

$$\langle \mathbf{p}^2 \rangle \geq 0 ,$$

(note that the expectation value of an operator of the form $A^\dagger A$ is always semi-positive definite) it follows that E_n satisfies

$$E_n > V_{\min} , \quad (3.2)$$

where V_{\min} is the minimum of the potential. *There cannot be any energy eigenstates with energy less than the minimum of the potential.*

Suppose that $V(\mathbf{r}) \rightarrow 0$ for $|\mathbf{r}| \rightarrow \infty$, but that the potential can be negative in some region of finite \mathbf{r} . All the energy eigenstates with $E < 0$ correspond to states in the discrete spectrum (bound states).

The value of the wave function is determined from the Schrödinger equation, and as a consequence the wave function in general does not vanish in the region where classically the particle cannot go, i.e., where $E < V(\mathbf{r})$. It follows from this simple general fact that the particle has a non-vanishing probability of penetrating through a finite potential barrier (the tunnel effect), which is one of the most characteristic quantum effects, to which we shall return repeatedly. See Figure 3.1.

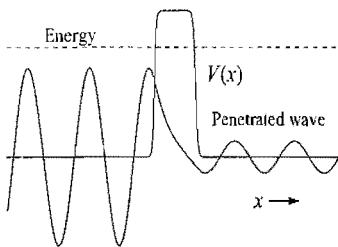


Fig. 3.1 The tunnel effect. For E less than $\frac{2}{3}V_{\max}$, the transmitted wave would have much too small an amplitude to be visible in the figure.

3.1.2 Ehrenfest's theorem

Consider the motion of a wave packet. The Hamiltonian is given by eqn (3.1). The following theorem by Ehrenfest holds for the expectation values of the position and momentum operators.

Theorem 3.1 *The expectation values of \mathbf{r} , \mathbf{p} , and the derivatives of the potential $V(\mathbf{r})$ satisfy the “Newtonian” equations*

$$\frac{d}{dt} \langle m\mathbf{r} \rangle = \langle \mathbf{p} \rangle ; \quad \frac{d}{dt} \langle \mathbf{p} \rangle = -\langle \nabla V \rangle .$$

Proof The expectation values of a generic time-independent operator satisfy

$$i\hbar \frac{d}{dt} \langle O \rangle = \langle [O, H] \rangle .$$

¹Note that $[AB, C] = A[B, C] + [A, C]B$; $[A, BC] = B[A, C] + [A, B]C$ for any A , B , and C .

For $O = m\mathbf{r}$ the commutator is¹

$$[m\mathbf{r}, H] = \left[m\mathbf{r}, \frac{\mathbf{p}^2}{2m} \right] = i\hbar\mathbf{p} ,$$

where use was made of $[\mathbf{x}, p_x^2] = 2p_x[\mathbf{x}, p_x] = 2i\hbar p_x$, etc., as well as the fact that $[\mathbf{r}, V(\mathbf{r})] = 0$. For $O = \mathbf{p}$, the needed commutator is $[\mathbf{p}, V(\mathbf{r})] = -i\hbar\nabla V$.

Proof The proof is not as trivial as it might look at first sight, though it is quite straightforward:

$$\begin{aligned} \frac{\partial}{\partial g} \int \psi_n^* H \psi_n &= \int \psi_n^* \frac{\partial V}{\partial g} \psi_n + \int \psi_n^* H \frac{\partial}{\partial g} \psi_n + \int \left[\frac{\partial}{\partial g} \psi_n^* \right] H \psi_n \\ &= \left\langle \frac{\partial V}{\partial g} \right\rangle_n + E_n \frac{\partial \|\psi_n\|^2}{\partial g} = \left\langle \frac{\partial V}{\partial g} \right\rangle_n , \end{aligned}$$

where the fact that $\langle \psi_n | \psi_n \rangle = 1$ for any g has been used. The theorem is valid if the external parameter varies slowly with time, in which case it describes the adiabatic change of the energy level.

□

3.2 One-dimensional systems

The Schrödinger equation for a particle which moves in a one-dimensional potential is given by

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \psi(x) = E \psi(x) . \quad (3.7)$$

The study of this equation is an important theoretical laboratory where the working of quantum mechanics can be explored and its ideas tested. However, interest in these one-dimensional problems should not be thought to be a purely academic one: there are real three-dimensional problems which effectively reduce to one-dimensional ones, as in the case of a potential which depends only on one of the variables,

$$V = V(x, y, z) .$$

By the substitution of a factorized form $\psi(x, y, z) = \psi(x)\phi(y)\eta(z)$ the problem reduces to

$$\begin{aligned} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \psi(x) &= E_1 \psi(x); \\ -\frac{\hbar^2}{2m} \frac{d^2}{dy^2} \phi(y) &= E_2 \phi(y); \\ -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} \eta(z) &= E_3 \eta(z); \\ E &= E_1 + E_2 + E_3 . \end{aligned}$$

The first of these is precisely the one-dimensional Schrödinger equation (the others being free one-dimensional Schrödinger equations).

Another important case in which the equation become effectively one-dimensional is the problem of a particle moving in a spherically symmetric potential $V = V(r)$, in three dimensions (see Section 6.1.) By separating the variables in spherical coordinates as

$$\psi(\mathbf{r}) = \frac{\chi(r)}{r} \Phi(\theta, \phi) ,$$

we see that the radial function $\chi(r)$ satisfies the one-dimensional Schrödinger equation,

$$\frac{d^2\chi}{dr^2} + \left[\frac{2m}{\hbar^2} (E - V_{\text{eff}}(r)) \right] \chi = 0 ,$$

where

$$V_{\text{eff}}(r) = V(r) + \frac{\ell(\ell+1)\hbar^2}{2mr^2}, \quad r \geq 0 . \quad (3.8)$$

The second term in $V_{\text{eff}}(r)$ obviously represents the centrifugal potential. As the regularity of the wave function requires $\chi(0) = 0$, the problem is equivalent to that of a particle moving on a half line $r \geq 0$ (or with $V_{\text{eff}}(r) = \infty$ for $r < 0$ and with eqn (3.8) for $r \geq 0$).

3.2.1 The free particle

For a free particle ($V = 0$) the Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\psi'' = E\psi ,$$

or

$$\psi'' = -k^2\psi, \quad k = \sqrt{\frac{2mE}{\hbar^2}} . \quad (3.9)$$

For $E \geq 0$, eqn (3.9) has two solutions which are bounded, though non-normalizable:

$$e^{\pm ikx}, \quad E = \frac{k^2\hbar^2}{2m} .$$

Each positive energy level is therefore doubly degenerate, corresponding to particles traveling towards right and left. A general solution is of the form,

$$\psi = Ae^{ikx} + Be^{-ikx} ,$$

and the corresponding time-dependent solution is

$$\psi(x, t) = e^{-iEt/\hbar}(Ae^{ikx} + Be^{-ikx}) .$$

For $E < 0$, the solution is $\psi \propto \exp \pm |k|x$, unbounded and having an exponential growth, hence the values $E < 0$ are excluded from the spectrum.

Another simple way to see this is to note that the Hermitian momentum operator has the spectrum $-\infty < p < \infty$. From the relation $E = p^2/2m$ it follows that $E \geq 0$.

In this case, the completeness of the energy eigenstates reduces to the well-known fact that any square-integrable function (L^2) has a Fourier transform of the form

$$f(x) = \int_{-\infty}^{\infty} dq \tilde{f}(q) e^{iqx} = \int_0^{\infty} dk \tilde{f}(k) e^{ikx} + \int_0^{\infty} dk \tilde{f}(-k) e^{-ikx} .$$

An interesting system is that of a free particle moving in a space having the topology of a circle S^1 . Another way to say the same thing is that in such a space the point x and the point $x + L$ are identified.

The boundary condition of the wave function must be consistent with such a structure of the space in which the particle moves. For instance, a natural boundary condition is

$$\psi(x + L) = \psi(x) : \quad (3.10)$$

the wave function itself is periodic. The wave number is accordingly constrained to take one of the values, $k = 2\pi n/L$, $n = 0, 1, 2, 3, \dots$. In this case the spectrum is discrete,

$$E_n = \frac{(2\pi n)^2 \hbar^2}{2mL^2} ; \quad (3.11)$$

each positive energy level is doubly degenerate, while the ground state is non-degenerate. We leave to the reader to demonstrate the completeness of the energy eigenstates, which in this case reduces to Fourier's theorem: any periodic function can be expanded in Fourier series.

3.2.2 Topologically nontrivial space

The system just considered above, a free particle moving along a line, having the topology of a circle,

$$x \equiv x + L ,$$

has interesting generalizations. In quantum mechanics, these systems can possess a physical parameter that has no direct analogue in classical mechanics. In fact, the well-known arbitrariness of the phase of wave functions allows for a more general boundary condition than (3.10),

$$\psi(x + L) = e^{i\theta} \psi(x) , \quad (3.12)$$

where θ is a constant characterizing the quantum system. The solution of the Schrödinger equation is $\psi = e^{ikx}$, $E = k^2 \hbar^2 / 2m$, but the generalized boundary condition requires that

$$kL = 2\pi n + \theta, \quad n = 0, \pm 1, \pm 2, \dots ,$$

so that

$$E_n = \frac{\hbar^2}{2mL^2} (2\pi n + \theta)^2 .$$

The corresponding eigenstate is

$$\psi_n(x) = \frac{1}{\sqrt{L}} \exp\left(i \frac{2\pi n + \theta}{L} x\right) . \quad (3.13)$$

Let us note that eqns (3.13) are momentum eigenstates,

$$\frac{\hbar}{i} \frac{\partial}{\partial x} \psi_n(x) = \hbar \frac{2\pi n + \theta}{L} \psi_n(x) .$$

For a generic θ , the double degeneracy of the energy levels found for $\theta = 0$ is lost, $E_n \neq E_{-n}$. For a particular value of θ , $\theta = \pi$, the energy levels are

$$E_n = \frac{\hbar^2 (2\pi)^2}{2mL^2} \left(n + \frac{1}{2}\right)^2 :$$

in this case *all levels, including the ground state*, are doubly degenerate. They correspond to the pairs of states $(0, -1)$, $(1, -2)$, $(2, -3)$, and so on.

Another interesting special case is $\theta = 2\pi$. In this case, the spectrum is identical to the $\theta = 0$ system, even though the ground state is now $n = -1$ and non-degenerate. Other states form degenerate pairs $((0, -2)$, $(1, -3)$, etc.) The fact that the spectrum is the same for $\theta = 0$ and for $\theta = 2\pi$ is to be expected because θ is an angular parameter, defined modulo 2π ! We just have to relabel the states $n \rightarrow n - 1$ to see that the two systems are indeed identical.

But there is something far from trivial. Suppose that the external parameter θ varies with time very slowly (adiabatically) from 0 to 2π . As we shall see later (Section 12.3), during an adiabatic variation of the system, if the system is originally in one of the stationary states, $|n\rangle$, it will remain in the “instantaneous energy eigenstate” $|n; t\rangle$ as the energy levels go up and down. After the system has gone through a full cycle, $\theta = 0 \rightarrow 2\pi$, the spectrum returns to the original one, but the quantum system is now in a shifted state $|n + 1\rangle$! This phenomenon is known as “spectral flow”; it has interesting applications in *non-Abelian gauge theories*².

Let us point out that these phenomena occur essentially because the space in question S^1 has a nontrivial topological structure: it is multiply connected. In the usual case of a particle moving in \mathbb{R}^3 , the uniqueness (the single-valuedness) of the wave function does not allow for such phenomena. It is necessary that the space is effectively multiply connected in order for the wave function to have nontrivial periodic conditions. We shall see interesting physical phenomena of this sort later on (the Aharonov-Bohm effect, some semi-classical systems).

3.2.3 Special properties of one-dimensional Schrödinger equations

Theorem 3.4 *The discrete energy levels in a one-dimensional potential well are non-degenerate.*

Proof We assume the contrary and suppose that there are two eigenfunctions ψ_1 and ψ_2 corresponding to the same energy eigenvalue, E , i.e.,

$$\psi_1'' = -\frac{2m}{\hbar^2}(E - V(x))\psi_1, \quad \psi_2'' = -\frac{2m}{\hbar^2}(E - V(x))\psi_2.$$

Since the Hamiltonian is Hermitian, $V(x)$ and E are real. The Schrödinger equation, eqn (3.7), has real coefficients, and so the bound state solutions can be taken to be real. Multiplying the first by ψ_2 and the second by ψ_1 , respectively, and subtracting term by term, one finds that

$$\psi_1''\psi_2 - \psi_2''\psi_1 = 0,$$

and integrating it,

$$\psi_1'(x)\psi_2(x) - \psi_2'(x)\psi_1(x) = \text{const.} \quad (3.14)$$

²This is a name given to field theories similar to quantum electrodynamics (QED), but with gauge transformations involving non-Abelian groups, such as $SU(2)$, $SU(3)$, instead of just the phase transformation ($U(1)$ group) of QED. As far as we know, fundamental interactions are basically all—except gravity—described by this type of theory.

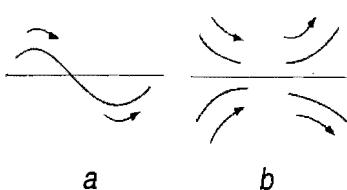


Fig. 3.2 General behavior of the wave function. (a) is the situation in the region $E > V(x)$; (b) in the region $E < V(x)$.

But $\psi_1 = \psi_2 = 0$ at $x = \pm\infty$ (normalizability), so const. = 0 in eqn (3.14):

$$\psi'_1(x)\psi_2(x) - \psi'_2(x)\psi_1(x) = 0.$$

This can be integrated again to give

$$\log \psi_1 = \log \psi_2 + \text{const.} \quad \psi_1 = \text{const.} \psi_2 :$$

that is, ψ_1 and ψ_2 actually describe the same eigenstate, contrary to the assumption. \square

The general behavior of the wave function can be deduced directly from the Schrödinger equation:

$$\psi'' = \frac{2m(V(x) - E)}{\hbar^2} \psi. \quad (3.15)$$

If $\psi'' > 0$ the function $\psi(x)$ is concave, while for $\psi'' < 0$ it is convex. In the interval where $E > V(x)$ (classically accessible region)

$$\begin{cases} \psi'' > 0 & \text{if } \psi < 0, \\ \psi'' < 0 & \text{if } \psi > 0, \end{cases}$$

i.e., $\psi(x)$ is oscillatory. Vice versa, in the region of x where $E < V(x)$ (classically forbidden region) the wave function behaves as

$$\begin{cases} \psi'' > 0 & \text{if } \psi > 0, \\ \psi'' < 0 & \text{if } \psi < 0, \end{cases}$$

which is an unstable behavior. In both cases the absolute value of the curvature $|\psi''|$ increases with $|E - V(x)|$. See Fig. 3.2.

If one takes these general behaviors into account, it is straightforward to show the following theorem.

Theorem 3.5. (The oscillation theorem) *The wave function of the n -th discrete energy level has $n - 1$ nodes (zeros).*

Proof Suppose that $V(x) \rightarrow \infty$ at $x \rightarrow \pm\infty$, so that the spectrum is purely discrete. Equation (3.15) has two independent solutions: in search of a normalizable solution, one can choose a solution ψ which tends to zero at $x \rightarrow -\infty$. Without loss of generality, ψ can be assumed to be positive at $x < 0$ and with $|x|$ sufficiently large. The normalization of ψ can be taken so that $\psi(x_1) = 1$, where x_1 is some arbitrarily chosen reference point. Let us first take $E < V_{\min}$ and study how the situation changes as E is gradually increased.

(I) For $E < V(x)$, $\forall x$, ψ is concave; it increases monotonically at all x and necessarily diverges at $x \rightarrow \infty$. There are no eigenvalues below V_{\min} .

(II) When E is just above V_{\min} , let x_1 and x_2 be the roots of $E - V(x) = 0$, so that $E > V(x)$ for $x_1 < x < x_2$ and $E < V(x)$ otherwise. ψ increases from $x = -\infty$ to $x = x_1$; in the interval (x_1, x_2) ψ is convex, and at $x > x_2$, ψ is again concave. For continuity, ψ continues to diverge at $x \rightarrow \infty$, unless E reaches some finite value above V_{\min} , E_1 . (Fig. 3.3.)

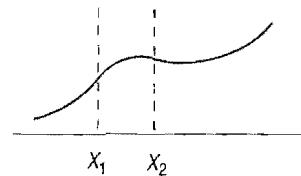


Fig. 3.3 The wave function for $V_{\min} < E < E_1$.

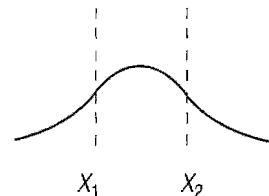


Fig. 3.4 The wave function at $E = E_1$ exactly (the ground state).

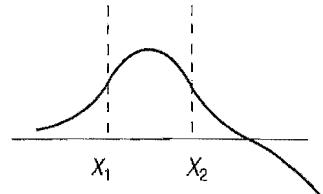


Fig. 3.5 The wave function at energies just above the ground state energy. $E_1 < E < E_2$.

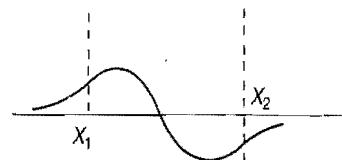


Fig. 3.6 $\psi(x)$ at $E = E_2$ (the first excited level)

- (III) $E = E_1$. As E increases, the interval x_1, x_2 where the function ψ is convex widens, and at the same time the curvature at fixed x increases indefinitely. Therefore there must be a first value of E , E_1 , where ψ tends to zero at $x = \infty$: ψ is normalizable at this value of E . The system is in its ground state. Clearly ψ has no nodes. (Fig. 3.4.)
- (IV) When the energy is further raised the function ψ overshoots zero, becomes unstable now in the negative, and again diverges. The normalizability is lost. (Fig. 3.5)
- (V) If one continuously increases E , again there will be a point $E = E_2$ at which ψ exactly tends to zero at $x = \infty$, this time approaching the x axis from below. The system is in the first excited state: the wave function has a node. (Fig. 3.6.)
- (VI) By repeating the arguments at ever-increasing values of E , one arrives at the theorem. The n -th energy eigenfunction has $n - 1$ modes. When the potential has a more complicated form with more than one local minima and maxima, the proof must be done more carefully.

□

3.3 Potential wells

3.3.1 Infinitely deep wells (walls)

Let us first consider a particle bound in an infinitely deep well,

$$V(x) = \begin{cases} 0 & 0 < x < a, \text{ II}, \\ \infty & x \leq 0 \quad \text{I}, \quad x \geq a \quad \text{III}. \end{cases} \quad (3.16)$$

The solution outside the well is $\psi = 0$. Inside the well, the Schrödinger equation describes a free particle,

$$-\frac{\hbar^2}{2m} \psi'' = E \psi,$$

with a general solution

$$\psi = A \sin(kx + \delta).$$

The condition of continuity at $x = 0$ imposes

$$A \sin \delta = 0 \Rightarrow \sin \delta = 0;$$

while at $x = a$ it gives

$$\psi = A \sin(ka + \delta) = 0 \Rightarrow \sin(ka + \delta) = 0.$$

The momentum (energy) eigenvalues are then given by

$$k a = n \pi, \quad E_n = \frac{k_n^2 \hbar^2}{2m} = \frac{\pi^2 \hbar^2}{2ma^2} n^2, \quad n = 1, 2, 3, \dots \quad (3.17)$$

Note that the eigenstates correspond to the normal modes of oscillations in the interval of length a (with wavelengths $2a/n$, $n = 1, 2, \dots$). The n -th eigenfunction is

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi n}{a}x\right).$$

3.3.2 The finite square well

Consider now a finite potential well (see Fig. 3.7)

$$\begin{aligned} V(x) &= -V_0, \quad -\frac{a}{2} < x < \frac{a}{2}, \quad \text{II}; \\ V(x) &= 0, \quad x \leq -\frac{a}{2} \quad \text{I}; \quad x \geq \frac{a}{2}, \quad \text{III} \end{aligned}$$

The Schrödinger equation is then

$$\psi'' = \begin{cases} -\frac{2m}{\hbar^2} E \psi, & x < -\frac{a}{2}; x > \frac{a}{2}, \\ -\frac{2m}{\hbar^2} (E + V_0) \psi, & -\frac{a}{2} < x < \frac{a}{2}. \end{cases} \quad (3.18)$$

For $E > 0$, eqn (3.18) has solutions of the form e^{ikx} , non-normalizable but bounded, so such a region of E corresponds to the continuous spectrum.

We have already shown (eqn (3.2)) that there are no physical states for $E < -V_0$. The spectrum of the Hamiltonian is therefore in the range $[-V_0, \infty]$. The bound states, if they exist, will lie in the range $[-V_0, 0]$. By setting

$$q = \frac{\sqrt{2m(V_0 - |E|)}}{\hbar} > 0, \quad \kappa = \frac{\sqrt{2m|E|}}{\hbar} > 0,$$

one has

$$\psi'' = \begin{cases} \kappa^2 \psi, & x \in \text{I, III} \\ -q^2 \psi, & x \in \text{II} \end{cases}.$$

Note that q and κ satisfy

$$q^2 + \kappa^2 = \frac{2mV_0}{\hbar^2}. \quad (3.19)$$

In region II the solution is

$$\psi_{\text{II}} = A \sin(qx + \delta).$$

In regions I and III, the solution instead has the form $e^{\pm \kappa x}$: by taking into account the normalization condition, we have

$$\psi_{\text{I}} = B e^{\kappa x}; \quad \psi_{\text{III}} = C e^{-\kappa x}.$$

As the Hamiltonian is invariant under $x \rightarrow -x$ and because the one-dimensional discrete levels are non-degenerate, the energy eigenfunctions have a definite parity, either even or odd under $x \leftrightarrow -x$. Let us then set

$$\psi_{\text{II}} = A \cos qx \quad \text{or} \quad \psi_{\text{II}} = A \sin qx.$$

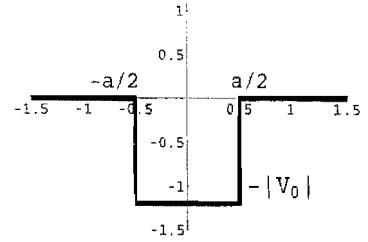


Fig. 3.7 A potential well

In regions I or III, the solution is of the form $e^{\pm\kappa x}$, so

$$\psi_I = B e^{\kappa x}; \quad \psi_{III} = C e^{-\kappa x}.$$

The continuity at $x = \frac{a}{2}$ imposes the condition $\psi_{II} = \psi_{III}$; $\psi'_{II} = \psi'_{III}$. As the function is either even or odd, the continuation condition at $x = -\frac{a}{2}$ is then automatically satisfied. For an even function ($B = C$) one finds that

$$q \tan \frac{qa}{2} = \kappa. \quad (3.20)$$

Analogously for an odd eigenfunction the condition is

$$-q \cot \frac{qa}{2} = \kappa. \quad (3.21)$$

Equations (3.19) and (3.20) together give the even energy levels; (3.19) and (3.21) the odd levels. The solutions of the coupled equations can be nicely visualized by using graphs, by setting

$$qa/2 \equiv \xi; \quad \kappa a/2 \equiv \eta, \quad (\xi, \eta > 0).$$

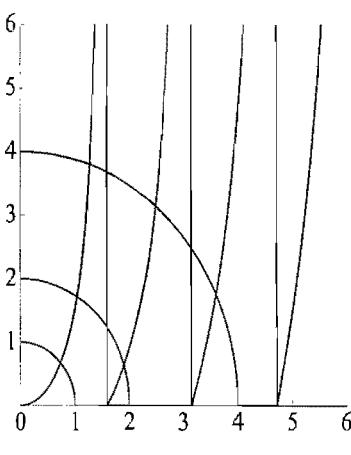


Fig. 3.8 Graphic solution of eqns (3.22) and (3.24), or eqns (3.23) and (3.24).

ξ, η satisfy

$$\xi \tan \xi = \eta, \quad (\text{even}), \quad (3.22)$$

or

$$\xi \cot \xi = -\eta, \quad (\text{odd}), \quad (3.23)$$

together with the constraint

$$\xi^2 + \eta^2 = \frac{m a^2 V_0}{2 \hbar^2}. \quad (3.24)$$

The intersections between the curves eqn (3.22) and eqn (3.24), or those between eqn (3.23) and eqn (3.24), in the quadrant $\xi > 0, \eta > 0$ represent the energy eigenvalues (see Fig. 3.8).

It is not difficult to see that the number of bound states is n if $\frac{(n-1)\pi}{2} < \sqrt{\frac{m a^2 V_0}{2 \hbar^2}} \leq n\pi/2$. In fact,

- (i) for $0 < \sqrt{\frac{m a^2 V_0}{2 \hbar^2}} \leq \frac{\pi}{2}$, there is only one solution with an even wave function: a small one-dimensional well has one and only one bound state;
- (ii) if $\frac{\pi}{2} < \sqrt{\frac{m a^2 V_0}{2 \hbar^2}} \leq \pi$, there is one (even) solution with $0 < qa/2 < \pi/2$, and another (odd) solution with $\pi/2 \leq qa/2 < \pi$;
- (iii) for $\pi < \sqrt{\frac{m a^2 V_0}{2 \hbar^2}} \leq \frac{3\pi}{2}$, there are three bound states, etc. It is easy to check that the oscillation theorem is satisfied.

Remarks

- One-dimensional square-well potentials always possess at least one bound state. In a three-dimensional square-well potential the situation is different: the potential must have a minimum width or depth in order to have at least one bound state (Section 6.2).

- For more general one-dimensional potentials (such that $V(x) \rightarrow 0$, at $x \rightarrow \infty$ and/or at $x \rightarrow -\infty$) the existence of negative energy bound states is not always guaranteed. An example of a sufficient condition for having at least one negative-energy bound state, for a potential vanishing at both asymptotic regions $x \rightarrow \pm\infty$, is that

$$\int_{-\infty}^{\infty} dx V(x) < 0$$

is satisfied. For more discussion, see [Schechter (1981)].

- Critical cases.** The special cases

$$\sqrt{\frac{ma^2V_0}{2\hbar^2}} = \frac{\pi n}{2}, \quad q_c = \sqrt{\frac{2mV_0}{\hbar^2}} = \frac{\pi n}{a}, \quad n = 1, 2, \dots,$$

deserve comment. Consider varying the parameters V_0, a, m slowly and ask how the number of bound states changes. As $\sqrt{\frac{ma^2V_0}{2\hbar^2}}$ passes one of these critical values, $\frac{\pi n}{2}$, the number of bound states will increase by one. More precisely, a state from the continuum becomes normalizable and enters the discrete spectrum. See Fig 3.9. Exactly at a critical value of $\sqrt{\frac{ma^2V_0}{2\hbar^2}}$, the energy of the state is zero ($\kappa = 0$) and the “new bound state” is not normalizable: it represents a state of the continuum which is *about to become a bound state*.

- Consider the limit $a \rightarrow 0, V_0 \rightarrow \infty$, with $g = aV_0$ fixed. In this limit the potential becomes a delta function, $V(x) = -g\delta(x)$. As $\sqrt{\frac{ma^2V_0}{2\hbar^2}}$ approaches zero, the system has only one bound state. Though η approaches zero, the energy (or κ) approaches a finite limit,

$$\kappa = \frac{mg}{\hbar^2}, \quad E_0 = -\frac{mg^2}{2\hbar^2},$$

while the wave function approaches the limit

$$\psi = \sqrt{\kappa} e^{-\kappa|x|}.$$

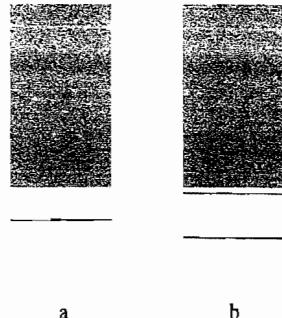


Fig. 3.9 The spectrum in a square potential well for $\sqrt{ma^2V_0/2\hbar^2}$ slightly below $\pi/2$ (a), and slightly above $\pi/2$ (b).

3.3.3 An application

It is possible to make a rudimentary model of a gas confined in a box, by using the solution of the system (3.16). Suppose that a particle is in the n -th energy level inside the box. Its energy is

$$E_n = \left(\frac{\pi n}{a}\right)^2 \frac{\hbar^2}{2m}.$$

Suppose that the wall of the box is compressed by $a \rightarrow a - \delta a$: the work needed is equal to

$$E_n(a - \delta a) - E_n(a) = \frac{\pi^2 n^2 \hbar^2}{2m} \left(\frac{1}{(a - \delta a)^2} - \frac{1}{a^2} \right) = \frac{\pi^2 n^2 \hbar^2}{m a^3} \delta a \equiv p \cdot \delta a,$$

and therefore the pressure the particle exerts on the wall is given by

$$p = \frac{\pi^2 n^2 \hbar^2}{m a^3} = \frac{2}{a} E_n . \quad (3.25)$$

Let us now think about a gas made of N such particles, in thermal equilibrium with the wall at temperature T . The energy distribution is given by the Boltzmann distribution

$$P_n = \mathcal{N} e^{-E_n/kT} ,$$

with \mathcal{N} being the normalization constant. For a particle in the n -th level, $E_n = An^2$, $A = (\frac{\pi}{a})^2 \frac{\hbar^2}{2m}$. The mean energy is

$$\langle E \rangle = \sum_n E_n P_n .$$

For the gas of N particles, whose interactions are negligible,

$$E_{(n_1, n_2, \dots, n_N)} \simeq E_{n_1} + E_{n_2} + \dots + E_{n_N} ,$$

with the mean value

$$\begin{aligned} \langle E \rangle^{(N)} &= \frac{\sum_{(n_1, n_2, \dots, n_N)} E_{(n_1, n_2, \dots, n_N)} e^{-E_{(n_1, n_2, \dots, n_N)}/kT}}{\sum_{(n_1, n_2, \dots, n_N)} e^{-E_{(n_1, n_2, \dots, n_N)}/kT}} \\ &= N \frac{\sum_{n_1} E_{n_1} e^{-E_{n_1}/kT}}{\sum_{n_1} e^{-E_{n_1}/kT}} = N \langle E \rangle . \end{aligned}$$

At high temperatures $\frac{A}{kT} \ll 1$, and the sum over n can be approximated by an integral, i.e. having set $\sqrt{A}n \equiv x$, one has

$$\langle E \rangle \sim \frac{\int dx x^2 e^{-x^2/kT}}{\int dx e^{-x^2/kT}} = \frac{1}{2} kT .$$

The energy of the system is given by the classical formula

$$U = \langle E \rangle^{(N)} = \frac{1}{2} N k T$$

from which follows the usual formula for the specific heat for a one-dimensional ideal gas $C = \frac{\partial U}{\partial T} = \frac{1}{2} N k$.

At low temperatures, the sum in $\langle E \rangle$ is dominated by the ground state,

$$\langle E \rangle \simeq E_1 ,$$

so that the specific heat tends to zero when $T \rightarrow 0$.

As for the pressure, one finds, from eqn (3.25),

$$P = \frac{2}{a} N \langle E \rangle = \frac{2}{a} N \langle E \rangle \simeq \frac{2}{a} N \frac{kT}{2} = \frac{1}{a} N k T ,$$

at room temperatures. This is nothing but the (one-dimensional) equation of perfect gas, $PV = NkT$.

3.4 The harmonic oscillator

3.4.1 The wave function and Hermite polynomials

The one-dimensional harmonic oscillator is described by the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2,$$

where the mass m and the angular frequency ω are constant. The Schrödinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2}m\omega^2x^2 \right) \psi = 0$$

can be slightly simplified by a rescaling,

$$\sqrt{\frac{m\omega}{\hbar}}x \rightarrow x,$$

and introducing

$$\epsilon \equiv \frac{2E}{\hbar\omega} > 0,$$

which is simply the energy measured in the unit of $\omega\hbar/2$. The dimensional constants (for x and for E) can be easily recovered at the end, by a dimensional consideration. For large x , $\psi'' \sim x^2\psi$, so the asymptotic behavior for ψ is

$$\psi \sim (\text{polynomial}) e^{-x^2/2}.$$

Set

$$\psi(x) = \chi(x) e^{-x^2/2},$$

the equation for χ is

$$\chi'' - 2x\chi' + (\epsilon - 1)\chi = 0. \quad (3.26)$$

As the wave function must be regular at the origin, we expand χ as a power series,

$$\chi(x) = a_0 + a_1x + a_2x^2 + \dots$$

Substituting this into eqn (3.26) gives

$$\begin{aligned} 2a_2 - (1 - \epsilon)a_0 &= 0; \\ 6a_3 - (3 - \epsilon)a_1 &= 0; \\ &\dots \quad \dots \\ (n+2)(n+1)a_{n+2} - (2n+1-\epsilon)a_n &= 0; \\ &\dots \quad \dots \end{aligned}$$

Let us first assume that $a_0 \neq 0$. In this case the recursion relations generate a_2, a_4, \dots , to give a partial sum

$$w^{(\text{even})}(x) = \sum_{m=0}^{\infty} a_{2m} x^{2m}.$$

The series may or may not terminate. If it does not, the asymptotic behavior of $w^{(\text{even})}(x)$ can easily be determined from the large- n behavior of a_{2m} ,

$$\frac{a_{n+2}}{a_n} \sim \frac{2}{n}, \quad \therefore a_{2m+2} \sim \frac{1}{m!};$$

$$\psi(x) = e^{-x^2/2} w(x) \sim e^{+x^2/2},$$

and the wave function is not normalizable. Therefore in order to have a normalized eigenfunction, the series must terminate, i.e., w must be a polynomial. This is possible if for some even integer n it happens that $2n + 1 - \epsilon = 0$, i.e., if ϵ is an integer of the form

$$\epsilon = 4m + 1, \quad m = 0, 1, 2, \dots$$

Note that for such values of energy ($E = \epsilon \omega \hbar/2$), the odd series cannot terminate and would give rise to a non-normalizable wave function. However, a normalizable solution can be obtained by simply setting all odd coefficients to zero, which is certainly consistent with the recursion relations. Thus one gets a purely even normalizable wave function,

$$\psi^{2n}(x) = e^{-x^2/2} \sum_{m=0}^n a_{2m} x^{2m}, \quad \epsilon = 2n + 1, \quad n = 0, 2, 4, \dots \quad (3.27)$$

If instead $a_0 = 0$, all even coefficients vanish by recursion relations. In this case a_1 cannot vanish, as otherwise the whole function $w(x)$ would vanish. One now has a purely odd solution,

$$w^{(\text{odd})}(x) = \sum_{m=0}^{\infty} a_{2m+1} x^{2m+1}, \quad a_1 \neq 0.$$

The condition for normalizability in this case is again that the series terminate at a finite n , $2n + 1 - \epsilon = 0$ for some odd integer n : the energy must satisfy

$$\epsilon = 4m + 3, \quad m = 0, 1, 2, \dots$$

The odd energy levels are described by the wave functions

$$\psi^{2n+1}(x) = e^{-x^2/2} \sum_{m=0}^n a_{2m+1} x^{2m+1}, \quad \epsilon = 2n + 1, \quad n = 1, 3, 5, \dots, \quad (3.28)$$

where the coefficients are all determined by the recursion relations apart from the overall normalization.

Combining the solutions (3.27) and (3.28), we have derived the famous energy levels

$$E_n = \omega \hbar \left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, \dots \quad (3.29)$$

for a linear oscillator and corresponding eigenfunctions.

The fact that the energy levels of a harmonic oscillator are equally spaced is of fundamental importance for physics. This allows us to interpret and to introduce an appropriate formalism (see below) to describe

the n -th excited state as a state with n non-interacting phonons, each with energy $\omega \hbar$. A special case of electromagnetic field oscillations—in this case the phonon is called a *photon*—has been already discussed in Chapter 1. Such a simplification is fundamental in the physics of many degrees of freedom, solids, elementary-particles, etc.

To find more systematically the energy eigenstates it is useful to note that the equation for w for the n -th state has the form

$$H_n'' - 2xH_n' + 2nH_n = 0, \quad (3.30)$$

which is the well-known Hermite equation. Its polynomial solutions are the Hermite polynomials:

The Hermite polynomials can be defined through its generating function

$$S(x, s) = e^{-s^2 + 2sx} = e^{x^2 - (s-x)^2} = \sum_{n=0}^{\infty} \frac{s^n}{n!} H_n(x). \quad (3.31)$$

where s is a parameter. By comparing the two ways of writing $\partial S / \partial x$ one obtains a recursion formula

$$H_n' = 2n H_{n-1},$$

while an analogous consideration of $\partial S / \partial s$ leads to

$$H_{n+1} = 2xH_n - 2nH_{n-1}.$$

Equation (3.30) can be found by combining the two.

An explicit formula

$$H_n(x) = (-)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}$$

can be easily found from eqn (3.31). By explicitly calculating the derivatives, one finds

$$\begin{aligned} H_0(x) &= 1, & H_1(x) &= 2x, \\ H_2(x) &= 4x^2 - 2, & H_3(x) &= 8x^3 - 12x, \\ H_4(x) &= 16x^4 - 48x^2 + 12, & \dots & \dots \end{aligned}$$

which of course coincide with the results found from the recursion relations. The Hermite polynomials are orthogonal with respect to the following measure:

$$\int_{-\infty}^{\infty} dx e^{-x^2} H_n(x) H_m(x) = \delta_{n,m} \sqrt{\pi} 2^n n!.$$

This can be shown from the study of

$$\int_{-\infty}^{\infty} dx e^{-x^2} S(x, s) S(x, t) = \sum_{n,m=0}^{\infty} \frac{s^n t^m}{n! m!} \int_{-\infty}^{\infty} dx e^{-x^2} H_n(x) H_m(x).$$

If one reinstates the constants, the n -th energy eigenfunction is given by

$$\psi_n(x) = C_n H_n(\alpha x) e^{-\frac{1}{2}\alpha^2 x^2} = C_n H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-\frac{m\omega}{2\hbar}x^2}, \quad (3.32)$$

where

$$C_n = \left(\frac{\alpha}{\pi^{1/2} 2^n n!}\right)^{1/2} = \left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \left(\frac{1}{2^n n!}\right)^{1/2}; \quad \alpha \equiv \sqrt{\frac{m\omega}{\hbar}}.$$

The ground state wave function is simply a Gaussian distribution

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2},$$

(3.33)

and has the energy

$$E_0 = \frac{1}{2} \hbar\omega,$$

known as the *zero-point energy*. The zero-point energy (often also called the *vacuum energy*) thus represents the minimum quantum fluctuation allowed by Heisenberg's uncertainty principle. A particle confined in a finite region (thus with finite Δx) cannot have a vanishing momentum uncertainty, which implies a non-vanishing kinetic energy.³ The zero-point energy, as well as the extension of the ground state wave function $\sqrt{\hbar/m\omega}$, may be understood from Heisenberg's uncertainty relation. Suppose that the ground state is the state in which the product $\Delta x \Delta p$ is minimum, $\Delta x \Delta p \simeq \hbar/2$. Minimizing the expectation value of the Hamiltonian $H = p^2/2m + m\omega^2 x^2/2$, and setting $\langle p^2 \rangle = (\Delta p)^2$, $\langle x^2 \rangle = (\Delta x)^2$ with respect to Δx (or Δp), one finds $E_0 \simeq (1/2)\hbar\omega$.

It is often useful to consider the *matrix elements* of the operators x , p , x^2 , and so on. For instance,

$$x_{nm} = \langle n | x | m \rangle \equiv \int dx \psi_n^*(x) x \psi_m(x),$$

$$(x^2)_{nm} = \langle n | x^2 | m \rangle \equiv \int dx \psi_n^*(x) x^2 \psi_m(x).$$

These can be determined easily by making use of the generating function, which yields

$$x_{nm} = \begin{cases} \frac{1}{\alpha} \sqrt{\frac{n+1}{2}}, & \text{if } m = n+1, \\ \frac{1}{\alpha} \sqrt{\frac{n}{2}}, & \text{if } m = n-1, \end{cases}$$

$$(x^2)_{nm} = \begin{cases} \frac{1}{\alpha^2} \sqrt{\frac{(n+1)(n+2)}{4}}, & \text{if } m = n+2, \\ \frac{1}{\alpha^2} \sqrt{\frac{n(n-1)}{4}}, & \text{if } m = n-2, \\ \frac{1}{\alpha^2} \frac{2n+1}{2}, & \text{if } m = n, \end{cases}$$

where

$$\alpha \equiv \sqrt{\frac{m\omega}{\hbar}}.$$

³The zero-point energy gives rise to interesting observable effects (*Casimir effects*) when a system with infinite degrees of freedom (such as quantized electromagnetic fields) is confined in some bounded region of space.

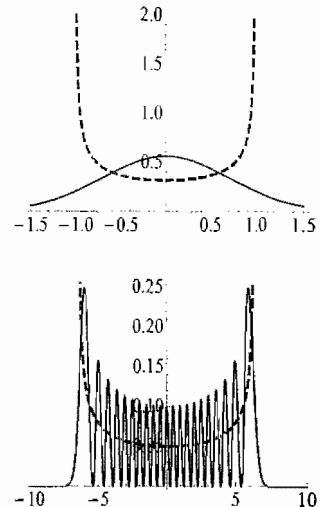
Analogously,

$$p_{mn} = \langle m | p | n \rangle = -i \sqrt{\frac{m\omega\hbar}{2}} (\delta_{m,n-1}\sqrt{n} - \delta_{m,n+1}\sqrt{n+1}).$$

It is an instructive exercise to compare the probability of finding the particle in certain region of x , $(x, x+dx)$ in a quantum mechanical oscillator and in a corresponding classical oscillator. In quantum mechanics such a probability is given by $|\psi_n(x)|^2 dx$, while in the classical oscillator we shall consider the length of time the particle spends in such a region, averaged over many oscillations. Such a probability is thus inversely proportional to its velocity in a given region of x , so

$$p_c(x)dx = 2 \frac{dt}{T} = \frac{2}{T} \frac{dt}{dx} dx = \frac{2}{T} \frac{dx}{v},$$

where T is the period of a full oscillation. In Fig. 3.10 such a comparison is made. As is clearly seen, the quantum mechanical result is in good agreement with the classical one, if the peaks and troughs are smoothed out for highly excited states, while for the ground states they do not look at all similar.



3.4.2 Creation and annihilation operators

There is an elegant way of describing the harmonic oscillator. Let us introduce

$$a = \sqrt{\frac{m\omega}{2\hbar}} x + i \sqrt{\frac{1}{2m\omega\hbar}} p \quad (3.34)$$

and its Hermitian conjugate

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}} x - i \sqrt{\frac{1}{2m\omega\hbar}} p, \quad (3.35)$$

called respectively the *annihilation operator* and the *creation operator*. The inverse is

$$x = \sqrt{\frac{\hbar}{2m\omega}} (a + a^\dagger); \quad p = -i \sqrt{\frac{m\omega\hbar}{2}} (a - a^\dagger).$$

The commutation relation between a and a^\dagger follows from that of x and p :

$$[a, a^\dagger] = 1. \quad (3.36)$$

In terms of these, the Hamiltonian takes a very simple form,

$$H = \frac{\omega\hbar}{2} (aa^\dagger + a^\dagger a) = \omega\hbar \left(a^\dagger a + \frac{1}{2} \right), \quad (3.37)$$

where we have used (3.36). By using the known matrix elements of the operators x and p , one finds that the only non-vanishing elements of a and a^\dagger are ($n = 0, 1, 2, \dots$)

$$\langle n-1 | a | n \rangle = \sqrt{n}; \quad \langle n+1 | a^\dagger | n \rangle = \sqrt{n+1}.$$

Fig. 3.10 Classical (dashed line) and quantum mechanical probabilities for finding the particle in near x for the state at the same energy corresponding to the $n = 0$ and $n = 20$ levels.

Or equivalently, one can write

$$a|n\rangle = \sqrt{n}|n-1\rangle, \quad a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle. \quad (3.38)$$

It follows then that

$$a^\dagger a|n\rangle = n|n\rangle; \quad (3.39)$$

the operator $\mathcal{N} \equiv a^\dagger a$ is the *number operator*. The Hamiltonian and its eigenvalues are simply:

$$H|n\rangle = \omega\hbar(\mathcal{N} + \frac{1}{2})|n\rangle = \omega\hbar(n + \frac{1}{2})|n\rangle,$$

which is of course the same as the results found earlier. It is natural to interpret the n -th eigenstate $|n\rangle$ as the state with n phonons. The ground state $|0\rangle$ is the state with no phonons; the operator a^\dagger creates a phonon, a annihilates one. The number operator $\mathcal{N} \equiv a^\dagger a$ counts the number of phonons. In the simple harmonic oscillator there is only one kind of phonon, with energy $\omega\hbar$.

The main results for the harmonic oscillator can be reproduced by working directly with the new formalism, starting from the expression of the Hamiltonian, eqn (3.37). First of all, let us note that the energy spectrum lies in the domain

$$E \geq \frac{\hbar\omega}{2},$$

as the expectation value of the operator $a^\dagger a$ is non-negative. If now $|E\rangle$ is a normalized energy eigenstate with eigenvalue, E , such that

$$Ha|E\rangle = aH|E\rangle + [H, a]|E\rangle = Ea|E\rangle - \hbar\omega a|E\rangle = (E - \hbar\omega)a|E\rangle,$$

we conclude that there is another energy eigenstate, $a|E\rangle$, which has energy $E - \hbar\omega$ and a positive norm as long as $E > \hbar\omega/2$. It follows that we must assume the existence of a ground state such that

$$a|0\rangle = 0, \quad \langle 0|0\rangle = 1, \quad E_0 = \frac{\hbar\omega}{2},$$

for otherwise the chain of states with energies $E, E - \hbar\omega, E - 2\hbar\omega, \dots$ would eventually lead to states with a negative norm.

Starting from the ground state, one can repeatedly use the creation operator to generate the (normalized) energy eigenstates

$$|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle, \quad n = 1, 2, \dots, \quad H|n\rangle = \omega\hbar(n + \frac{1}{2})|n\rangle.$$

All the matrix elements of x , p , and their powers can easily be reproduced by repeated use of eqn (3.38).

Coherent states

An important application in which the formalism of creation and annihilation operators shows its power is the so-called *coherent states*. They

represent the most compact wave packets, in which the product of the uncertainties of x and of p takes the minimum value. A coherent state is a wave packet which most closely resembles a classical particle.

The coherent state can be defined as an eigenstate of the annihilation operator,

$$a|\beta\rangle = \beta|\beta\rangle, \quad (3.40)$$

where β is a complex number. To construct the state $|\beta\rangle$ explicitly, consider the unitary operator

$$U(\beta) = e^{\beta a^\dagger - \beta^* a},$$

Then

$$|\beta\rangle = U(\beta)|0\rangle,$$

where $|0\rangle$ is the ground state, $a|0\rangle = 0$. By using

$$aU(\beta) = U(\beta)(a + \beta) \quad (3.41)$$

one can easily show eqn (3.40).⁴ By using the Baker–Campbell–Hausdorff–Weyl formula

$$e^X e^Y = e^{X+Y+\frac{1}{2}[X,Y]}, \quad (3.42)$$

valid if $[X, Y]$ is a c -number (i.e., if it commutes with all operators), the unitary operator U can be written as

$$U(\beta) = e^{-|\beta|^2/2} e^{\beta a^\dagger} e^{-\beta^* a}.$$

Thus

$$|\beta\rangle = e^{-|\beta|^2/2} e^{\beta a^\dagger} |0\rangle.$$

By expanding the exponential, one gets

$$|\beta\rangle = \sum_n A_n |n\rangle, \quad A_n = e^{-|\beta|^2/2} \frac{\beta^n}{\sqrt{n!}}. \quad (3.43)$$

The probability of observing n phonons in the coherent state $|\beta\rangle$ is therefore

$$P_n = |\langle n|\beta\rangle|^2 = e^{-|\beta|^2} \frac{|\beta|^{2n}}{n!}, \quad (3.44)$$

which is a Poisson distribution, with average occupation number

$$\langle \beta | a^\dagger a | \beta \rangle = |\beta|^2.$$

It is not difficult to show that

- (i) the product of the uncertainties $\langle (\Delta x)^2 \rangle \cdot \langle (\Delta p)^2 \rangle$ takes the minimum value, $\hbar^2/4$;
- (ii) the wave function in the x representation takes the form

$$\psi(x) = \langle x|\beta\rangle = \mathcal{N} \exp \left[-\frac{(x - x_0)^2}{4D} + i \frac{p_0 x}{\hbar} \right], \quad (3.45)$$

where

$$\begin{aligned} x_0 &= \sqrt{\frac{\hbar}{2m\omega}}(\beta + \beta^*) \equiv A \cos \varphi, \\ p_0 &= i\sqrt{\frac{\hbar m\omega}{2}}(\beta^* - \beta) = m\omega A \sin \varphi, \end{aligned} \quad (3.46)$$

$$\beta = |\beta| e^{-i\varphi}, \quad A = \sqrt{\frac{2\hbar}{m\omega}} |\beta|,$$

$$D = \langle (\Delta x)^2 \rangle = \frac{\hbar}{2m\omega}.$$

Equation (3.45) can be easily found by integrating eqn (3.40) in the x representation. (See also [Davydov (1965)]). In the x representation what distinguishes the coherent state from generic wave packets is the particular value of the width $D = \frac{1}{2}$ (in the unit $m = \omega = \hbar = 1$).

The coherent states have interesting generalizations called “squeezed states” recently studied in connection with quantum optics. In generic squeezed states the uncertainties $\langle (\Delta x)^2 \rangle$ and $\langle (\Delta p)^2 \rangle$ vary, while their product remains at the minimum value.

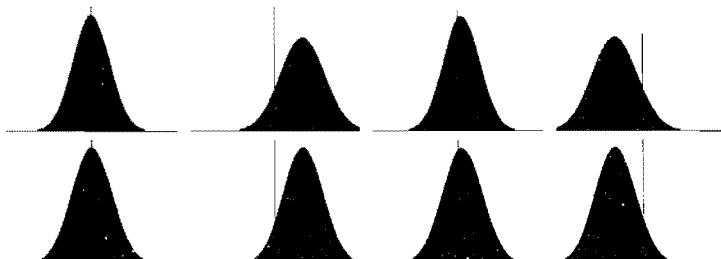


Fig. 3.11 Snapshots of time evolution for a Gaussian wave packet in a harmonic oscillator. The first row is a generic packet, the second one a coherent state. See NB-3.4.

The time evolution of a coherent state can be easily analyzed. As $|n(t)\rangle = e^{-iE_n t/\hbar} |n(0)\rangle$ it follows from eqn (3.43) that

$$|\beta(t)\rangle = e^{-i\frac{\omega t}{2}} e^{-|\beta|^2/2} \frac{\beta^n}{\sqrt{n!}} e^{-in\omega t} |n\rangle = e^{-i\frac{\omega t}{2}} |e^{-i\omega t} \beta\rangle. \quad (3.47)$$

In other words, during the time evolution a coherent state remains so at all times: the parameter β receives a phase variation $e^{-i\omega t}$. We see from eqn (3.46) that the evolution can be expressed as the time variation of the center of mass and its mean momentum,

$$x_0(t) = A \cos(\varphi + \omega t) \quad p_0(t) = m\omega A \sin(\varphi + \omega t). \quad (3.48)$$

This is nothing but the motion of a classical oscillator! As the width of the packet $D = \langle (\Delta x)^2 \rangle$ is constant, a coherent state oscillates as a classical oscillator maintaining its shape, while a generic wave packet ($D \neq \frac{1}{2}$) pulsates. See Numerical Analysis 3.4 at the end of this chapter.

3.5 Scattering problems and the tunnel effect

Let us now turn to the study of the physics of the continuum, continuing to restrict ourselves to one-dimensional systems. Our interest is not so much in the energy spectrum itself (which, in most cases, is simply $\infty > E \geq 0$) as in the physical phenomena associated with it, such as scattering, the tunnel effect, and so on.

Typically one has a situation in which the potential is non-vanishing in a finite region of x , so that asymptotically (at $x \rightarrow -\infty$ and at $x \rightarrow \infty$) the particle becomes free.

A free particle moving in the direction of \hat{k} is described by a plane wave,

$$\psi_{\mathbf{k}} = A e^{i \mathbf{k} \cdot \mathbf{x}}.$$

The coefficient A depends on the normalization used. As the current density

$$\mathbf{j} = \frac{\hbar}{2m_i} (\psi^* \nabla \psi - \psi \nabla \psi^*)$$

indicates the number of particles (on the average) passing through a unit area perpendicular to the direction of the motion, the normalization corresponding to a unit flux is

$$\psi_{\mathbf{k}} = \frac{1}{v} e^{i \mathbf{k} \cdot \mathbf{x}}, \quad v = \frac{|\mathbf{p}|}{m} \equiv \frac{\hbar |\mathbf{k}|}{m}.$$

In the one-dimensional case $|\psi|^2$ is a probability per unit length, and accordingly the flux j measures the number of particles per unit interval of time. In one dimension there exist only two types of plane waves: right movers e^{ikx} and left movers e^{-ikx} .

A typical situation is illustrated in Fig. 3.12.

N.B. A more physical description would be to use a wave packet to represent the particle. The relation between the present approach using stationary states and one using wave packets will be discussed in Subsection 20.4.1.

We shall discuss a few simple problems first.

3.5.1 The potential barrier and the tunnel effect

As a first example, consider the case of the potential barrier (see Fig. 3.13)

$$V = \begin{cases} 0 & \text{if } x < 0, \text{ (I), } x > a \text{ (III),} \\ V_0 > 0 & \text{if } 0 \leq x \leq a, \text{ (II).} \end{cases}$$

Without losing generality one can consider a particle incident from $x = -\infty$. The final state will consist of a plane wave propagating towards $x = +\infty$ —the transmitted wave—and one propagating back towards the left, the reflected wave. In the stationary state approach we are adopting, one must solve the time-independent Schrödinger equation $H\psi = E\psi$ with appropriate boundary conditions. Let us consider the cases $E > V_0$ and $E < V_0$, separately.

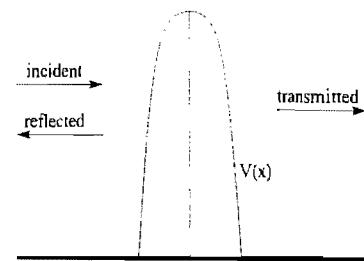


Fig. 3.12 The tunnel effect: an incident wave gives rise to transmitted and reflected waves.

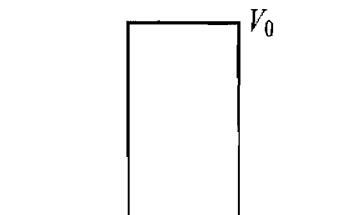


Fig. 3.13 A potential barrier

Case 1: $E > V_0$

A classical particle incident from the left of the barrier, having an energy above the barrier height, will just go on its way towards the right, apart from suffering a deceleration during the passage. In quantum mechanics the general solution of the Schrödinger equation is of the form

$$\begin{aligned}\psi_{\text{I}} &= e^{ikx} + A e^{-ikx}, \quad k = \frac{\sqrt{2mE}}{\hbar}; \\ \psi_{\text{II}} &= B e^{ik'x} + B' e^{-ik'x}, \quad k' = \frac{\sqrt{2m(E - V_0)}}{\hbar}; \\ \psi_{\text{III}} &= C e^{ikx}.\end{aligned}\quad (3.49)$$

In writing eqn (3.49) we have imposed the boundary condition that on the right of the barrier the solution consists purely of the transmitted wave, while on the left of the barrier there are both the incident and reflected waves. The coefficient in front of the incident wave has been arbitrarily set to unity. It will shortly be clear that it is not possible to assume that $A = 0$ without getting the trivial solution $\psi = 0$. This means that in general the particle has a non-vanishing probability of being reflected, even if its energy is above the barrier height.

In fact, the continuity condition between regions I and II is

$$1 + A = B + B', \quad ik(1 - A) = ik'(B - B'),$$

while that between II and III is

$$\begin{aligned}B e^{ik'a} + B' e^{-ik'a} &= C e^{ika} \equiv C'; \\ ik'(B e^{ik'a} - B' e^{-ik'a}) &= ik C e^{ika} = ik C'.\end{aligned}$$

This system can be solved easily, by eliminating B, B' . The result is

$$\begin{aligned}A &= -\frac{i(k^2 - k'^2) \sin k'a}{2kk' \cos k'a - i(k^2 + k'^2) \sin k'a}; \\ C' &= e^{ika} C = \frac{2kk'}{2kk' \cos k'a - i(k^2 + k'^2) \sin k'a}.\end{aligned}$$

We wish to calculate the *transmission coefficient*

$$D \equiv \frac{|j_{\text{trans}}|}{|j_{\text{inc}}|} \quad (3.50)$$

and the *reflection coefficient*

$$R \equiv \frac{|j_{\text{refl}}|}{|j_{\text{inc}}|}, \quad (3.51)$$

where $j_{\text{inc}} = k\hbar/m$, $j_{\text{trans}} = k\hbar|C'|^2/m$, and $j_{\text{refl}} = k\hbar|A|^2/m$ represent the current density of the incident, transmitted, and reflected waves, respectively. We find that

$$D = |C'|^2 = |C|^2, \quad R = |A|^2;$$

that is

$$D = \frac{4k^2 k'^2}{4k^2 k'^2 + (k^2 - k'^2)^2 \sin^2 k' a},$$

$$R = \frac{(k^2 - k'^2)^2 \sin^2 k' a}{4k^2 k'^2 + (k^2 - k'^2)^2 \sin^2 k' a}.$$

Remarks

- $D + R = 1$, as is expected for the total probability.
- As anticipated, $R \neq 0$ in general, while for a classical particle we expect $D = 1$, $R = 0$.
- For certain values of the incident energy ($\sqrt{2m(E - V_0)}a/\hbar = n\pi$, $n = 1, 2, \dots$), there is a complete transmission ($D = 1$). This is an analogue of Ramsauer-Townsend effect in three dimensions.
- In the high-energy limit $E \gg V_0$ one has $D \rightarrow 1$, $R \rightarrow 0$.

Case 2: $E < V_0$

In this case, a classical particle will be reflected one hundred percent of the time ($D = 0$; $R = 1$); the behavior of the quantum particle is quite different. The solution can be written in this case as

$$\psi_I = e^{ikx} + A' e^{-ikx}, \quad k = \frac{\sqrt{2mE}}{\hbar};$$

$$\psi_{II} = B' e^{-\kappa x} + B'' e^{\kappa x}, \quad \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar};$$

$$\psi_{III} = C e^{ikx}.$$

Note that the behavior in the intermediate region is now of real exponential type. The condition of continuity at $x = 0$ and at $x = a$ can be solved as before, yielding the coefficients A' and C needed to determine D and R .

Actually, as the manipulations for solving these systems of equations are purely algebraic, there is no need to repeat the calculation. It suffices to make the substitution

$$k' \rightarrow ik$$

to get these coefficients for the case $E < V_0$. By noting that $\sin k' a \rightarrow i \sinh \kappa a$ and $\cos k' a \rightarrow \cosh \kappa a$, one quickly arrives at

$$A = \frac{(k^2 + \kappa^2) \sinh \kappa a}{2k\kappa i \cosh \kappa a + (k^2 - \kappa^2) \sinh \kappa a},$$

$$C' = \frac{2k\kappa i}{2k\kappa i \cosh \kappa a + (k^2 - \kappa^2) \sinh \kappa a}.$$

The transmission and reflection probabilities are given by

$$D = \frac{4k^2 \kappa^2}{4k^2 \kappa^2 + (k^2 + \kappa^2)^2 \sinh^2 \kappa a};$$

$$R = \frac{(k^2 + \kappa^2)^2 \sinh^2 \kappa a}{4k^2 \kappa^2 + (k^2 + \kappa^2)^2 \sinh^2 \kappa a}.$$

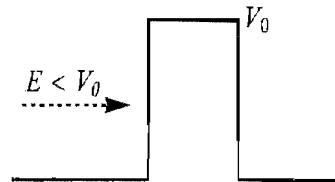


Fig. 3.14

Remarks

- Thus we find that $D \neq 0$, $D > 0$ even though the incident energy is not sufficient to overcome the potential barrier from the classical point of view. This is an example of the celebrated “tunnel effect”, a characteristic feature of quantum mechanical particles.
- In the limit of a large barrier, $V_0 \rightarrow \infty$ and/or $a \rightarrow \infty$, the transmission probability behaves as

$$D \sim e^{-2\sqrt{2m(V_0-E)a/\hbar}};$$

⁵More precisely the tunnel effect turns out to be characterized by the classical action in the motion with time continued analytically to the Euclidean time, $t = -it_E$.

it is exponentially small, the exponent being twice the classical “action”, $\int dx |p|$.⁵

A careful reader should have noticed the fact that, in computing j_{inc} and j_{refl} , we have neglected the interference terms between the two terms of eqn (3.49). In order to justify such a passage it is necessary to consider the wave packets (linear combinations of plane waves) and study the time evolution of these; see Section 20.4.

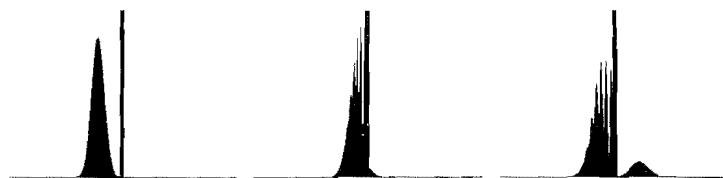


Fig. 3.15 Three snapshots of a wave packet against a barrier, from an animation in notebook NB-3.3.

3.5.2 The delta function potential

The case of the delta-function potential well or barrier is interesting both as an exactly soluble model where the general theory and ideas can be tested, and as a particular type of singular physical interaction.

General considerations: the discontinuity condition

Let us consider the motion of a particle in a delta potential,

$$H = \frac{p^2}{2m} - g \delta(x). \quad (3.52)$$

Owing to the singularity at $x = 0$, the condition of the matching of the wave function on both sides of the singularity requires particular care. The continuity of the probability density itself requires that

$$\psi(x)|_{x \rightarrow 0+} = \psi(x)|_{x \rightarrow 0-}, \quad \psi_-(0) = \psi_+(0),$$

as before. The condition on the first derivative of the wave function must take into account the $\delta(x)$ singularity. Indeed, by integrating the Schrödinger equation

$$-\frac{\hbar^2}{2m}\psi'' - g\delta(x)\psi = E\psi,$$

in the interval $[-\epsilon, \epsilon]$, we find that

$$-\frac{\hbar^2}{2m} (\psi'(\epsilon) - \psi'(-\epsilon)) - g\psi(0) = O(\epsilon).$$

If we now take the limit $\epsilon \rightarrow 0$, the matching condition for the derivatives of the wave function is

$$\psi'_+(0) - \psi'_-(0) = -\frac{2mg}{\hbar^2} \psi(0). \quad (3.53)$$

The same condition follows by directly substituting the wave function of the form

$$\psi(x) = \psi_-(x)\theta(-x) + \psi_+(x)\theta(x) \quad (3.54)$$

into the Schrödinger equation and using $\theta'(x) = \delta(x)$, i.e., requiring that the wave function (3.54) indeed satisfies the condition everywhere, including $x = 0$.

The discrete spectrum (bound state)

Normalizable solutions must have the behavior $e^{\mp\kappa x}$, at $x > 0$ and $x < 0$, respectively, with $\kappa = \sqrt{-2mE/\hbar^2}$. The quantization condition

$$\kappa = \frac{mg}{\hbar^2}, \quad E_0 = -\frac{mg^2}{2\hbar^2} \quad (3.55)$$

then follows from eqn (3.53). The normalized eigenstate is

$$\psi(x) = \sqrt{\kappa} [\theta(-x)e^{\kappa x} + \theta(x)e^{-\kappa x}] : \quad (3.56)$$

there is only one bound state. Obviously, the bound state exists only for an attractive delta potential, $g > 0$ in eqn (3.52).

The continuum

For $E \geq 0$, $k = \sqrt{2mE/\hbar^2}$ we set

$$\psi(x) = \theta(-x)[Ae^{ikx} + Be^{-ikx}] + \theta(x)[Ce^{ikx} + De^{-ikx}]. \quad (3.57)$$

The condition of continuity at the boundary of I and II is

$$A + B = C + D. \quad (3.58)$$

The condition on the derivative (3.53) reads

$$C - D = A - B + \frac{2img}{k\hbar^2}(A + B) = (1 + 2i\alpha)A - (1 - 2i\alpha)B, \quad (3.59)$$

where

$$\alpha = \frac{mg}{k\hbar^2} > 0. \quad (3.60)$$

Solving eqn (3.58) and eqn (3.59) for C, D , we have

$$C = (1 + i\alpha)A + i\alpha B,$$

$$D = -i\alpha A + (1 - i\alpha)B,$$

or

$$\begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} 1+i\alpha & i\alpha \\ -i\alpha & 1-i\alpha \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} \equiv \Omega \cdot \begin{pmatrix} A \\ B \end{pmatrix}. \quad (3.61)$$

The matrix Ω ,

$$\Omega = \begin{pmatrix} 1+i\alpha & i\alpha \\ -i\alpha & 1-i\alpha \end{pmatrix}, \quad \Omega^{-1} = \begin{pmatrix} 1-i\alpha & -i\alpha \\ i\alpha & 1+i\alpha \end{pmatrix}, \quad (3.62)$$

is known as the *transition matrix*:

$$\begin{pmatrix} A \\ B \end{pmatrix} = \Omega^{-1} \begin{pmatrix} C \\ D \end{pmatrix} = \begin{pmatrix} 1-i\alpha & -i\alpha \\ i\alpha & 1+i\alpha \end{pmatrix} \begin{pmatrix} C \\ D \end{pmatrix}. \quad (3.63)$$

For any real value of k , eqn (3.57) with coefficients given by eqn (3.63) represents an eigenstate of H . The continuous spectrum looks quite similar for the attractive ($g > 0$) and repulsive potentials ($g < 0$), apart from the sign change in α .

Transmission and reflection

If the particle is incident from $x = -\infty$, the appropriate boundary condition is

$$D = 0,$$

i.e., only a right-mover on the right of the barrier. The transition matrix then gives

$$A = (1 - i\alpha)C, \quad B = i\alpha C,$$

from which the probabilities for transmission and reflection,

$$D = \frac{1}{1 + \alpha^2}, \quad R = \frac{\alpha^2}{1 + \alpha^2}. \quad (3.64)$$

follow immediately. Note that for a one-dimensional delta function potential, these probabilities are independent of the sign of the potential.

The double delta potential

These results can be easily generalized to the cases of more than one delta functions, such as case of a double delta potential,

$$V = g [\delta(x) + \delta(x - a)]. \quad (3.65)$$

The wave function has the form

$$\begin{aligned} \psi(x) = & \theta(-x)[Ae^{ikx} + Be^{-ikx}] + \theta(x)\theta(a-x)[Ce^{ikx} + De^{-ikx}] \\ & + \theta(x-a)[Fe^{ikx} + Ge^{-ikx}]. \end{aligned} \quad (3.66)$$

By defining

$$F' = Fe^{ik_a}, \quad G' = Ge^{-ik_a}, \quad C' = Ce^{ik_a}, \quad D' = De^{-ik_a},$$

one sees that C, D are given in terms of A, B as in (3.61), while

$$\begin{pmatrix} F' \\ G' \end{pmatrix} = \begin{pmatrix} 1 - i\beta & -i\beta \\ i\beta & 1 + i\beta \end{pmatrix} \cdot \begin{pmatrix} C' \\ D' \end{pmatrix} \equiv \Omega \cdot \begin{pmatrix} e^{ika} & 0 \\ 0 & e^{-ika} \end{pmatrix} \cdot \Omega \cdot \begin{pmatrix} A \\ B \end{pmatrix},$$

or

$$\begin{pmatrix} F \\ G \end{pmatrix} = \begin{pmatrix} e^{-ika} & 0 \\ 0 & e^{ika} \end{pmatrix} \cdot \Omega \cdot \begin{pmatrix} e^{ika} & 0 \\ 0 & e^{-ika} \end{pmatrix} \cdot \Omega \cdot \begin{pmatrix} A \\ B \end{pmatrix}, \quad (3.67)$$

where

$$\Omega = \begin{pmatrix} 1 - i\beta & -i\beta \\ i\beta & 1 + i\beta \end{pmatrix}; \quad \beta = \frac{mg}{k\hbar^2}. \quad (3.68)$$

The difference between Ω here and in eqn (3.62) reflects the sign difference of the potential (cf. eqns (3.65) and (3.52)).

Physics in this case is definitely more interesting than in the case of a single delta potential. We find that the transmission and reflection coefficients are given by

$$D = \frac{1}{1 + 4\beta^2(\cos ka + \beta \sin ka)^2}, \quad R = \frac{4\beta^2(\cos ka + \beta \sin ka)^2}{1 + 4\beta^2(\cos ka + \beta \sin ka)^2}.$$

As a check, note that for $a \rightarrow 0$ we have the result for the single delta potential with $g \rightarrow 2g$. For a generic value of the incident energy the situation is qualitatively similar to the case of the single delta; in particular, note that in the limit of strong repulsion (attraction) $\beta \rightarrow \infty$ ($g \rightarrow \infty$), the transmission coefficient approaches zero. For particular values of the energy,

$$\tan ka = -\frac{1}{\beta},$$

however, we get total transmission ($R = 0, D = 1$)! Note that in the limit $g \rightarrow \infty$, this occurs at

$$ka \simeq \pi n, \quad n = 1, 2, \dots :$$

these correspond precisely to the energy of the stationary states in the infinitely deep potential well with a width a (cf. eqn (3.17)). For generic non-resonant values of k we get, instead, total reflection ($R \rightarrow 1, D \rightarrow 0$) in the limit $g \rightarrow \infty$. In other words, the system works as a filter for selecting out the particular wavelengths⁶ $\lambda \simeq 2a/n, n = 1, 2, \dots$. The situation is illustrated in Fig. 3.16.

The generalization of the formula (3.67) in the case of the N -tuple delta potential with a coupling constant g is given by

$$\begin{pmatrix} A_N \\ B_N \end{pmatrix} = \begin{pmatrix} e^{-iNka} & 0 \\ 0 & e^{iNka} \end{pmatrix} \cdot [\begin{pmatrix} e^{ika} & 0 \\ 0 & e^{-ika} \end{pmatrix} \cdot \Omega]^N \cdot \begin{pmatrix} A_1 \\ B_1 \end{pmatrix}. \quad (3.69)$$

3.5.3 General aspects of the scattering problem

We shall now generalize the results seen above in simple examples, studying the constraints on Ω imposed by the symmetries of the system, for a generic potential such as in Fig. 3.12.

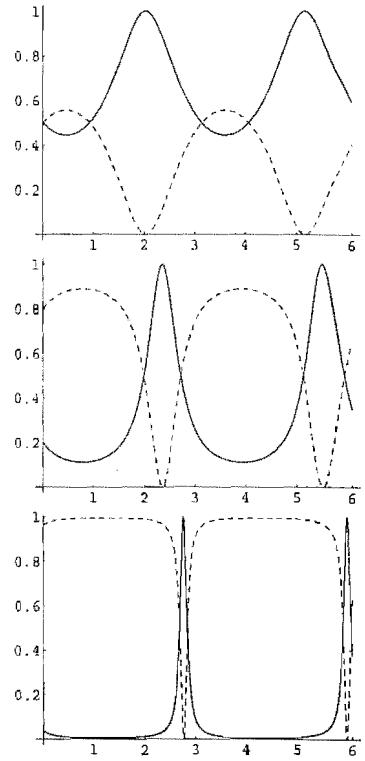


Fig. 3.16 Transmission and reflection coefficients D (continuous line) and R (dashed line) for a double delta potential, for three different values of the potential strength ($\beta = 0.5, 1, 2.5$), as functions of $k a$.

⁶It is easy to interpret this result. For these wavelengths the waves trapped between the two barriers and traveling back and forth are in phase with the waves which go straight from the first to the second barrier: they are enhanced by positive interference. Particles with wrong wavelengths interfere destructively. A device known as the Fabry-Pérot interferometer, often used to measure the wavelength of light precisely, works on the same principles.

For simplicity we shall assume that the potential has a finite range, $V(+\infty) = V(-\infty) = 0$. A general solution of the Schrödinger equation then has the *asymptotic* form

$$\psi(x) = \begin{cases} a e^{ikx} + b e^{-ikx}, & x \rightarrow -\infty, \\ a' e^{ikx} + b' e^{-ikx}, & x \rightarrow +\infty, \end{cases} \quad (3.70)$$

where $k = \sqrt{2mE}/\hbar$. For such solutions the current density is given by

$$\lim_{x \rightarrow \infty} j(x) = \frac{\hbar k}{m} (|a'|^2 - |b'|^2), \quad \lim_{x \rightarrow -\infty} j(x) = \frac{\hbar k}{m} (|a|^2 - |b|^2),$$

in the asymptotic regions. As the current density is conserved, one has

$$|a'|^2 - |b'|^2 = |a|^2 - |b|^2. \quad (3.71)$$

For concreteness let us first consider a solution corresponding to a particle incident from the left (a right-mover):

$$\psi_R(x) \xrightarrow{x \rightarrow -\infty} e^{ikx} + A_R e^{-ikx}; \quad \psi_R(x) \xrightarrow{x \rightarrow \infty} A_T e^{ikx}. \quad (3.72)$$

We have chosen the boundary condition $b' = 0$, adequate for this type of solution, and moreover arbitrarily set the coefficient of the incident plane wave to unity. Clearly the amplitudes A_T and A_R represent the transmitted and reflected waves respectively, and accordingly the transmission and reflection coefficients are given by

$$D = |A_T|^2, \quad R = |A_R|^2. \quad (3.73)$$

The current conservation equation (3.71) tells us that

$$|A_T|^2 = 1 - |A_R|^2 \Rightarrow 1 = D + R. \quad (3.74)$$

An incident particle has a probability D of passing the barrier and a probability $R = 1 - D$ of being reflected.

Note that as $V(x)$ is real, a second, linearly independent solution can be found by taking the complex conjugate: $\psi_A(x) = \psi_R^*(x)$ with the asymptotic behavior

$$\psi_A(x) \xrightarrow{x \rightarrow -\infty} e^{-ikx} + A_R^* e^{ikx}; \quad \psi_A(x) \xrightarrow{x \rightarrow \infty} A_T^* e^{-ikx}. \quad (3.75)$$

Thanks to the linearity of the Schrödinger equation, the solution to the problem with the particle incident from $x = +\infty$ can be found by considering the linear combination $\psi_A - A_R^* \psi_R$. By using eqn (3.74) and dividing by A_T^* one gets the *left-mover solution*, $\psi_L = (1/A_T^*)(\psi_A - A_R^* \psi_R)$, with the asymptotic behavior

$$\psi_L(x) \xrightarrow{x \rightarrow -\infty} A_T e^{-ikx}; \quad \psi_L(x) \xrightarrow{x \rightarrow \infty} e^{-ikx} - \frac{A_R^* A_T}{A_T^*} e^{ikx}, \quad (3.76)$$

which indeed contains only the transmitted wave on the far left side of the potential. *One thus finds the same transmission and reflection coefficients as in the problem of the particle incident from the left.*

One can also make linear combinations so that on the left asymptotic region the wave consists of one or the other of the pure plane waves:

$$(1 - |A_R|^2)e^{ikx} \xrightarrow{x \rightarrow -\infty} \psi_R - A_R \psi_A \xrightarrow{x \rightarrow +\infty} A_T e^{ikx} - A_R A_T^* e^{-ikx}$$

$$(1 - |A_R|^2)e^{-ikx} \xrightarrow{x \rightarrow -\infty} \psi_A - A_R^* \psi_R \xrightarrow{x \rightarrow +\infty} A_T^* e^{-ikx} - A_R^* A_T e^{ikx}.$$

As the two types of plane waves obviously form a complete set in the asymptotic regions, we can think of these solutions as the basis of a two-dimensional vector space and represent them as (1,0) or (0,1). In this way we express the passage from the region $-\infty$ to the region $+\infty$ represented in eqn (3.77) in terms of an operator, a two-by-two matrix

$$\Omega \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1/A_T^* \\ -A_R/A_T \end{pmatrix}, \quad \Omega \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} -A_R^*/A_T^* \\ 1/A_T \end{pmatrix};$$

that is,

$$\Omega = \begin{pmatrix} 1/A_T^* & -A_R^*/A_T^* \\ -A_R/A_T & 1/A_T \end{pmatrix}, \quad (3.78)$$

where use was made of eqn (3.74). The operator Ω is called the *transition matrix*. It has the property

$$\det(\Omega) = \frac{1}{|A_T|^2} - \frac{|A_R|^2}{|A_T|^2} = 1. \quad (3.79)$$

In other words, the current conservation is translated into the requirement that Ω be a matrix belonging to $\text{SL}(2, \mathbb{R})$.⁷ The general solution is indeed

$$\begin{pmatrix} a' \\ b' \end{pmatrix} = \Omega \begin{pmatrix} a \\ b \end{pmatrix}. \quad (3.80)$$

Equation (3.78) is the most general form compatible with the real potential, or better, with the fact that ψ and ψ^* represent both solutions with the same energy (as will be seen later, this is a consequence of the invariance under *time reversal* of the system). The complex numbers A_R, A_T are constrained by the condition (3.74) so that there are only three real independent parameters involved. If, however, the system has some symmetry, the number of independent parameters can be further reduced, as in the example considered next.

⁷ $\text{SL}(N, \mathbb{R})$ denotes the group formed by real $N \times N$ matrices with unit determinant: see Section 20.6.

Parity

Let us now consider the cases the Hamiltonian is invariant under parity: $V(x) = V(-x)$. Invariance under parity implies that if $\varphi(x)$ is a solution of the Schrödinger equation, then so is $\varphi_P(x) \equiv \varphi(-x)$. That is, the left-mover solution, (3.76), and the right-mover solution, (3.72), must transform into each other by parity transformation, $x \rightarrow -x$. It follows that

$$A_R = -A_R^* \frac{A_T}{A_T^*}. \quad (3.81)$$

In other words, the ratio A_R/A_T is purely imaginary in these cases. It is easy to check this result in the cases of the square-well and the delta-function potentials, where the amplitudes have been explicitly calculated above. A_T and A_R can be written as

$$A_T = \cos \theta e^{i\alpha}, \quad A_R = i \sin \theta e^{i\alpha}. \quad (3.82)$$

3.6 Periodic potentials

3.6.1 The band structure of the energy spectrum

The behavior of a quantum mechanical particle in a periodic potential

$$V(x) = V(x + a) \quad (3.83)$$

(see Fig. 1.4) differs essentially from that of a classical particle. This problem can be thought as a prototype of systems of physical interest such as electrons in solids. Suppose that the energy of the particle is such that

$$0 < E \ll V_0,$$

where 0 and V_0 are, respectively, the minimum and maximum of the potential. Suppose furthermore that, in the limit of a high barrier ($V_0 \gg E$), the energy levels and the eigenfunctions in the n -th potential well are given by

$$E_1^{(0)}, E_2^{(0)}, \dots, E_i^{(0)}, \dots; \quad \psi_1(x; n), \psi_2(x; n), \dots, \psi_i(x; n), \dots \quad (3.84)$$

The energy levels in other wells are identical. In other words, in the approximation of neglecting the tunnel effects (transmission between different potential wells) each level is infinitely degenerate, having the wave functions $\{\psi_i(x; n)\}$, $n = \dots, -2, -1, 0, 1, 2, \dots$ localized in different wells. In the following let us concentrate our attention on one of these levels.

Owing to the tunnel effect, the localized wave functions $\{\psi(x; n)\}$ are not eigenstates of the Hamiltonian

$$H = \frac{p^2}{2m} + V;$$

in other words, H is not diagonal in this basis. Assuming the tunnel effects to be small (which should be true for low-lying levels), we might treat these effects as a small perturbation

$$H\psi(x; n) \simeq E^{(0)}\psi(x; n) - \epsilon [\psi(x; n+1) + \psi(x; n-1)], \quad n = 0, \pm 1, \pm 2, \dots, \quad (3.85)$$

where ϵ represents the tunneling amplitude from the n -th well to one of the adjacent wells.

Diagonalization of the Hamiltonian, in view of the fact that eqn (3.85) represents a system of an infinite number of equations, might appear to

be a formidable task. Actually it can be done without difficulty by a Fourier transform with respect to the discrete positions n

$$\tilde{\psi}_k(x) \equiv \sum_{n=-\infty}^{\infty} e^{ikan} \psi(x; n), \quad (3.86)$$

where k is a real parameter ($k\hbar = p$ is the “lattice momentum”, conjugate to n). As n is an integer, the lattice momentum ka is an angular parameter, $k \in [-\pi/a, \pi/a]$. Indeed, by multiplying both sides of eqn (3.85) with e^{ikan} and summing over n , we find that the linear combinations, eqn (3.86), are eigenstates of the energy:

$$H\tilde{\psi}_k(x) = [E^{(0)} - 2\epsilon \cos(ka)] \tilde{\psi}_k(x). \quad (3.87)$$

In other words, the single energy level, infinitely degenerate before taking into account the tunnel effect, has widened into a continuous strip of spectrum, $[E^{(0)} - 2\epsilon, E^{(0)} + 2\epsilon]$ (the *energy band*), parametrized by $p = k\hbar$. Each energy value inside the band is only doubly degenerate, $k = \pm|k|$, corresponding to right- or left-moving waves, with wave functions spread all over the space, $-\infty < x < \infty$.⁸

The eigenfunctions, (3.86), are not eigenstates of the momentum operator, $-i\hbar(d/dx)$; the translation invariance $x \rightarrow x + \Delta x$ is in fact broken by the potential. On the other hand, the Hamiltonian is invariant under the discrete translation, $x \rightarrow x \pm a$, and indeed the energy eigenstates satisfy

$$\tilde{\psi}_k(x \pm a) = e^{\pm ika} \tilde{\psi}_k(x)$$

(where we used $\psi(x+a; n) = \psi(x; n-1)$, etc.), which is reminiscent of a standard plane wave. Let us in particular consider the limit of small momentum $ka \ll 1$. The energy-momentum relation (sometimes called the dispersion relation) in this case becomes

$$E = E^{(0)} - 2\epsilon \cos(ka) \simeq E^{(0)} - 2\epsilon + \epsilon k^2 a^2. \quad (3.88)$$

Apart from a constant, this is just the standard energy-momentum relation of a free particle, with “mass”

$$m_{\text{eff}} = \frac{\hbar^2}{2\epsilon a^2}.$$

Naturally it is not the true mass but an effective mass the particle feels owing to the interactions with the lattice. Whatever the mass may be, the particle does propagate freely though the potential barriers! The range of the energy interval within which the particle can stay, and with which it moves around freely, is known as the *energy band* or the *conduction band*; the electrons in a crystal lattice typically sees such a band structure of levels. Vice versa, the energy region where no electron states exist, is called the *energy gap*. Electrons in the conduction band move freely in the metallic crystals, in spite of the fact that they are subject to interactions with all lattice atoms.

⁸Note that the eigenfunctions of the Hamiltonian differ essentially from those localized wave functions, even if the tunnel effect is a very small effect. The reason for such a large response to small “perturbation” lies in the degeneracy of the “unperturbed” system. This phenomenon is well known in quantum mechanics and is not really a paradox, as the basis of the “unperturbed states” could have been chosen arbitrarily, precisely because of the degeneracy. Even an infinitesimal “perturbation” will orient the system under such a circumstance.

In all this the crucial point is that the tunnel effect describes the penetration through barriers at the level of the *amplitudes* (or in the wave functions), and not directly in the *probability*. In this sense electrical conduction can be regarded as one of the most characteristic quantum effects in Nature.

3.6.2 Analysis

As preparation for the study of periodic potentials, let us first consider the following problem. Suppose that one has a particle moving in a potential $V(x)$, with compact support, and has calculated the transition matrix Ω for this system. What is the energy and what is the wave function of the system with a potential $V(x-d)$? By simply introducing the shifted position variable $z = x - d$, we see that the Schrödinger equation of the new problem reduces to the original one,

$$-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} \psi + V(z) = E\psi$$

so that the same matrix Ω ,

$$\begin{pmatrix} a' \\ b' \end{pmatrix} = \Omega \begin{pmatrix} a \\ b \end{pmatrix}, \quad (3.89)$$

describes the transition from the asymptotic state on the left $a e^{ikx} + b e^{-ikx}$ to the asymptotic solution $a' e^{ikz} + b' e^{-ikz}$ on the right of the potential. Ω is related to the tunneling (A_T) and reflection (A_R) amplitudes due to a single potential by eqn (3.78).

If we are interested in the transition matrix from the state $a e^{ikx} + b e^{-ikx}$ to the state $a' e^{ikx} + b' e^{-ikx}$, where $x = z + d$ is the original position variable, we must simply rename

$$U_d^{-1} \begin{pmatrix} a \\ b \end{pmatrix} \rightarrow \begin{pmatrix} a \\ b \end{pmatrix},$$

(and similarly for (a', b')), where

$$U_d = \begin{pmatrix} e^{ikd} & 0 \\ 0 & e^{-ikd} \end{pmatrix}, \quad (3.90)$$

so that the transition matrix for the potential $V(x-d)$ is⁹

$$\Omega_d = U_d^{-1} \Omega U_d. \quad (3.91)$$

It is now straightforward to iterate the procedure when the potential is given by (see Fig. 3.17)

$$W(x) = \sum_{j=1}^N V(x - jd).$$

At each step the transition matrix is given by Ω : we must only take into account the phase shift as we move from one region from another.

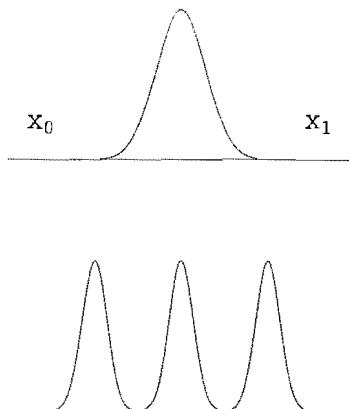


Fig. 3.17 A potential with finite support. On the second figure the potential consists of the several repetition of the original potential.

⁹This is an example of the large arbitrariness of the description of the states and operators present in quantum mechanics related to each other by "unitary transformations" $\psi \rightarrow U\psi$, $O \rightarrow UOU^\dagger$, where $U^\dagger = U^{-1}$. See Section 7.4.

By choosing the asymptotic wave function to be $a e^{ikx} + b e^{-ikx}$ on the far left, and $a_N e^{ikx} + b_N e^{-ikx}$ on the far right, of the whole potential region, the net effect is

$$\begin{pmatrix} e^{ikNd} & 0 \\ 0 & e^{-ikNd} \end{pmatrix} \begin{pmatrix} a_N \\ b_N \end{pmatrix} = (U_d \Omega)^N \begin{pmatrix} a \\ b \end{pmatrix},$$

or

$$\Omega_N = U_{Nd}^{-1} (U_d \Omega)^N. \quad (3.92)$$

Equation (3.92) agrees with eqn (3.69), obtained in the particular case of the chain of delta function potentials.

The problem becomes very interesting for $N \gg 1$, particularly so in the limit $N \rightarrow \infty$, where the potential becomes periodic. The matrix $U_d \Omega$ has unit determinant, so diagonalization by a similarity transformation will yield

$$S^{-1} U_d \Omega S = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}, \quad \lambda_1 \cdot \lambda_2 = 1. \quad (3.93)$$

The same, finite similarity matrix S can be used to diagonalize $(U_d \Omega)^N$ also, so

$$\Omega_N = S^{-1} U_{Nd}^{-1} S \begin{pmatrix} \lambda_1^N & 0 \\ 0 & \lambda_2^N \end{pmatrix}. \quad (3.94)$$

The transition matrix and the tunneling or reflection amplitudes are related as in eqn (3.78):

$$\Omega_N = \begin{pmatrix} 1/A_T^{(N)*} & -A_R^{(N)*}/A_T^{(N)*} \\ -A_R^{(N)}/A_T^{(N)} & 1/A_T^{(N)} \end{pmatrix}. \quad (3.95)$$

Let us now distinguish the following two cases:

- (1) The two eigenvalues λ_1, λ_2 of $U_d \Omega$ have different absolute values, for instance, $1/|\lambda_2| = |\lambda_1| > 1$. In this case, λ_1 dominates in the $N \rightarrow \infty$ limit, and by using the fact that S is a finite matrix independent of N , one sees easily that

$$|1/A_T^{(N)}| \sim \lambda_1^N \rightarrow \infty;$$

that is, $A_T \rightarrow 0$. No transmission is possible.

- (2) The two eigenvalues have the same absolute value, so $|\lambda_1| = |\lambda_2| = 1$.

Only in the second case can the particle move though the potential grid. The condition of unit moduli imposes a nontrivial constraint on the matrix $U_d \Omega$. In fact, let $e^{i\varphi}$ be one of the eigenvalues of $U_d \Omega$. Then

$$\begin{aligned} 0 &= \det \{U_d \Omega - e^{i\varphi}\} = \det \{\Omega - e^{i\varphi} U_d^{-1}\} \\ &= \det \begin{pmatrix} 1/A_T^* e^{i(\varphi-kd)} & -A_R^*/A_T^* \\ -A_R/A_T & 1/A_T - e^{i(\varphi+kd)} \end{pmatrix}; \end{aligned} \quad (3.96)$$

that is, by writing $A_T = |A_T|e^{i\delta}$, we have

$$\begin{aligned} 0 &= \frac{1}{|A_T|^2} - \frac{e^{i\varphi}}{|A_T|} \left[e^{i(kd+\delta)} + e^{-i(kd+\delta)} \right] + e^{2i\varphi} - \frac{|A_R|^2}{|A_T|^2} = \\ &= e^{i\varphi} \left[e^{-i\varphi} + 2 \frac{1}{|A_T|} \cos(kd + \delta) + e^{i\varphi} \right], \end{aligned}$$

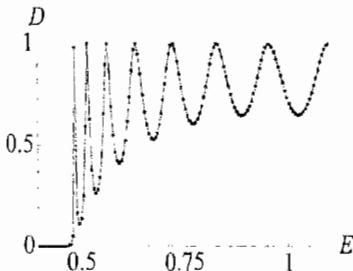


Fig. 3.18 The transmission coefficient D versus E for a quasi-periodic potential with 11 peaks. (see NB-3.6).

and so finally we get

$$\left| \frac{\cos(kd + \delta)}{|A_T|} \right| = |\cos(\varphi)| \leq 1. \quad (3.97)$$

Since A_T is a function of k , this means that the values of k which violate the above inequality are *not allowed*. This precisely corresponds to the energy gap mentioned in the preceding subsection, Section 3.6.1. Note that in going to the $N \rightarrow \infty$ limit, we have qualitatively changed the physical system to a purely periodic potential W :

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + W(x), \quad W = \sum_s V(x - s d). \quad (3.98)$$

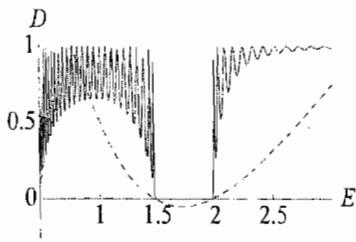


Fig. 3.19 The transmission coefficient D versus E for a quasi-periodic potential with 30 peaks. The constraint eqn (3.97) is also shown. (see NB-3.6)

For illustration, the result of the numerical calculation for the potential $W(x) = \sum_{j=1}^N V(x - j d)$, with

$$V(x) = \frac{V_0}{2} \left[1 + \cos \left(2\pi \frac{x}{d} \right) \right], \quad (3.99)$$

is shown in Figs. 3.18 ($N = 11$) and 3.19 ($N = 30$). (See Numerical Analysis, 9.1). In the second figure the emergence of the energy gap is clearly visible. Note that the forbidden region is bounded by the points at which the curve $1 - |\cos(kd + \delta)/|A_T||$ intercepts the energy axis. In the first figure the full curve represents the direct numerical solution of the Schrödinger equation, while the dots are from the calculation of Ω_N .

Guide to the Supplements

Supplement 20.3 illustrates and explicitly demonstrate the orthonormality and completeness relation in a system with a delta-function potential. These relations are interesting as both discrete (for the attractive potential) and continuum spectra are present. In another Supplement,

20.4, the S-matrix approach to the scattering problem is briefly discussed; a wave packet description of scattering processes is introduced and the relation to the approach used in the main text (using stationary waves) is elucidated.

Problems

- (3.1) Show that condition (3.53) is compatible with the continuity of the current density, $j = \frac{i\hbar}{2m} [(\psi^*)' \psi - \psi^* \psi']$.

- (3.2) A particle moves in a three-dimensional well

$$V(\mathbf{r}) = \begin{cases} 0, & 0 < x < a, 0 < y < b, 0 < z < c; \\ \infty, & \text{otherwise.} \end{cases}$$

Find the eigenvalues and eigenstates. Discuss the degeneracy for the low-lying levels, in particular for the cubic box, $a = b = c$.

- (3.3) A one-dimensional square well has a unique bound state, if its parameters are such that $\sqrt{\frac{m a^2 V_0}{2\hbar^2}} = \delta \ll 1$. Compute the energy of this state approximately, in the first nontrivial order in δ , expressing it as a function of V_0 and of δ .

- (3.4) Consider the limit $a \rightarrow 0$, $V_0 \rightarrow \infty$, with $aV_0 \equiv f$ fixed, in the problem of the finite square well potential of Section 3.3.2. Compare the result obtained with the bound state found in the delta function potential, eqns (3.55) and (3.56).

- (3.5) Find the transmission coefficient for the step potential

$$V = 0, \quad x < 0; \quad V = V_0 > 0 \quad x \geq 0.$$

for $E < V_0$ and for $E > V_0$.

- (3.6) Discuss the qualitative features of the low-lying energy levels in a deep double well potential, by using the symmetry argument (parity) and the non-degeneracy theorem.

- (3.7) A particle of mass m is confined in a potential well $V(x)$, with

$$V(x) = \begin{cases} 0, & 0 \leq x \leq a; \\ \infty, & x < 0 \text{ and } x > a. \end{cases}$$

The particle is in the ground state.

- (a) Compute the force exerted on the walls by the particle.
- (b) At time $t = 0$ the right wall (at $x = a$) moves suddenly to $x = 2a$. Compute the probabilities of finding the particle in various stationary states of the new well.

- (c) What is the final state if the wall moves adiabatically from $x = a$ to $x = 2a$? Compute the work done by the quantum particle during this process.

- (3.8) A particle of mass m is subject to the one-dimensional potential

$$V(x) = \begin{cases} -g \delta(x), & x \leq a; \\ \infty, & x > a. \end{cases}$$

- (a) Find the condition on parameters (m, g) for the existence of a bound state with $E < 0$.

- (b) Discuss the limit $a \rightarrow \infty$.

- (c) Is there degeneracy in the continuum spectrum?

- (3.9) A particle of mass m is subject to the one-dimensional potential

$$V(x) = \begin{cases} \infty, & x < -a; \\ g \delta(x), & -a \leq x \leq 2a \\ \infty, & x > 2a. \end{cases}$$

We want to study the first two energy levels. Let us call the wave functions for negative and positive x $\psi_-(x)$ and $\psi_+(x)$ respectively. Note that the vanishing of the wave function at the boundaries $-a$ and $2a$ allows us to write $\psi_-(x) = A \sin(x+a)$ and $\psi_+(x) = A \sin(-2a)$.

- (a) Obtain the relations for (A, B, k) following from matching $\psi_+(x)$ and $\psi_-(x)$ at $x = 0$. Show that these relations lead to a set of stationary states with exact energy eigenvalues, for which $\psi(0) = 0$.

- (b) Show that there is another group of levels for which $\psi(0) \neq 0$. Show using graphs that the ground state of the system belongs to this group of levels, and compute its energy in the limits, $g \rightarrow 0$ and $g \rightarrow \infty$.

- (3.10) A particle of mass m and energy $E < 0$ moves in a one-dimensional potential

$$V(x) = f \delta(x) - g \delta(x-a), \quad g > 0.$$

- (a) For a single delta-function well ($f = 0$) compute the energy of the ground state and its normalized eigenfunction.

- (b) Assume now that $f \neq 0$ and $g > 0$. Write the conditions for the existence of a bound state.

- (c) By using the condition found in problem (3.3) show that a bound state exists for $|f|$ sufficiently small. Show that for $(2gma)/\hbar^2 < 1$ and for $f > 0$ with sufficiently large $|f|$, no bound states exist.

- (3.11) A particle of mass m moves in the one-dimensional potential ($V_0 > 0$)

$$V(x) = \begin{cases} \infty, & x < 0; \\ 0; & 0 \leq x \leq a \\ V_0 & x > a. \end{cases}$$

- (a) Find the condition for having only one bound state.
 (b) Find approximately the ground state wave function for large V_0 .
 (c) Suppose that at time $t = 0$ the particle is in such a bound state. The part $x > 2a$ of the potential suddenly gets modified to 0. Compute the decay rate, i.e., the probability per unit time of finding the particle outside the potential well ($x > 2a$).

- (3.12) Consider the three-dimensional space divided into two regions, separate by a plane. The potential energy is 0 and $-U_0$ in the two half-spaces. A plane wave impinges on the plane with an incidence angle α . Describe the reflection and the transmission (refracted wave) of the wave. Write and verify the condition for conservation of the number of particles.

- (3.13) A particle of mass m moves in one dimension, subject to an elastic force $-kx$. At time $t = 0$ the center of the force is suddenly shifted by x_0 . The particle is assumed to be in the ground state initially ($t < 0$).

- (a) Compute the mean value of the energy for $t > 0$.
 (b) Compute the probability of finding the particle in the ground state and in the first excited state of the new system at $t > 0$.
 (c) Compute the behavior at $t \rightarrow 0^\pm$ for the expectation values of Heisenberg operators x, p, \dot{x}, \dot{p} .

- (3.14) A neutron interferometer is shown schematically in Fig. 3.20. The Hamiltonian describing neutron motion is

$$H = \frac{p_x^2 + p_z^2}{2m} + mgz,$$

$M \simeq 1.7 \times 10^{-24}$ g is the neutron mass, $g \simeq 980 \text{ cm s}^{-2}$, z is the vertical direction, and x the

horizontal direction, the incident direction of the beam. Assume that at $t = 0$ the plane $BCED$ is vertical, while ABD is on the x axis.

- (a) Write the wavelength of the de Broglie wave for the incident neutron as a function of the momentum p .
 (b) Assuming $p^2/2M \gg Mgz$, compute the phase difference $\Delta\Phi$ in the wave function between the two paths $ABCEF$ and $ABDEF$, in terms of the parameters shown in the figure. Find the condition for maximal interference.
 (c) The plane $BCED$ containing the apparatus is now rotated by an angle φ around the x axis, ABD . As φ varies, the intensity I of the neutrons detected by the counter F changes, showing various maxima and minima. Find how many maxima there are as φ varies from 0 to $\pi/2$.

This effect has been observed experimentally [Colella, et. al. (1975)].

- (3.15) An excited nucleus (with excitation energy G) decays into the ground state by emitting a photon.

- (a) Compute the energy of the emitted photon in the approximation of infinite nuclear mass.
 (b) Suppose now that the free nucleus of finite mass M is initially at rest. Compute the energy of the emitted photon, taking the recoil of the final nucleus into account. Assume $Mc^2 \gg G$.
 (c) Assume now, instead, that the nucleus is bound in a harmonic potential (e.g., a crystal lattice):

$$H = \frac{\mathbf{P}^2}{2M} + \frac{1}{2}M\omega^2 \mathbf{r}^2,$$

where \mathbf{r} is the position of the center of mass of the nucleus. Before decaying, the nucleus is in the ground state ψ_0 of the above oscillator (its internal state is in the excited state, as in the previous problems). Find the possible values of energy E_γ for the emitted photon in this case.

- (d) Justify the approximation according to which the amplitude for the process is given by the matrix element of $\exp(ikz)$, where the momentum of the emitted photon is $(0, 0, \hbar k)$. By using such an approximation, compute the probability $P(E_\gamma)$ of the nucleus emitting a photon with energy E_γ , one of the energies found in part (c) above.

This analysis shows that a fraction of absorption and re-emission of a gamma ray from a nucleus occurs in a recoil-free manner, when the nucleus is bound in a crystal solid. This phenomenon is known as the *Mössbauer effect*.

- (3.16) An electron (of mass m and charge $-e$) moves in the $x-y$ plane, subject to a magnetic field directed along z : $\mathbf{B} = (0, 0, B)$. In the following the electron spin is neglected. The Hamiltonian is

$$H = \frac{1}{2m} \left(\mathbf{p} + \frac{e}{c} \mathbf{A} \right)^2,$$

where \mathbf{A} is the electromagnetic vector potential.

- (a) Compute the spectrum of the Hamiltonian in the gauge $\mathbf{A} = (-By, 0, 0)$ for the vector potential.
 (b) Do the same computation in the gauge $\mathbf{A} = (-By/2, Bx/2, 0)$.

(Laudau levels: see Section 14.3 for further discussions.)

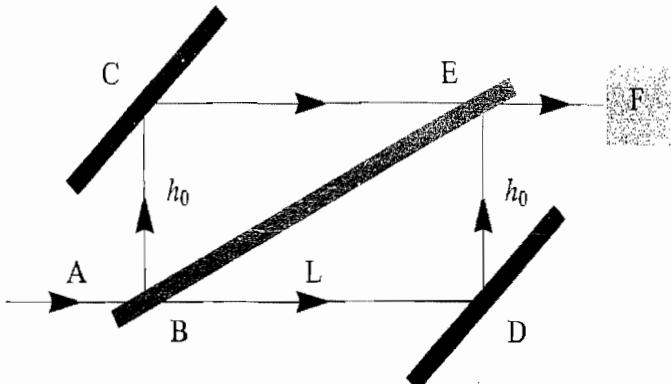


Fig. 3.20 A neutron interferometer

Numerical analyses

- (3.1) Solve numerically the eigenvalue problem

$$H\psi = E\psi; \quad H = \frac{p^2}{2} + V[x], \quad (3.100)$$

by discretizing the coordinate x . Check the method in the harmonic oscillator problem.

- (3.2) Solve the eigenvalue problem, eqn (3.100), with the *shooting method*.

- (3.3) Solve numerically the eigenvalue problem $H\psi = E\psi$ using matrix mechanics. Write a finite-dimensional approximation to variables p, q by using harmonic oscillator basis functions. Study the approximation with polynomial potentials (harmonic and anharmonic oscillator) and the Morse potential

$$V[x] = A(e^{-2\alpha x} - 2e^{-\alpha x}).$$

- (3.4) Study the time evolution of a wave packet in an external potential by three methods:

- the discretization of space and time,
- the Mathematica function NDSolve,
- the expansion in eigenvalues of H .

In particular study the tunneling process for a double well potential.

- (3.5) Study numerically the transmission of a wave packet through a rectangular barrier. Use both a discretization method and NDSolve to solve the Schrödinger equation. Use a Fourier analysis of the solution to get the momentum content of the transmitted wave and compare the result with the theoretical expectations.

- (3.6) Study numerically the transmission of a wave packet through a quasi-periodic potential.
- (3.7) Study numerically the evolution problem presented in Problem 3.11. Verify that it is possible to describe the decay probability by the law $\exp(-\Gamma t)$.

4

Angular momentum

A central role is played by the angular momentum variables in three-dimensional problems. In quantum mechanics angular momentum turns out to be quantized in a universal manner, i.e., independently of the system considered, as a consequence of its characteristic commutation relations and of the positivity of the norm of the state.

4.1 Commutation relations

The Schrödinger equation for a particle moving in a three-dimensional spherically symmetric potential,

$$H\psi = \left(-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) \psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (4.1)$$

reads, in spherical coordinates,

$$\begin{aligned} \Delta\psi &= \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \right\} \psi \\ &= -\frac{2m}{\hbar^2} (E - V(r)) \psi. \end{aligned} \quad (4.2)$$

If we separate the variables in spherical coordinates,

$$\psi = R(r)\Phi(\theta,\phi),$$

the equation of motion reads

$$\frac{1}{R(r)} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{2m}{\hbar^2} r^2 (E - V(r)) \right] R(r) = \frac{1}{\Phi(\theta,\phi)} \hat{L}^2 \Phi(\theta,\phi) = \lambda,$$

where \hat{L}^2 is defined by

$$\hat{L}^2 \Phi(\theta,\phi) = - \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \Phi(\theta,\phi). \quad (4.3)$$

\hat{L}^2 turns out to be the square of the angular momentum $(\mathbf{r} \times \mathbf{p})^2$ (see Section 4.5), so if λ is its eigenvalue, the radial equation takes the form

$$\left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{2m}{\hbar^2} (E - V(r)) - \frac{\lambda}{r^2} \right] R(r) = 0.$$

The quantum mechanical angular momentum operator can be defined as

$$\mathbf{L} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = -i\hbar \mathbf{r} \times \nabla.$$

4.1 Commutation relations	89
4.2 Space rotations	91
4.3 Quantization	92
4.4 The Stern-Gerlach experiment	95
4.5 Spherical harmonics	96
4.6 Matrix elements of \mathbf{J}	98
4.7 The composition rule	101
4.8 Spin	105
Guide to the Supplements	108
Problems	109

In components, they are

$$L_x \equiv L_1 = y p_z - z p_y = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right);$$

$$L_y \equiv L_2 = z p_x - x p_z = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right);$$

$$L_z \equiv L_3 = x p_y - y p_x = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right).$$

As the pairs of position and momentum operators which are not canonically conjugate commute with each other ($[y, p_z] = 0$, etc.), there is no ambiguity of definition in the above.

If the system involves more than one particle, the total angular momentum is defined by

$$\mathbf{L}_{\text{tot}} = \sum_a (\mathbf{r}_a \times \mathbf{p}_a)$$

where the sum is over the particles present.

It is convenient to introduce a constant tensor (the Levi–Civita tensor)

$$\epsilon_{ijk} = \begin{cases} 1, & \text{if } (ijk) = (123) \text{ or even permutations} \\ -1, & \text{if } (ijk) = (213) \text{ or odd permutations} \\ 0 & \text{otherwise} \end{cases}$$

ϵ_{ijk} is totally asymmetric under a pairwise exchange of indices; moreover it is invariant under cyclic permutations,

$$\epsilon_{ijk} = \epsilon_{jki} = \epsilon_{kij}.$$

The i -component of the angular momentum is

$$L_i = \epsilon_{ijk} x_j p_k,$$

where summing over repeated indices is understood.

Use of the standard commutation relations

$$\begin{aligned} [x_i, x_j] &= [p_i, p_j] = 0, \\ [x_i, p_j] &= i\hbar \delta_{ij}, \quad i = 1, 2, 3 \end{aligned} \tag{4.4}$$

straightforwardly leads to the commutation relations among the L_i 's,

$$[L_1, L_2] = i\hbar L_3, \quad [L_2, L_3] = i\hbar L_1, \quad [L_3, L_1] = i\hbar L_2,$$

or

$$[L_i, L_j] = i\hbar \epsilon_{ijk} L_k. \tag{4.5}$$

The same commutation relations hold for the components of the total angular momentum, as the angular momenta of different particles commute with each other trivially.

The angular momentum operators are all Hermitian. They also satisfy the commutation relations

$$[L_i, x_j] = i\hbar \epsilon_{ijk} x_k, \quad (4.6)$$

$$[L_i, p_j] = i\hbar \epsilon_{ijk} p_k \quad (4.7)$$

with the components of x and p . Consider now the square of the angular momentum,

$$\mathbf{L}^2 = L_1^2 + L_2^2 + L_3^2.$$

It is easy to verify that the operator¹ \mathbf{L}^2 commutes with each component L_i ,

$$[\mathbf{L}^2, L_i] = 0, \quad i = 1, 2, 3.$$

For instance,

$$[\mathbf{L}^2, L_1] = [L_2^2, L_1] + [L_3^2, L_1] = i\hbar(-L_2 L_3 - L_3 L_2 + L_3 L_2 + L_2 L_3) = 0.$$

As a consequence, \mathbf{L}^2 and one of the components, e.g. L_3 , can be diagonalized simultaneously. L_1, L_2 do not commute with L_3 ; as a consequence they cannot have definite values² in the eigenstates $|\mathbf{L}^2, L_3\rangle$.

¹We shall see that the operator \mathbf{L}^2 coincides with the operator $\hat{\mathbf{L}}^2$ that appears as the angular part of the Laplacian, expressed in spherical coordinates, eqn (4.3).

4.2 Space rotations

The fact that formulas (4.5), (4.6), and (4.7) have the same structure is not accidental. It means that the angular momentum, position, and momentum operators all transform as vectors: they transform in the same way under the rotation of the coordinate axes. Recall that the momentum operator $\mathbf{p} = -i\hbar\nabla$ is the generator of the *space translation*: a generic operator $O(\mathbf{r}, \mathbf{p})$ is transformed like this:

$$e^{i\mathbf{p}\cdot\mathbf{r}_0/\hbar} O(\mathbf{r}, \mathbf{p}) e^{-i\mathbf{p}\cdot\mathbf{r}_0/\hbar} = O(\mathbf{r} + \mathbf{r}_0, \mathbf{p}).$$

The translation acts on the wave function as follows:

$$e^{i\mathbf{p}\cdot\mathbf{r}_0/\hbar} \psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{r}_0).$$

Analogously the angular momentum operators generate space rotations. Consider

$$U \psi = e^{i\mathbf{L}\cdot\boldsymbol{\omega}/\hbar} \psi(\mathbf{r})$$

for an infinitesimal $\boldsymbol{\omega}$. One has

$$\begin{aligned} e^{i\mathbf{L}\cdot\boldsymbol{\omega}/\hbar} \psi(\mathbf{r}) &\simeq \left(1 + i\frac{\mathbf{L}\cdot\boldsymbol{\omega}}{\hbar}\right) \psi(\mathbf{r}) = \left(1 + \omega_i \epsilon_{ijk} x_j \frac{\partial}{\partial x_k}\right) \psi \\ &\simeq \psi(\mathbf{r} + \boldsymbol{\omega} \times \mathbf{r}). \end{aligned}$$

As the translation operator is $e^{i\mathbf{p}\cdot\mathbf{r}_0/\hbar}$, the operator $U = e^{i\mathbf{L}\cdot\boldsymbol{\omega}/\hbar}$ can be regarded as a *unitary transformation*: a generic operator O is transformed like this:

$$O \rightarrow U O U^\dagger.$$

²The only exception is a state with $\mathbf{L}^2 = 0$: in this case each component has a definite value, $L_i = 0$.

In particular, $O = \mathbf{r}$ gets transformed as follows:

$$\mathbf{r} \rightarrow \tilde{\mathbf{r}} = e^{i\mathbf{L}\cdot\omega/\hbar} \mathbf{r} e^{-i\mathbf{L}\cdot\omega/\hbar} = \mathbf{r} + \frac{i\omega_i}{\hbar} [L_i, \mathbf{r}] + \dots = \mathbf{r} + \boldsymbol{\omega} \times \mathbf{r} + \dots,$$

where commutators (4.6) have been used. The operator $U = e^{i\mathbf{L}\cdot\omega/\hbar}$ thus represents a three-dimensional rotation of the coordinate axes by an angle $|\omega|$ around the direction of the vector $\boldsymbol{\omega}$.

Remarks

- Angular momentum has the dimensions of an action $[L] = [\mathbf{r} \times \mathbf{p}]$, and indeed will be found to be quantized in units of $\frac{1}{2}\hbar$. In the following, throughout the book, we shall indicate by L the dimensionless operator \mathbf{L}/\hbar . In this way all the commutation relations involving angular momenta will be free from the ubiquitous factor \hbar .³
- The commutators among the components of the angular momentum L_i yield linear combinations of the same set of operators. In such a circumstance the operators L_i are said to form an *algebra*. A particular algebra is specified by the set of constants—called structure constants—that appear on the right-hand side of the commutators, and characterizes infinitesimal transformations under the associated group. In the present case of angular momentum algebra, the structure constants are just the tensor ϵ_{ijk} ; they characterize the three-dimensional rotational group $SO(3)$. See more about these points in Supplement 20.6 of this chapter.

In what follows it turns out to be very useful to introduce the following “raising” and “lowering” operators L_+ and L_-

$$L_+ \equiv L_1 + iL_2, \quad L_- \equiv L_1 - iL_2,$$

and rewrite the angular momentum algebra as

$$[L_+, L_-] = 2L_3, \quad [L_3, L_+] = L_+, \quad [L_3, L_-] = -L_-. \quad (4.8)$$

The square of the angular momentum can be expressed as

$$L^2 = L_+L_- + L_3^2 - L_3 = L_-L_+ + L_3^2 + L_3. \quad (4.9)$$

4.3 Quantization

In Nature most elementary particles (the electron, the proton, the neutron, etc.) carry an intrinsic angular momentum, known as *spin*. The spin of a particle is unrelated to the orbital motion of the particle; intuitively it is closer to the revolution of a particle around itself, as proposed by G. Uhlenbeck and S. Goudsmit for the electron spin. We introduce a symbol \mathbf{S} or \mathbf{s} to describe the spin operators. By hypothesis the spin operators satisfy the same commutation relations as generic angular momentum operators.

³Note on the notation. From now on, the symbols \mathbf{L} , \mathbf{S} , \mathbf{s} and \mathbf{J} will stand for the various types of angular momentum operators, measured *in the unit of \hbar* .

As is customary in the literature, we shall indicate by the symbol \mathbf{J} or \mathbf{j} the generic angular momentum operator, for instance the sum of the spin and orbital angular momentum of a single particle, reserving the letters \mathbf{L} , ℓ for the orbital angular momentum and \mathbf{S} , s for spin.

The first fundamental result concerning angular momentum is that owing to the commutation relations

$$[J_i, J_j] = i \epsilon_{ijk} J_k$$

and to the positivity of the norm of the states, the eigenvalues of an angular momentum operator are always quantized, in a universal manner. Let us see how this comes about.

We start by recalling the commutation relations

$$[J_+, J_-] = 2J_3, \quad [J_3, J_+] = J_+, \quad [J_3, J_-] = -J_-, \quad (4.10)$$

$$[\mathbf{J}^2, J_i] = 0, \quad i = 1, 2, 3.$$

The square of the angular momentum can be expressed in terms of J_\pm and J_3 as

$$\mathbf{J}^2 = J_+ J_- + J_3^2 - J_3 = J_- J_+ + J_3^2 + J_3. \quad (4.11)$$

We choose a basis in which \mathbf{J}^2 and J_3 are diagonal, with the corresponding eigenstate

$$J_3 |j, m\rangle = m |m\rangle,$$

where j indicates the as yet unknown eigenvalue of \mathbf{J}^2 . From commutation relations (4.10), it follows that

$$J_3 J_+ |j, m\rangle = (J_+ J_3 + J_+) |j, m\rangle = (m + 1) J_+ |j, m\rangle;$$

i.e., the state $J_+ |j, m\rangle$, if not a null vector, is another eigenstate of J_3 , with eigenvalue $m + 1$. Analogously,

$$J_3 J_- |j, m\rangle = (m - 1) J_- |j, m\rangle$$

tells us that $J_- |j, m\rangle$ is either a null vector or is an eigenstate $|j, m - 1\rangle$. Note that as \mathbf{J}^2 and J_\pm commute, the states $|j, m \pm 1\rangle$ continue to be eigenstates of the former, with the same eigenvalues (hence the notation). The operators J_+ and J_- thus act as the raising and lowering operators:

$$J_\pm |j, m\rangle = \text{const.} |j, m \pm 1\rangle,$$

$$J_\pm^2 |j, m\rangle = \text{const.} |j, m \pm 2\rangle,$$

etc. The non-null states $J_\pm^n |m\rangle$, $n = 0, 1, 2, \dots$ form a tower of states belonging to the same eigenvalues of \mathbf{J}^2 , but with eigenvalues of J_3 differing by integer units.

Now what is the relation between the eigenvalue of \mathbf{J}^2 and those of J_3 ? Let us indicate by T the eigenvalue of \mathbf{J}^2 . From the relation

$$\langle \mathbf{J}^2 - J_3^2 \rangle = \langle J_1^2 + J_2^2 \rangle \geq 0 \quad (4.12)$$

(which the reader should be able to verify easily) the constraint

$$\sqrt{T} \geq m \geq -\sqrt{T}.$$

follows. Therefore, given the value T (the eigenvalue of \mathbf{J}^2), there must be a state with the maximum value of m (limited by \sqrt{T}), which we indicate by j . According to the notation introduced above, it is the state $|j, j\rangle$.

Classically such a situation occurs when the angular momentum vector is directed towards the positive z axis: its z component then coincides with the magnitude of the vector itself. The quantum mechanical situation is not quite the same.

The relation between T and j can in fact be found as follows. As the state $|j, j\rangle$ is by definition the state with the maximum value of m , a further action of the raising operator should annihilate it,

$$J_+ |j, j\rangle = 0,$$

for otherwise it would generate another eigenstate of J_3 with eigenvalue $j + 1$, contradicting the assumption. It follows from eqn (4.11) that

$$\mathbf{J}^2 |j, j\rangle = (J_- J_+ + J_3^2 + J_3) |j, j\rangle = j(j+1) |j, j\rangle.$$

Namely

$$T = j(j+1) :$$

in contrast to the classical expectation, in a system with the angular momentum $\sqrt{j(j+1)}$ its z component can reach only j , and furthermore can take only the quantized values, $j, j-1, j-2$, etc.

We are not yet done. As we have seen, starting from the “highest” state $|j, j\rangle$, a tower of states belonging to the same angular momentum multiplet (i.e., with the same $T = j(j+1)$) can be generated by using J_- repeatedly,

$$J_-^n |j, j\rangle \propto |j-n\rangle; \quad n = 0, 1, 2, \dots$$

How far can we go? It follows from eqn (4.12) that there must also be a state with the *lowest* m . There must be an integer n such that

$$J_- |j, j-n\rangle = 0.$$

By virtue of the first of eqns (4.9), one finds that

$$\mathbf{J}^2 |j, j-n\rangle = (J_+ J_- + J_3^2 - J_3) |j, j-n\rangle = ((j-n)^2 - (j-n)) |j, j-n\rangle.$$

But this state belongs to the same multiplet as $|j, j\rangle$, so

$$(j-n)^2 - (j-n) = j(j+1), \quad \therefore \quad n = 2j, \quad n = 0, 1, 2, \dots$$

This result looks innocent enough, but actually we have just proven one of the fundamental results of quantum mechanics: the modulus of

angular momentum j can assume *a priori* an integer or half-integer value only,

$$j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots \quad (4.13)$$

The angular momentum is always quantized, independently of its nature, orbital or spin, elementary or composite. The operator corresponding to the square of the angular momentum \mathbf{J}^2 can *a priori* only take values

$$j(j+1) = 0, \frac{3}{4}, 2, \frac{15}{4}, 6, \dots$$

In fact, it will be shown in Section 4.5 that the *orbital* angular momentum can take integer values, $j = \ell = 0, 1, 2, \dots$ only.

For a given j , there is a tower of $2j+1$ states

$$\left\{ \begin{array}{l} |j, j\rangle \\ |j, j-1\rangle \\ \dots \\ |j, -j\rangle \end{array} \right. \quad (4.14)$$

related by the raising and lowering operators J_{\pm} . They correspond classically to those states with the angular momentum vector directed in various directions. What is remarkable about eqn (4.14) is that quantum mechanics predicts the quantization of the z -component J_z (indicating its eigenvalues by m ,

$$m = j, j-1, \dots, -j; \quad (4.15)$$

but it is up to us which space direction to call the z axis. Put differently, *whichever* component $\mathbf{J} \cdot \mathbf{n}$ is chosen, where \mathbf{n} is an arbitrary unit vector, its eigenvalues are always quantized in the same way, as in eqn (4.15).⁴ Of course, the relative probability of finding various values of m depends on the particular *state* considered.

In Nature these theoretical predictions are obeyed without exception. The spin of the elementary particles turns out to be either half-integer or integer: electrons, protons and neutrons all carry spin $s = \frac{1}{2}$ (units of \hbar); pions and kaons have no spin, W and Z particles have spin 1, and so on. Orbital angular momenta always have integer values.

⁴This truly remarkable aspect of quantum mechanical angular momentum was called “directional quantization” in the early days of quantum mechanics.

4.4 The Stern-Gerlach experiment

One of the first experiments to prove the existence of spin and verify the “directional quantization” predicted by quantum mechanics was performed by Stern and Gerlach (1922). In their experiment, a well-collimated beam of silver atoms is sent through a region with an inhomogeneous magnetic field, before hitting a photographic plate (see Fig.4.1). The magnetic field is directed perpendicular to the beam, and has a strong gradient

$$\frac{\partial B_z}{\partial z} \neq 0,$$

so that the beam made of atoms with a magnetic moment will be bent toward the z or $-z$ axis. As the magnetic moment will be proportional to its spin, such an experiment can be thought of as a measurement of the z component of the spin, S_z .

If the incident beam is unpolarized, the atoms composing the beam will have the magnetic moment pointing in various random directions. Classically, then, we expect that the beam will broaden and upon reaching the plate will leave a wide band of images. Experimentally, the beam is found to split into just two sub beams, and the photographic image consists of two split regions of spots, separated in the z direction, confirming quantization of angular momentum dramatically and, in particular, spin. Such an experimental outcome, which implied the value $\frac{1}{2}$ for the spin, was quite a surprise at the time. The experiment can be done with the orientation of the magnets rotated in any direction: the result (doubly split images of the beam) is always the same, even though the relative intensity of the two images in general depends on the direction of the magnet, unless the incident beam is completely unpolarized (see Section 7.7).

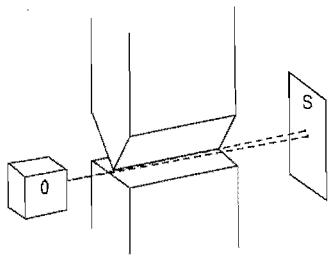


Fig. 4.1 The Stern–Gerlach experiment. Atoms ejected from the oven O are collected on the screen S .

4.5 Spherical harmonics

All the preceding discussions are, of course, valid for the angular momenta due to orbital motion, $\mathbf{L} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$. However, the requirement that the wave function be single-valued turns out to imply that only integer values are allowed for ℓ . In spherical coordinates (r, θ, ϕ) ,

$$r = \sqrt{x^2 + y^2 + z^2}; \quad \theta = \tan^{-1} \frac{\sqrt{x^2 + y^2}}{z}; \quad \phi = \tan^{-1} \frac{y}{x}.$$

The components of $\mathbf{L} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$ are

$$\begin{aligned} L_3 &= -i \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = -i \frac{\partial}{\partial \phi}; \\ L_+ &= -(x + iy) \frac{\partial}{\partial z} + z \left(\frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right) = e^{i\phi} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right); \\ L_- &= -L_+(i \rightarrow -i) = e^{-i\phi} \left(-\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right). \end{aligned}$$

Thus

$$\mathbf{L}^2 = L_+ L_- + L_3^2 - L_3 = - \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right],$$

as anticipated in Section 4.1.

Let us now solve the eigenvalue equation for \hat{L}^2 ,

$$\hat{L}^2 \Phi(\theta, \phi) = - \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \Phi(\theta, \phi) = \ell(\ell+1) \Phi(\theta, \phi). \quad (4.17)$$

As $L_3 = -i\frac{\partial}{\partial\phi}$ commutes with \hat{L}^2 , it is convenient to solve first

$$L_3\psi(\phi) = -i\frac{\partial}{\partial\phi}\psi(\phi) = m\psi(\phi) :$$

The solution is obviously

$$\psi(\phi) = \Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}.$$

The factor $1/\sqrt{2\pi}$ was chosen to satisfy the normalization condition

$$\int_0^{2\pi} \Phi_{m'}(\phi)^* \Phi_m(\phi) d\phi = \delta_{m'm}.$$

But the wave function must be a well-defined function of ϕ , so

$$m = 0, \pm 1, \pm 2, \dots$$

Since m (called the *azimuthal quantum number*) can take only the quantized values

$$-\ell, -\ell + 1, \dots, +\ell,$$

it follows that ℓ can also take only integer values

$$\ell = 0, 1, 2, 3, \dots$$

Thus the orbital angular momentum is quantized, with eigenvalues taking integer multiples⁵ of \hbar only.

Now substitute

$$\Phi(\theta, \phi) = \Phi_m(\phi)\Theta_{\ell,m}(\theta)$$

into eqn (4.17). One finds that

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\Theta_{\ell,m}(\theta)\right) - \frac{m^2}{\sin^2\theta}\Theta_{\ell,m}(\theta) + \ell(\ell+1)\Theta_{\ell,m}(\theta) = 0,$$

or, in terms of the variable $x \equiv \cos\theta$,

$$\frac{d}{dx}(1-x^2)\frac{d}{dx}\Theta_{\ell,m} - \frac{m^2}{1-x^2}\Theta_{\ell,m} + \ell(\ell+1)\Theta_{\ell,m} = 0. \quad (4.18)$$

This equation is well-known. Its solutions, which are finite and single-valued in the range $-1 \leq x \leq 1$ and for $\ell \geq |m|$, are known as the *associated Legendre polynomials* and usually indicated as $P_\ell^m(x)$. For more on Legendre polynomials and associated Legendre polynomials, see the Supplement to the chapter.

The solution of eqn (4.18) properly normalized as

$$\int_0^\pi d\theta \sin\theta |\Theta_{\ell,m}(\theta)|^2 = \int_{-1}^1 dx |\Theta_{\ell,m}|^2 = 1,$$

⁵This property of orbital angular momenta reflects the simply-connected structure of the three-dimensional space, \mathbf{R}^3 . There are interesting physical situations in which the space becomes effectively non-simply connected. See, for instance, Section 14.2.

and is given by ($x \equiv \cos \theta$)

$$\Theta_{\ell,m} = (-)^m \sqrt{\frac{(2\ell+1)(\ell-m)!}{2(\ell+m)!}} P_\ell^m(x), \quad m \geq 0, \quad (4.19a)$$

$$\Theta_{\ell,-|m|} = (-)^m \Theta_{\ell,|m|}.$$

The solution for $\Phi(\theta, \phi)$ is then

$$\Phi(\theta, \phi) = Y_{\ell,m}(\theta, \phi) = (-)^{(m+|m|)/2} \sqrt{\frac{(2\ell+1)(\ell-|m|)!}{4\pi(\ell+|m|)!}} P_\ell^{|m|}(x) e^{im\phi}.$$

The functions $Y_{\ell,m}(\theta, \phi)$ are known as *spherical harmonics*: they represent the simultaneous eigenstates of the operators \mathbf{L}^2 (with eigenvalue $\ell(\ell+1)$) and L_3 (with eigenvalue m). The spherical harmonic functions $Y_{\ell,m}(\theta, \phi)$ are normalized as

$$\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi Y_{\ell',m'}(\theta, \phi)^* Y_{\ell,m}(\theta, \phi) = \delta_{\ell\ell'} \delta_{mm'}.$$

The $(2\ell+1)$ functions $Y_{\ell,m}(\theta, \phi)$ for a given value of ℓ are just the coordinate representation of the states $|\ell, m\rangle$, or

$$\langle \theta, \phi | \ell, m \rangle = Y_{\ell,m}(\theta, \phi).$$

Let us explicitly write down some of the spherical harmonics $Y_{\ell,m}$:

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}},$$

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta, \quad Y_{2,0} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1),$$

$$Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}, \quad Y_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \cos \theta \sin \theta e^{\pm i\phi},$$

$$Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}, \quad (4.20)$$

⁶Another convention often used for $Y_{\ell,m}$ is the one used in the book [Landau and Lifshitz (1976 c)]: there is an additional phase i^ℓ there.

etc⁶. Some of the important properties of $Y_{\ell,m}(\theta, \phi)$ are

$$Y_{\ell,m}(\pi - \theta, \phi + \pi) = (-)^\ell Y_{\ell,m}(\theta, \phi),$$

$$Y_{\ell,m}^* = (-)^m Y_{\ell,-m}.$$

4.6 Matrix elements of \mathbf{J}

We have seen that results such as

$$J_\pm |m\rangle = \text{const.} |m \pm 1\rangle, \quad (4.21)$$

$$\mathbf{J}^2 |j\rangle = j(j+1) |j\rangle,$$

follow from the commutation relations of J_i . Let us now determine the constants in front of the right-hand side of these relations. Consider the expectation value of the operator

$$\mathbf{J}^2 = (J_+ J_- + J_3^2 - J_3)$$

in the state $|j, m\rangle$. One has

$$\begin{aligned}\langle j, m | \mathbf{J}^2 | j, m \rangle &= \langle j, m | J_+ J_- | j, m \rangle + \langle j, m | J_3^2 | j, m \rangle - \langle j, m | J_3 | j, m \rangle, \\ j(j+1) &= \sum_{m'} \langle j, m | J_+ | j, m' \rangle \langle j, m' | J_- | j, m \rangle + m^2 - m.\end{aligned}$$

We have used here the completeness relation

$$\sum_{j', m'} |j', m'\rangle \langle j', m'| = \mathbb{1},$$

and the fact that the operators J_{\pm} do not modify the value of j . From the last relation it follows, by taking into account eqn (4.21), that only one term contributes in the sum over m' :

$$\langle j, m | J_+ | j, m-1 \rangle \langle j, m-1 | J_- | j, m \rangle = j(j+1) - m^2 + m = (j+m)(j-m+1).$$

Since $J_+ = J_-^\dagger$, the two matrix elements on the left-hand side are related:

$$\langle j, m | J_+ | j, m-1 \rangle = \langle j, m-1 | J_- | j, m \rangle^*.$$

Thus

$$|\langle j, m-1 | J_- | j, m \rangle|^2 = (j+m)(j-m+1),$$

and with a convenient choice of phase we find that

$$\langle j, m-1 | J_- | j, m \rangle = \langle j, m | J_+ | j, m-1 \rangle = \sqrt{(j+m)(j-m+1)}; \quad (4.22)$$

clearly all other matrix elements of J_+, J_- vanish.

The matrix elements of J_1 and J_2 follow from those of J_{\pm} via

$$J_1 = \frac{J_+ + J_-}{2}, \quad J_2 = \frac{J_+ - J_-}{2i}.$$

The non-vanishing matrix elements are therefore

$$\begin{aligned}\langle j, m-1 | J_1 | j, m \rangle &= \frac{1}{2} \sqrt{(j+m)(j-m+1)}, \\ \langle j, m+1 | J_1 | j, m \rangle &= \frac{1}{2} \sqrt{(j+m+1)(j-m)},\end{aligned} \quad (4.23)$$

and

$$\begin{aligned}\langle j, m-1 | J_2 | j, m \rangle &= +\frac{i}{2} \sqrt{(j+m)(j-m+1)}, \\ \langle j, m+1 | J_2 | j, m \rangle &= -\frac{i}{2} \sqrt{(j+m+1)(j-m)}.\end{aligned} \quad (4.24)$$

These together with the known matrix elements of J_3 ,

$$\langle j, m | J_3 | j, m \rangle = m, \quad (4.25)$$

determine *all* the matrix elements of the operators J_i .

Returning to eqn (4.21), we have found that

$$\begin{aligned}J_- | j, m \rangle &= \sqrt{(j+m)(j-m+1)} | j, m-1 \rangle, \\ J_+ | j, m \rangle &= \sqrt{(j-m)(j+m+1)} | j, m+1 \rangle.\end{aligned} \quad (4.26)$$

Note that $J_+ | j, j \rangle = 0$ and $J_- | j, -j \rangle = 0$, as expected.

The choice of the above phases (with non-negative, real matrix elements for J_{\pm}), is part of the so-called *Condon-Shortley convention*.

4.6.1 Spin- $\frac{1}{2}$ and Pauli matrices

The component J_z in the case $j = \frac{1}{2}$ has only two possible eigenvalues $m = \pm \frac{1}{2}$. The matrix elements of the operators J_i , $i = 1, 2, 3$ can all be represented as 2×2 matrices:

$$\begin{aligned}\langle \frac{1}{2}, m' | J_1 | \frac{1}{2}, m \rangle &= \frac{1}{2}(\sigma_1)_{m',m}; \\ \langle \frac{1}{2}, m' | J_2 | \frac{1}{2}, m \rangle &= \frac{1}{2}(\sigma_2)_{m',m}; \\ \langle \frac{1}{2}, m' | J_3 | \frac{1}{2}, m \rangle &= \frac{1}{2}(\sigma_3)_{m',m},\end{aligned}$$

where

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (4.27)$$

These are known as *Pauli matrices*. They act in the space of *spinor* states,

$$\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = c_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} + c_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

The base spinor states

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \left| \frac{1}{2}, \frac{1}{2} \right\rangle = |\uparrow\rangle, \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \left| \frac{1}{2}, -\frac{1}{2} \right\rangle = |\downarrow\rangle,$$

represent the states of *spin-up* or *spin-down*.

Note that the spin operators $s_i = \frac{1}{2}\sigma_i$ satisfy the same algebra as eqn (4.5):

$$\left[\frac{\sigma_i}{2}, \frac{\sigma_j}{2} \right] = i \epsilon_{ijk} \frac{\sigma_k}{2}.$$

In other words, these matrices represent the algebra of the group $SO(3)$. The Pauli matrices possess important properties

$$\sigma_i^2 = \mathbb{1}, \quad (i = x, y, z); \quad \sigma_i \sigma_j = -\sigma_j \sigma_i = i \epsilon_{ijk} \sigma_k, \quad (i \neq j); \quad (4.28)$$

these show that Pauli's matrices (more precisely $i \sigma_i$'s) are a representation of *quaternions*—generalized imaginary numbers.

Exercise:

A spin- $\frac{1}{2}$ system is in the eigenstate of the operator $\boldsymbol{\sigma} \cdot \mathbf{n}$ with eigenvalue 1, where \mathbf{n} is a generic direction $\mathbf{n} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$. (Fig. 4.2) Find the spin wave function.

Answer:

$$|\psi_{\mathbf{n}}\rangle = \begin{pmatrix} e^{-i\phi/2} \cos \frac{\theta}{2} \\ e^{i\phi/2} \sin \frac{\theta}{2} \end{pmatrix}. \quad (4.29)$$

Such a state can be “prepared” by sending the particles through a set of Stern–Gerlach magnets aligned in the \mathbf{n} direction and selecting the beam bent upwards or downwards, depending on the sign of the gyromagnetic ratio.

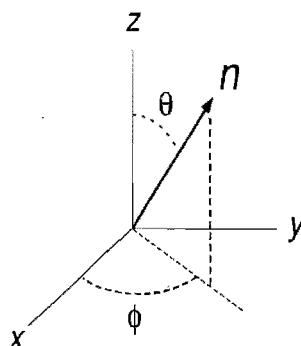


Fig. 4.2

4.7 The composition rule

Consider now a system with more than one angular momentum operator. The nature of the two angular momenta depends on the particular system considered. They might correspond to two orbital angular momenta, two particles with spin, or to the orbital angular momentum and spin of a single particle. The addition law of the angular momenta \mathbf{J}_1 and \mathbf{J}_2 follows from their commutation relations and is universal. Any state of such a system can be expressed as a linear combination of the states of the form $|j_1, m_1\rangle |j_2, m_2\rangle$, i.e. the *direct product* of the eigenstates of \mathbf{J}_1^2, J_{1z} and those of \mathbf{J}_2^2, J_{2z} .

The total angular momentum is defined as

$$\mathbf{J} = \mathbf{J}_1 \otimes \mathbb{1} + \mathbb{1} \otimes \mathbf{J}_2 \equiv \mathbf{J}_1 + \mathbf{J}_2. \quad (4.30)$$

Because the two angular momenta commute trivially,

$$[J_{1i}, J_{2j}] = 0$$

(they act on two distinct spaces), the total angular momentum \mathbf{J} obeys the same commutation relations,

$$[J_i, J_j] = i \epsilon_{ijk} J_k,$$

as those satisfied by \mathbf{J}_1 and \mathbf{J}_2 .

We ask two questions.

Question 1: Given the quantum numbers j_1 and j_2 for \mathbf{J}_1 and \mathbf{J}_2 , what are the possible values of j for the total angular momentum?

Question 2: What are the relations between the states of the component angular momenta, $|j_1, m_1\rangle |j_2, m_2\rangle$, and the eigenstates of the total angular momentum operators, \mathbf{J}^2 and J_z ?

The starting point from which to answer these questions is the observation that there are two natural bases of the angular momentum eigenstates:

- (i) a basis in which the operators $\mathbf{J}_1^2, J_{1z}, \mathbf{J}_2^2$, and J_{2z} are diagonal, with eigenstates

$$|j_1, m_1, j_2, m_2\rangle = |j_1, m_1\rangle \otimes |j_2, m_2\rangle = |j_1, m_1\rangle |j_2, m_2\rangle,$$

- (ii) an alternative basis in which the operators $\mathbf{J}^2, J_z, \mathbf{J}_1^2$, and \mathbf{J}_2^2 have definite values simultaneously,

$$|j_1, j_2; J, M\rangle,$$

with the properties

$$\mathbf{J}^2 |j_1, j_2; J, M\rangle = J(J+1) |j_1, j_2; J, M\rangle,$$

$$J_z |j_1, j_2; J, M\rangle = M |j_1, j_2; J, M\rangle.$$

The reader should verify that the operators in each group commute among themselves, and in each case, there are no other operators which commute with all of the operators already present. In other words, they form two alternative maximal sets of compatible observables. They will be called below the first and second basis, respectively.

To start with, let us consider the state in which the eigenvalues of J_{1z} and J_{2z} both take the maximum possible values,

$$|j_1, j_1, j_2, j_2\rangle = |j_1, j_1\rangle |j_2, j_2\rangle. \quad (4.31)$$

This is the *highest* state in the first basis. As the addition rule (4.30) is simply additive for the component J_z , $M = m_1 + m_2$, the above state must correspond to the state in which M also takes the maximum possible value, which is found to be $j_1 + j_2$. As $J \geq M$, this means that state (4.31) also represents the state in which J itself is maximum, and takes the value $j_1 + j_2$. Indeed

$$\begin{aligned} J^2 |j_1, j_1, j_2, j_2\rangle &= (J_1^2 + J_2^2 + 2\mathbf{J}_1 \cdot \mathbf{J}_2) |j_1, j_1, j_2, j_2\rangle \\ &= (J_1^2 + J_2^2 + J_{1+}J_{2-} + J_{1-}J_{2+} + 2J_{1z}J_{2z}) |j_1, j_1, j_2, j_2\rangle \\ &= (j_1 + j_2)(j_1 + j_2 + 1) |j_1, j_1, j_2, j_2\rangle \end{aligned}$$

shows that state (4.31) is an eigenstate of J^2 with eigenvalue $(j_1 + j_2)(j_1 + j_2 + 1)$, that is

$$|j_1, j_1, j_2, j_2\rangle = |j_1, j_2; j_1 + j_2, j_1 + j_2\rangle. \quad (4.32)$$

This is the first nontrivial result relating the two bases. To be precise, the relative phase in this relation has been arbitrarily set to unity. This will turn out to be part of the phase convention we are going to adopt.

Let us now act upon the highest state (4.32) with the lowering operator $J_{1-} + J_{2-} = J_-$. On the one hand (in the total angular momentum basis) this gives

$$J_- |j_1, j_2; j_1 + j_2, j_1 + j_2\rangle = \sqrt{2(j_1 + j_2)} |j_1, j_2; j_1 + j_2, j_1 + j_2 - 1\rangle,$$

where we have made use of eqn (4.26) and the fact that the action of J_- does not change the magnitude of the total angular momentum J . On the other hand, we also have

$$(J_{1-} + J_{2-}) |j_1, j_1, j_2, j_2\rangle = \sqrt{2j_1} |j_1, j_1 - 1, j_2, j_2\rangle + \sqrt{2j_2} |j_1, j_1, j_2, j_2 - 1\rangle,$$

and so this yields the second relation

$$\begin{aligned} &|j_1, j_2; j_1 + j_2, j_1 + j_2 - 1\rangle \\ &= \sqrt{\frac{j_1}{j_1 + j_2}} |j_1, j_1 - 1, j_2, j_2\rangle + \sqrt{\frac{j_2}{j_1 + j_2}} |j_1, j_1, j_2, j_2 - 1\rangle. \end{aligned} \quad (4.33)$$

Note that a particular linear combination of the two states with $M = j_1 + j_2 - 1$ appears in eqn (4.33). Since there are two linearly independent states with this value of $J_{1z} + J_{2z}$ in the first basis, there must be two states in the second basis also. One is eqn (4.33). Where is the other?

This second state must necessarily have $j_1 + j_2 \geq J \geq j_1 + j_2 - 1$. As the state with $J = j_1 + j_2$, $M = j_1 + j_2 - 1$ was already found, eqn (4.33), the only possibility is $J = j_1 + j_2 - 1$: the “missing state” is necessarily $|j_1, j_2; J = j_1 + j_2 - 1, M = j_1 + j_2 - 1\rangle$. What should it look like, in terms of the states of the first basis? It can be constructed “by hand”, so that it is orthogonal to eqn (4.33), that is

$$\begin{aligned} & |j_1, j_2; j_1 + j_2 - 1, j_1 + j_2 - 1\rangle \\ = & e^{i\alpha} \left(\sqrt{\frac{j_2}{j_1 + j_2}} |j_1, j_1 - 1, j_2, j_2\rangle - \sqrt{\frac{j_1}{j_1 + j_2}} |j_1, j_1, j_2, j_2 - 1\rangle \right), \end{aligned} \quad (4.34)$$

where α is a phase, undetermined for the moment.

At the next step, acting on eqns (4.33) and (4.34) with the operator $J_{1-} + J_{2-} = J_-$, we find two states

$$|j_1, j_2; j_1 + j_2, j_1 + j_2 - 2\rangle, \quad |j_1, j_2; j_1 + j_2 - 1, j_1 + j_2 - 2\rangle,$$

with $M = j_1 + j_2 - 2$. In general there will be three states having the value of J_z equal to $M = j_1 + j_2 - 2$ so that there must be another state in the total angular momentum basis as well. By reasoning analogous to those used above, we conclude that the third state must necessarily be the highest state of the multiplet with $J = j_1 + j_2 - 2$, whose explicit composition in terms of the states of the component angular momenta can be found by imposing orthogonality on the two states already found. And so on.

By continuing this way, we find at the n -th step $n + 1$ linearly independent states with $M = j_1 + j_2 - n$, of which one corresponds to the “new” multiplet with $J = j_1 + j_2 - n$. In other words, at each step the number of linearly independent states increases by one. This, however, does not continue forever: this process continues until n reaches $\min\{2j_1, 2j_2\}$ (the smaller of the two). When $n = 2j_1$ for instance, assuming $j_1 < j_2$, another action of the lowering operator simply annihilates the state $|j_1, -j_1, j_2, j_2\rangle$ so no new multiplet appears. A little thought convinces us that the value of the total angular momentum lies only in the range

$$J = j_1 + j_2, j_1 + j_2 - 1, j_1 + j_2 - 2, \dots, |j_1 - j_2|. \quad (4.35)$$

As a check, let us count the total number of linearly independent states in the two bases. In the first basis, we obviously have

$$(2j_1 + 1)(2j_2 + 1).$$

In the second basis, assuming eqn (4.35), one gets (for $j_1 < j_2$)

$$\sum_{J=j_2-j_1}^{j_2+j_1} (2J + 1) = (2j_1 + 1)(2j_2 + 1),$$

which shows that eqn (4.35) is indeed correct. In other words, the product of two multiplets decomposes as

$$\underline{j_1} \otimes \underline{j_2} = \underline{j_1 + j_2} \oplus \underline{j_1 + j_2 - 1} \oplus \cdots \oplus \underline{|j_1 - j_2|}$$

into various multiplets of definite angular momentum.

Let us examine a few examples. The case of two spin doublets, $s_1 = s_2 = \frac{1}{2}$, is of particular importance. In the notation already introduced, the product states decompose into a spin triplet ($S = 1$),

$$|\uparrow\rangle|\uparrow\rangle, \quad \frac{|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle}{\sqrt{2}}, \quad |\downarrow\rangle|\downarrow\rangle,$$

and a singlet,

$$\frac{|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle}{\sqrt{2}}.$$

The former combinations are all symmetric under the exchanges of the two spins and are often said to be in states with *parallel spins*, the latter (spin antisymmetric) combination is in a state with *anti-parallel* spin configuration.

For $j_1 = j_2 = 1$, there are nine states, which in the basis of total angular momentum decompose into a multiplet of $J = 2$ (5 states), a state with $J = 1$ (a triplet), and one with $J = 0$ (a singlet).

4.7.1 The Clebsch–Gordan coefficients

The above discussion answers Question 1. The discussion really also answered Question 2, apart from the phases appearing in relations such as eqn (4.34), which must be determined consistently. Each state in one basis can be expanded as a linear combination of the states of the other basis:

$$|j_1, m_1, j_2, m_2\rangle = \sum_{J, M} |j_1, j_2; J, M\rangle \langle j_1, j_2; J, M| j_1, m_1, j_2, m_2\rangle$$

and vice versa,

$$|j_1, j_2; J, M\rangle = \sum_{m_1, m_2} |j_1, m_1, j_2, m_2\rangle \langle j_1, m_1, j_2, m_2| j_1, j_2; J, M\rangle.$$

The expansion coefficients,

$$\langle j_1, j_2; J, M| j_1, m_1, j_2, m_2\rangle, \quad \langle j_1, m_1, j_2, m_2| j_1, j_2; J, M\rangle \quad (4.36)$$

are known as the *Clebsch–Gordan coefficients*, or simply, CG coefficients. The coefficients we found by an explicit construction, eqns (4.32), (4.33), and (4.34), are in fact examples of the CG coefficients. As already noted, the CG coefficients depend on the phase convention among various states. The convention frequently used, which we adopt in this book, is known as the Condon–Shortley convention. It consists of the following three rules:

- (1) The highest states in the two bases are identified with the coefficient 1, as in eqn (4.32): this fixes the global relative phases of the states in the first basis and those in the second basis.

- (2) All the matrix elements of the lowering operators J_{1-} , J_{2-} , J_- are real and semi-positive definite: this rule fixes the relative phases among the states within a multiplet.
- (3) The matrix elements

$$\langle j_1, j_2; J, M | J_{1z} | j_1, j_2; J \pm 1, M \rangle$$

are all real and semi-positive definite.

In this convention the CG coefficients are all real: the two expressions in eqn (4.36) are equal. For the reader's convenience the CG coefficients for small values of (j_1, j_2) are given in a Table (Figure 24.5) at the end of the book. In Mathematica, the command to get the CG coefficient, eqn (4.36), is simply: ClebschGordan[{ j_1, m_1 }, { j_2, m_2 }, { J, M }]

Note that due to the third rule of Condon-Shortley, the CG coefficients are in general not symmetric under the exchange, $(j_1, m_1) \leftrightarrow (j_2, m_2)$.

4.8 Spin

Let us come back to the transformation properties of wave functions under space rotations of the coordinate axes. For a particle without spin, the wave function transforms, under a rotation of the axes around a fixed axis ω , as a scalar, i.e. as

$$\mathbf{r} \rightarrow \mathbf{r}' = \mathbf{r} - \boldsymbol{\omega} \times \mathbf{r} + \dots;$$

$$\begin{aligned} \psi(\mathbf{r}) \rightarrow \psi(\mathbf{r}) &= \psi(\mathbf{r}' + \boldsymbol{\omega} \times \mathbf{r}') \\ &= \psi'(\mathbf{r}') = e^{i\boldsymbol{\omega} \cdot \hat{\mathbf{L}}} \psi(\mathbf{r}'). \end{aligned} \quad (4.37)$$

In other words, for $S = 0$, the value of the wave function in the same space point is invariant, but its *functional form* changes by virtue of the coordinate change (Fig. 4.3).

Such a change of functional form of wave functions can be regarded as a representation of the $SO(3)$ group. From the point of view of the transformation group, it is important to know which set of functions form an *irreducible* representation of the group, i.e. a set of objects which transform among themselves. Clearly since the space rotations do not change the magnitude of the angular momentum, such irreducible representations correspond to the *multiplets* of states with a fixed eigenvalue of \mathbf{J}^2 . For particles without spin, they are sets of eigenstates with a fixed orbital angular momentum \mathbf{L}^2 . They are precisely the spherical harmonics of index ℓ , $Y_{\ell,m}(\theta, \phi)$, $m = \ell, \ell-1, \dots, -\ell$. A generic wave function can be expanded in terms of the spherical harmonics,

$$\psi(\mathbf{r}) = \sum_{\ell,m} R_{\ell,m}(r) Y_{\ell,m}(\theta, \phi).$$

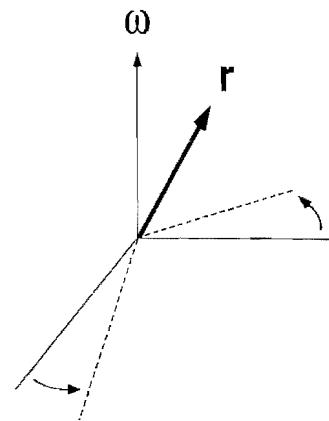


Fig. 4.3 As the axes are rotated by angle ω around the axis ω the physical position where the wave function is calculated remains unchanged, but its coordinates are rotated by $-\boldsymbol{\omega} \times \mathbf{r}$

The rotation of the coordinate system induces the transformation

$$\psi \rightarrow \psi' = e^{i\omega \cdot \hat{\mathbf{L}}} \psi = \sum_{\ell,m} R_{\ell,m}(r) e^{i\omega \cdot \hat{\mathbf{L}}} Y_{\ell,m}(\theta, \phi).$$

But as the operators \mathbf{L} cannot modify the value of ℓ , one has

$$e^{i\omega \cdot \hat{\mathbf{L}}} Y_{\ell,m}(\theta, \phi) = \sum_{m'=-\ell}^{\ell} D_{m',m}^{\ell}(\omega) Y_{\ell,m'}. \quad (4.38)$$

The matrix

$$D_{m',m}^{\ell}(\omega) \equiv \langle \ell, m' | e^{i\omega \cdot \hat{\mathbf{L}}} | \ell, m \rangle \quad (4.39)$$

is called *rotation matrix*.

The wave function of a particle with spin s has $2s+1$ components; they transform according to the law

$$\psi \rightarrow e^{i\omega \cdot (\hat{\mathbf{L}} + \hat{\mathbf{s}})} \psi.$$

$$\psi(\mathbf{r}) = \begin{pmatrix} \psi_1(\mathbf{r}) \\ \psi_2(\mathbf{r}) \\ \vdots \\ \psi_{2s+1}(\mathbf{r}) \end{pmatrix}.$$

The operator \mathbf{L} acts on the dependence on \mathbf{r} of each component (they are differential operators with respect to angular variables), while the spin operator acts on the spinor space,

$$\psi'_{\sigma} = \sum_{\sigma'} (e^{i\omega \cdot \hat{\mathbf{s}}})_{\sigma, \sigma'} \psi_{\sigma'}.$$

The matrix elements of \mathbf{s} have been determined in eqns (4.23), (4.24), and (4.25) (read $J_1 \rightarrow s_x$, $J_2 \rightarrow s_y$, $J_3 \rightarrow s_z$).

Remarks

- If the Hamiltonian is independent of the spin operators, its eigenstates can be taken to be in a factorized form,

$$\psi_{\sigma}(\mathbf{r}) = \psi(\mathbf{r}) \chi_{\sigma}.$$

For instance, the hydrogen atom is described, in the non-relativistic approximation, by

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r}. \quad (4.40)$$

The first relativistic corrections to eqn (4.40) are given by the terms

$$\Delta H = -\frac{\mathbf{p}^4}{8m^3} + \frac{e^2}{2m^2 r^3} \mathbf{L} \cdot \mathbf{s} + \frac{\pi e^2}{2m^2} \delta^3(\mathbf{r}).$$

Observe that the total Hamiltonian, $H + \Delta H$, is invariant under spatial rotations. In fact,

$$[\mathbf{J}, H + \Delta H] = 0,$$

where $\mathbf{J} = \mathbf{L} + \mathbf{s}$.

- In the case of a particle with spin- $\frac{1}{2}$, the spin operators are given by the Pauli matrices, $s_i = \frac{1}{2}\sigma_i$. An identity

$$e^{i\mathbf{a} \cdot \boldsymbol{\sigma}} = \cos|\mathbf{a}| + i \frac{\mathbf{a}}{|\mathbf{a}|} \cdot \boldsymbol{\sigma} \sin|\mathbf{a}|, \quad (4.41)$$

where \mathbf{a} is a constant vector, is useful to obtain explicit form of the rotation matrices.

4.8.1 Rotation matrices for spin $\frac{1}{2}$

Under a rotation of angle ϕ around the direction \mathbf{n} , the wave function of spin $\frac{1}{2}$ transforms as

$$\chi \rightarrow \exp \left[\frac{i}{2} \phi (\mathbf{n} \cdot \boldsymbol{\sigma}) \right] \psi \equiv U(\phi \mathbf{n}) \psi.$$

Using identity (4.41), we can easily calculate the rotation matrix:

$$U(\phi \mathbf{n}) = \cos \frac{\phi}{2} + i \mathbf{n} \cdot \boldsymbol{\sigma} \sin \frac{\phi}{2}.$$

For example, for a rotation around the z axis,

$$U_z(\phi) = \begin{pmatrix} e^{i\frac{\phi}{2}} & 0 \\ 0 & e^{-i\frac{\phi}{2}} \end{pmatrix};$$

while for rotations around the x or y axes,

$$U_x(\phi) = \begin{pmatrix} \cos \frac{\phi}{2} & i \sin \frac{\phi}{2} \\ i \sin \frac{\phi}{2} & \cos \frac{\phi}{2} \end{pmatrix}; \quad U_y(\phi) = \begin{pmatrix} \cos \frac{\phi}{2} & \sin \frac{\phi}{2} \\ -\sin \frac{\phi}{2} & \cos \frac{\phi}{2} \end{pmatrix}.$$

Observe that for a rotation of angle 2π ,

$$U_x(2\pi) = -\mathbb{1}; \quad U_y(2\pi) = -\mathbb{1}; \quad U_z(2\pi) = -\mathbb{1};$$

the wave function of a spin- $\frac{1}{2}$ particle changes sign! From the point of view of group theory, consideration of these wave functions constitutes particular types of representation, known as spinor (or projective) representations of the $SO(3)$ group. “Spinor” is just the name given to these objects to distinguish them, for instance, from ordinary vectors. The wave function of a spin-1 particle does transform as a vector, for which obviously $U(2\pi) = \mathbb{1}$ holds.

The rotation matrix for a generic rotation for spin $\frac{1}{2}$ can be expressed in terms of three Euler angles, α , β and γ , defined in Fig. 4.4.

$$\begin{aligned} D^{1/2} \equiv U(\alpha, \beta, \gamma) &= U_z(\gamma) U_y(\beta) U_z(\alpha) \\ &= \begin{pmatrix} e^{i(\alpha+\gamma)/2} \cos \frac{\beta}{2} & e^{-i(\alpha-\gamma)/2} \sin \frac{\beta}{2} \\ -e^{i(\alpha-\gamma)/2} \sin \frac{\beta}{2} & e^{-i(\alpha+\gamma)/2} \cos \frac{\beta}{2} \end{pmatrix}. \end{aligned} \quad (4.42)$$

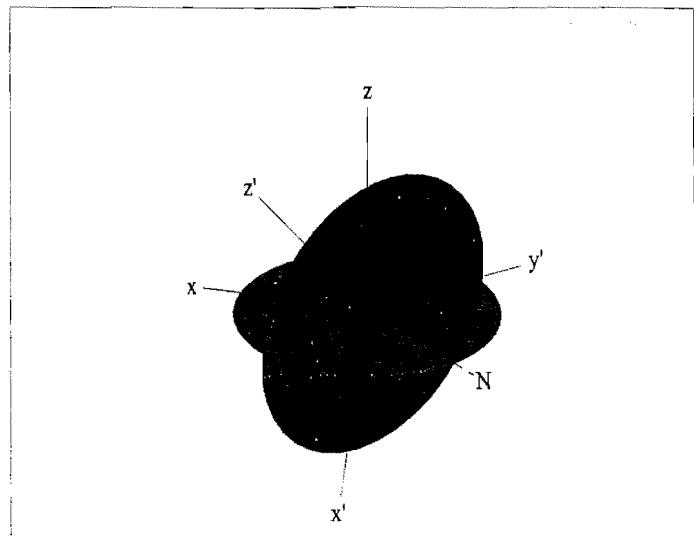


Fig. 4.4 Euler angles

The rotation matrix for a particle with arbitrary spin

The rotation matrix for a particle with spin $S = \frac{n}{2}$, $n = 1, 2, 3, \dots$, can be found in the following way. Take n spinors, each with spin $\frac{1}{2}$, and construct their products, totally symmetric under exchange of spins. There are exactly $n + 1$ such combinations, analogous to the triplet of states found earlier on the case of $n = 2$. Clearly the highest state,

$$|\uparrow\uparrow\dots\uparrow\rangle, \quad (4.43)$$

having $S_z = \frac{n}{2}$, must be a state of $S = \frac{n}{2}$. Other states which are totally symmetric can be obtained from eqn (4.43) by repeatedly acting with $S_- = s_{1-} + s_{2-} + \dots + s_{n-}$. For instance, the next-to-highest state is

$$\frac{1}{\sqrt{n}} (|\downarrow\uparrow\dots\uparrow\rangle + |\uparrow\downarrow\uparrow\dots\uparrow\rangle + \dots + |\uparrow\dots\uparrow\downarrow\rangle).$$

Since the action of the operator S_- does not change the value of S , these $n + 1$ states precisely form the multiplet with $S = \frac{n}{2}$.

The rotation matrix for spin S is therefore just the direct product of $n = 2S$ matrices (4.42), totally symmetrized with respect to the spins. It follows that the wave function of a particle with an integer spin (even n) returns to the original value after a 2π rotation, while the wave function of any half-integer spin particle (odd n) changes sign.

Guide to the Supplements

Supplement 20.5 briefly discusses the properties of the Legendre polynomials. Supplement 20.6 reviews some elementary aspects of the group theory. Supplement 20.7 is a collection of the formulas used in the angular momentum theory.

Problems

- (4.1) Two particles of spin $\frac{1}{2}$ interact with a Hamiltonian $H_0 = \frac{1}{2}\mathbf{s}_1 \cdot \mathbf{s}_2$. List all the conserved quantities and write the energy eigenvalues. An external field \mathbf{B} is applied to the system. Assume that this field interacts only with the first particle, with $V = \mathbf{B} \cdot \mathbf{s}_1$. Find the conserved quantities and determine the spectrum of $H_0 + V$.
- (4.2) Write the components of a spinor ($s = \frac{1}{2}$) with projection of spin $\frac{1}{2}$ along an axis lying in the y, z plane and making an angle θ with the z axis. Generalize the computation to an arbitrary axis ζ defined through the spherical angles (θ, φ) .
- (4.3) The particle Λ^0 with spin $\frac{1}{2}$, decays into $p + \pi$ in its rest system. Assume that Λ^0 is polarized along the z axis. Write the most general amplitude for the process and the angular distribution of the secondary particles. What are the constraints if parity is conserved? Write the expression for the average value of the longitudinal polarization of the proton (projection of spin along the direction of motion).
- (4.4) A particle of spin S interacts with an external uniform magnetic field \mathbf{B} ,

$$H = -\mu \cdot \mathbf{B} = -\beta S_z.$$

At time $t = 0$ the spin is oriented along $\mathbf{n} = (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$, i.e. $\mathbf{S} \cdot \mathbf{n}|0\rangle = |0\rangle$.

- a) Compute the mean values $\langle S_x \rangle, \langle S_y \rangle, \langle S_z \rangle$ at time $t = 0$. (Suggestion: consider an equivalent system composed of $N = 2S$ particles of spin $\frac{1}{2}$).
- b) Compute the probabilities of finding the different S_z values with a measure of S_z at $t = 0$.
- c) Consider the Heisenberg operators $S_x^H(t), S_y^H(t), S_z^H(t)$. Write and solve the Heisenberg equations of motion. From the computation extract the values of $\langle t|S_x|t\rangle, \langle t|S_y|t\rangle, \langle t|S_z|t\rangle$ for the Schrödinger operators at time t . Find the minimum value t such that $\langle t|S_x|t\rangle$ has the initial value.
- (4.5) A particle of mass m , spin $\frac{1}{2}$ and charge e is bound in a three-dimensional harmonic potential. A weak uniform magnetic field is applied to the system. The Hamiltonian is

$$H = \frac{1}{2m} \left(\mathbf{p} - \frac{e}{c} \mathbf{A} \right)^2 + \frac{1}{2} m \omega^2 \mathbf{r}^2 - \mu \cdot \mathbf{B},$$

with

$$\mu = g \mu_B \mathbf{s} = \frac{g}{2} \mu_B \sigma; \quad \mu_B = \frac{e\hbar}{2mc}.$$

- a) With $\mathbf{B} = 0$, compute the first few energy levels of the system, their orbital angular momentum, and the total angular momentum.
- b) Consider now a weak magnetic field, with a vector potential $\mathbf{A} = (-B\frac{y}{2}, B\frac{x}{2}, 0)$. List the conserved operators, neglecting order B^2 effects.
- c) Using previous results, compute, in the weak field approximation, the energy for the first two levels of the system.

- (4.6) A constant electric field directed along the z axis acts on a particle of mass m and charge q .

- a) Write and solve the Heisenberg equations for the position $\mathbf{r}(t)$ and the momentum $\mathbf{p}(t)$.
- b) Find the operator $\mathbf{L}(t)$ using the results of part a). Verify that the result is consistent with equations of motion for $\mathbf{L}(t)$.
- c) Compute the mean value of $\mathbf{L}(t)$, knowing that

$$\langle \mathbf{r}(0) \rangle = 0; \quad \langle \mathbf{p}(0) \rangle = p_0 \hat{\mathbf{x}}; \quad \langle \mathbf{L}(0) \rangle = 0.$$

- (4.7) A particle of mass m and spin $\frac{1}{2}$ is described by a one-dimensional Hamiltonian

$$H = \frac{1}{2m} \mathbf{p}^2 + V(x); \quad V[x] = \frac{\sigma_3 + 1}{4} m \omega^2 x^2.$$

- a) Compute the spectrum of H and its eigenfunctions.
- b) At time $t = 0$ the particle is in the state

$$\psi(0, x) = \psi_0(x) \frac{|+\rangle - |-\rangle}{\sqrt{2}},$$

where $|\pm\rangle$ are up and down eigenstates of s_z , and $\psi_0(x) = (m\omega/\pi\hbar)^{1/4} \exp(-\frac{m\omega}{2\hbar}x^2)$ is the ground-state wave function for the oscillator (frequency ω). Tell if this state is an eigenstate of H and compute the expectation value of H in it.

- c) Compute the wave function at time t . At time t a measurement of s_z is performed with a Stern-Gerlach experiment. Compute the probability of finding $s_z = -\frac{1}{2}$.

- (4.8) Let us consider the Hamiltonian of the hydrogen atom, together with the spin-orbit interaction term for the electron and the spin-spin interaction between electron and proton (hyperfine interaction):

$$H_{so} = A \mathbf{L} \cdot \mathbf{s}_e; \quad H_{ss} = B \mathbf{s}_p \cdot \mathbf{s}_e;$$

A and B are constants.

- a) Compute the degeneracy for the levels $n = 1$, $n = 2$ of the hydrogen atom taking into ac-

count electron and proton spin but neglecting the above interactions.

- b) Classify the same levels by neglecting only H_{ss} . Use the operators \mathbf{L}^2 , \mathbf{J}^2 , \mathbf{F}^2 , F_z , where $\mathbf{J} = \mathbf{L} + \mathbf{s}_e$, $\mathbf{F} = \mathbf{J} + \mathbf{s}_p$.
- c) Some of the states classified above are also eigenstates of the total Hamiltonian: find which and compute their eigenvalues.

5

Symmetry and statistics

Two concepts, of fundamental importance to quantum mechanics, will be discussed in this chapter. The first is that of symmetry. Even though the concept of symmetry is familiar in a wide range of natural sciences, the way symmetry constrains the consequences of quantum mechanics is rather subtle and, at the same time, far-reaching. The second is the symmetry property of the states under the exchange of two identical particles. Identical particles with a half-integer spin (fermions) obey the Fermi–Dirac statistics: the wave functions are totally antisymmetric under the exchange of the particles. Identical particles with an integer spin (bosons) are instead subject to the Bose–Einstein statistics. Their wave functions are totally symmetric.

5.1 Symmetries in Nature

Often the equations of a given physical system can be expressed by using different variables, such as position variables referring to alternative coordinate systems. We talk in general about transformations (e.g. canonical transformations in classical mechanics) of variables in describing the same physics.

A concept closely related is that of symmetry. When a transformation of variables leaves the Hamiltonian formally invariant, when expressed in terms of the new variables¹, we talk about a *symmetry*, or an *invariance* of physical laws. In fact, the equations of motion and the physical laws will look identical in two different descriptions of the same system.

Symmetries abound in Nature, from atoms and crystals to biological bodies.

A possible consequence of symmetry is the conservation law. Well-known examples from classical mechanics are energy conservation related to the homogeneity of time (the Hamiltonian is invariant under time translation), momentum conservation (if the Hamiltonian is invariant under space translations), and angular momentum conservation (if the space and the potential are isotropic). Electric charge conservation can also be related to the invariance under phase transformations of the wave function of charged particles. In many cases, the conservation law in physics is indeed a consequence of some underlying symmetry.

Symmetries can be classified into two types, discrete and continuous, according to whether the relevant transformations are of discrete or continuous type. There is an approximate left-right symmetry to many biological bodies, including human bodies, which is an example of

5.1 Symmetries in Nature	111
5.2 Symmetries in quantum mechanics	113
5.3 Identical particles: Bose–Einstein and Fermi–Dirac statistics	127
Guide to the Supplements	133
Problems	134

¹ Sometimes not only the form but also the value of the Hamiltonian is left invariant, but here we shall allow for both possibilities.

²In more modern terms, those electroweak interactions associated with the exchange of W and Z bosons violate parity.

³ C is a “charge conjugation” symmetry, i.e. symmetry under the exchange of particle and anti-particle; T is time reversal. See below.

⁴For non-derivative interactions, like $g\mu_B \mathbf{s} \cdot \mathbf{B}$ in non-relativistic quantum mechanics, the gauge principle quoted below requires that gauge potentials appear only as electric and magnetic fields, \mathbf{E}, \mathbf{B} .

a discrete symmetry. In elementary particle physics we have an analogous symmetry, parity, which is a good symmetry of strong (nuclear), electromagnetic and gravitational interactions, but is broken by weak interactions². CP , T , and CPT are other important examples of (very good) discrete symmetries of Nature.³

Symmetries related to continuous set of transformations are known as continuous symmetries. The three-dimensional rotational symmetry group $SO(3)$ (characterized by continuous Euler angles) is an example of a continuous symmetry.

Symmetries may also be divided into two categories: space-time (such as those involving invariance under time or space transformations) and internal symmetries (such as isospin, see below).

A great advance in 20th century theoretical physics was the notion that the requirement of symmetry can be strong enough to determine even the form of the interactions (type of forces). For instance, the form of the derivative⁴ interactions of a charged particle with electromagnetic fields is determined by the so-called minimal principle, with the following characteristic way in which the vector and scalar potentials enter the Hamiltonian,

$$H = \frac{(\mathbf{p} - \frac{q}{c}\mathbf{A})^2}{2m} + q\phi + \dots$$

As is well known (see Chap. 14), such a form is dictated by the requirement that it should be possible to re-parametrize the electron wave function by an arbitrary phase factor, with time- and space-dependent phase $f(\mathbf{r}, t)$, as

$$\psi(\mathbf{r}, t) \rightarrow e^{if(\mathbf{r}, t)} \psi(\mathbf{r}, t).$$

Even the necessity of the existence of the photon, whose wave function transforms inhomogeneously under gauge transformations, follows from such a requirement. Empirical laws such as the Lorentz force are now understood as a consequence of the minimal principle. This strong form of the symmetry requirement—that the system be invariant under transformations depending on space-time, and that the form of the interactions is uniquely determined by such a requirement—is known as the *gauge principle*.

In the case of electromagnetism, the transformation group is simply the phase transformation—the group $U(1)$ —which is commutative (Abelian). C. N. Yang and R. L. Mills [Yang and Mills (1954)] and R. Shaw [Shaw (1954)] extended the gauge principle by constructing a model in which the requirement of local transformation is applied to a set of multi-component wave functions, such as an isospin multiplet. The requirement is now that the theory be invariant under the re-labelling (gauge transformations) of the form

$$\psi(\mathbf{r}, t) \rightarrow U(\mathbf{r}, t) \psi(\mathbf{r}, t),$$

where $U(\mathbf{r}, t)$ is a matrix representing a group element of $SU(2)$, $SU(3)$, $SO(3)$, etc., depending on the model considered, in general a non-commutative (non-Abelian) group. They are known as Yang–Mills theories today.

It is a truly remarkable fact that the standard model of fundamental interactions—quantum chromodynamics for the strong interactions and the Glashow–Weinberg–Salam model of electroweak interactions—are all theories of this sort (with the $SU(3)$ group in the former and the $SU(2) \times U(1)$ group in the latter). The impressive success of the standard model in describing basically *all* of the known fundamental physical phenomena, with the exclusion of gravitational ones, suggests that a very highly nontrivial conceptual unification underlies the working of Nature ('t Hooft).⁵

Finally, a symmetry can be realized in two different ways, either manifest or hidden. The former is the usual way a symmetry is realized in Nature, yielding energy degeneracy among the states belonging to a multiplet of states, transformed among each other by the particular symmetry operation under consideration. However, this is not the only way a symmetry can be realized. It is possible that the physical laws and the Hamiltonian are invariant but the ground state is not.

In the example of the left-right symmetry of the human body, an exact symmetry may be realized in three different ways. Each individual is left-right symmetric, with the heart in the center; or, for each left-hearted person there is another individual with the heart on the right, but otherwise with identical characteristics (a parity partner); or finally, the option that everybody has the heart on the left side, even if all the physical and biological laws are symmetric,⁶ i.e., might have allowed for a left-hearted as well as right-hearted people (see Fig. 5.1). This last option, which Nature seems to have adopted, is known as “spontaneously broken” symmetry. See Subsection 5.2.1.

A well-known example of spontaneously broken symmetry is the spontaneous magnetization that occurs in certain metals (ferromagnets). Below some critical temperature, all the spins are directed in the same direction, thus “violating” the $SO(3)$ rotational invariance of the Hamiltonian. There are many important applications in solid-state and elementary particle physics of spontaneously broken symmetries.

C. N. Yang, in the concluding talk of the TH 2002 Conference in Paris, characterized the 20th century theoretical physics by three “melodies”.⁷

“Symmetry, quantization, and phase factor”

The challenge today is to find out whether we need some new principles or paradigm, in addition to these concepts, to understand Nature at a deeper level, beyond the standard model of fundamental interactions.

5.2 Symmetries in quantum mechanics

The presence of a symmetry in a quantum mechanical system is signaled by the existence of a unitary operator U which commutes with the Hamiltonian:

$$[U, H] = 0. \quad (5.1)$$

⁵To be precise, there is a part of the Glashow–Weinberg–Salam model, related to the so-called Higgs particle, which is not entirely determined by gauge principles. Future experiments, such as the Large Hadron Collider (LHC) experiments which has just started operating at CERN, Geneva, are hoped to give some indications whether the model should be extended and if so in which way.

⁶Of course, this is a blatant simplification for the sake of discussion. Biological systems are not left-right symmetric at the deeper levels also (e.g. DNA).

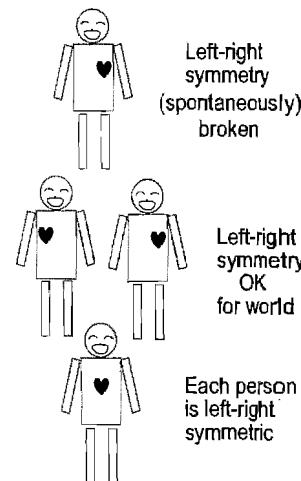


Fig. 5.1 Left-right symmetry might be realized in different ways

⁷For the “phase factor”, see Chapters 8 and 14.

As a unitary operator satisfies

$$UU^\dagger = U^\dagger U = \mathbf{1};$$

eqn (5.1) is equivalent to

$$U^\dagger H U = H : \quad (5.2)$$

U is a unitary transformation which leaves the Hamiltonian invariant. We have already seen some examples of such operators:

$$U = e^{i\hat{J} \cdot \omega}$$

describes spatial rotations;

$$U = e^{i\hat{p} \cdot r_0 / \hbar}$$

represents spatial translations.

Conservation

One of the possible consequences of a symmetry is the conservation of an associated charge. Suppose that the state $|\psi\rangle$ is an eigenstate of a dynamical quantity represented by a Hermitian operator G , such that

$$U \simeq \mathbf{1} - i\epsilon G + \dots,$$

i.e. G is a generator of U . From eqn (5.1) and eqn (5.2) it follows that

$$[G, H] = 0. \quad (5.3)$$

By assumption

$$G|\psi(0)\rangle = g|\psi(0)\rangle.$$

The state at time $t > 0$ is given by

$$|\psi(t)\rangle = e^{-iHt/\hbar}|\psi(0)\rangle,$$

so that

$$G|\psi(t)\rangle = Ge^{-iHt/\hbar}|\psi(0)\rangle = e^{-iHt/\hbar}G|\psi(0)\rangle = g|\psi(t)\rangle.$$

The system remains an eigenstate of G during the evolution; the charge g is conserved.

Electric charge conservation is similar. The charge operator Q acts on the particle state as follows:

$$\begin{aligned} Q|e\rangle &= -e|e\rangle; & Q|p\rangle &= +e|p\rangle; \\ Q|n\rangle &= 0; & Q|\pi^+\rangle &= +e|\pi^+\rangle, \end{aligned}$$

etc., where the kets stand for the state of a single electron, a proton, a neutron, and a pion, respectively. Q commutes with the Hamiltonian including all the known forces (the gravitational, electroweak, and strong

forces): this fact guarantees that the total electric charge of a system is conserved. In the non-relativistic approximation adopted in most of this book, charge conservation is a consequence of particle number conservation; vice versa, in the relativistic context where particles can be created or annihilated (only the total energy is conserved), electric charge conservation represents a nontrivial selection rule.

In general, conservation means (see Section 2.4.2)

$$0 = i\hbar \frac{dG}{dt} = i\hbar \frac{\partial G}{\partial t} + [G, H] \quad (5.4)$$

For operators which do not depend explicitly on time, this condition reduces to eqn (5.3). The additional term has a simple meaning in terms of symmetry. Let $G(\alpha, t)$ be a generator (or the associated unitary operator) which depends on some parameter and on t . Equation (5.4) is then equivalent to

$$G(\alpha, t) = e^{-iH(t-t_0)/\hbar} G(\alpha, t_0) e^{iH(t-t_0)/\hbar},$$

as can be checked by taking the time derivative. The previous equation means

$$G(\alpha, t) e^{-iH(t-t_0)/\hbar} = e^{-iH(t-t_0)/\hbar} G(\alpha, t_0). \quad (5.5)$$

In words: G is conserved (is a symmetry) if the transformation of the evolved state is equal to the evolution of the transformed state, i.e. if the transformation commutes with dynamical evolution. An example will be given below for Galilei boosts.

Degeneracy

Another possible consequence of a symmetry is the degeneracy of energy levels. Consider a stationary state

$$H|\psi_n\rangle = E_n|\psi_n\rangle,$$

and suppose that there exists an operator G which commutes with H . It follows from $[G, H] = 0$ that

$$H G |\psi_n\rangle = G H |\psi_n\rangle = E_n G |\psi_n\rangle.$$

There are several possibilities. The state $|\psi_n\rangle$ might not be in the domain of the operator G ($G|\psi_n\rangle \notin \mathcal{H}$); G may annihilate $|\psi_n\rangle$, $G|\psi_n\rangle = 0$; or $|\psi_n\rangle$ may happen to be an eigenstate of G :

$$G|\psi_n\rangle = \text{const.}|\psi_n\rangle.$$

In any of these cases no interesting result follows.

If, however, none of the above cases holds (i.e., $G|\psi_n\rangle \in \mathcal{H}$; $G|\psi_n\rangle \neq 0$; $G|\psi_n\rangle \neq |\psi_n\rangle$), then it follows that the level n is degenerate: we can find another energy eigenstate, $G|\psi_n\rangle$, with the same energy. By acting upon the state $|\psi_n\rangle$ with the operator G repeatedly one expects to find some degenerate set of states. We have already seen several examples of

this sort. For instance, if the Hamiltonian commutes with the angular momentum operators L_i , $i = 1, 2, 3$, that is, it is invariant under three-dimensional rotations, an energy level with a given orbital quantum number L is (at least) $2L + 1$ times degenerate. Such a degeneracy can be seen as the result of nontrivial actions of the operators L_x , L_y on an energy (and L_z) eigenstate $|E, \mathbf{L}^2, L_z\rangle$.

5.2.1 The ground state and symmetry

As stated in Section 5.1 the behavior of the ground state under symmetry transformations is of particular importance. In quantum mechanics, with a finite number of degrees of freedom the ground state is *invariant* under symmetry, and *unique*. Let us discuss this point informally. In the previous paragraph we have shown that if H commutes with a (unitary) operator U and if $|\psi_0\rangle$ is an eigenstate of H , then also $U|\psi_0\rangle$ is an eigenstate with the same energy. If the ground state is unique, it is therefore necessarily invariant. The uniqueness cannot be just a mathematical statement on self-adjoint operators, as the trivial example of a Hamiltonian multiple of the identity clearly has a non-unique ground state. To be a “bona fide” ground state, $|\psi_0\rangle$ must be *stable*, i.e. if we switch a small perturbation λV , the new ground state $|\lambda\rangle$ must satisfy $|\lambda\rangle \rightarrow |\psi_0\rangle$ as $\lambda \rightarrow 0$. This cannot be true for a ground state belonging to a degenerate subspace. The example of a two-state system

$$H = \begin{pmatrix} E_0 & \lambda V \\ \lambda V & E_0 \end{pmatrix} \quad (5.6)$$

is general enough: we can always think of a perturbation which acts only on the two “degenerate” states $|\pm\rangle$ out of the Hilbert space. In this case the true ground state (even for an infinitesimal non-diagonal element V) $|\lambda\rangle = (|+\rangle + |-\rangle)/\sqrt{2}$ is *not* a small perturbation of a supposed ground state $|+\rangle$ or $|-\rangle$. In any quantum mechanical system with a finite number of degrees of freedom, tunnel effects give rise to non-diagonal elements connecting different ground states.

It is reassuring that a very general theorem states that for “reasonable” Hamiltonians with the usual kinetic terms and two-body interaction potentials, if a ground state exists at all (i.e. if we have a discrete spectrum), then it is unique. This is a generalization of the non-degeneracy theorem of one-dimensional systems. In fact, the theorem proves more: the ground state function can be chosen to be positive everywhere. The interested reader can find a proof in Vol.4 of the book [Reed and Simon (1980b)]. This means that in physically realistic problems the ground state is indeed unique, and then symmetric.

An apparently harmless assumption in eqn (5.6), the existence of a “small” perturbation which can connect different vacuum states, must be reconsidered with more care in the case of systems with *infinite degrees of freedom*. It is precisely here that the situation can change in going from finite to infinite degrees of freedom, such as solids or quantum field theories. In the case of spontaneous magnetization, an infinite energy

is required to flip an infinite number of spins, and therefore no non-diagonal elements arise. The system chooses a ground state in which all spins are directed in one direction, at sufficiently low temperatures (where the energetics wins against the entropy effects in the free energy, $E - TS$). The rotational symmetry of the Hamiltonian is violated by the ground state.

In systems with infinite degrees of freedom, a symmetry can thus be realized in two ways: either having a symmetric, unique ground state—in this case, all the excited states will be in various degenerate multiplets, and symmetry is realized in the standard, “manifest” way—or by a ground state which is not symmetric. In the latter case one talks about “spontaneously broken symmetry”, even though symmetry is not really broken. In particular, if this second option is realized in a system with a *continuous symmetry*, the system necessarily develops some excitations of zero energy (Nambu–Goldstone excitations).⁸

5.2.2 Parity (\mathcal{P})

Parity is one of the approximate symmetries of Nature. It is a discrete symmetry, under the spatial reflection

$$\mathbf{r} \rightarrow -\mathbf{r}.$$

The wave function undergoes a transformation

$$\mathcal{P}\psi(\mathbf{r}) = \psi(-\mathbf{r})$$

while the operators transform as

$$\mathcal{P}O(\mathbf{r}, \mathbf{p})\mathcal{P}^{-1} = O(-\mathbf{r}, -\mathbf{p}).$$

If the Hamiltonian is invariant under parity,

$$\mathcal{P}H\mathcal{P}^{-1} = H,$$

or $\mathcal{P}H = H\mathcal{P}$, then parity is conserved. \mathcal{P} is a symmetry operator. As \mathcal{P} commutes with H , the stationary states *can* be chosen to be eigenstates of \mathcal{P} also. The eigenvalues of the latter are limited to be ± 1 , as obviously

$$\mathcal{P}^2 = \mathbf{1}.$$

The stationary states are then classified into parity-even states

$$\mathcal{P}\psi(\mathbf{r}) = \psi(-\mathbf{r}) = +\psi(\mathbf{r})$$

and -odd states

$$\mathcal{P}\psi(\mathbf{r}) = \psi(-\mathbf{r}) = -\psi(\mathbf{r}).$$

Parity is a good quantum number when the potential is spherically symmetric, $V(\mathbf{r}) = V(r)$. In such a case the angular momentum is also conserved and a state with definite angular momentum will have

⁸This is known as the Nambu–Goldstone theorem. See [Nambu (1960), Nambu and Jona-Lasinio (1961), Goldstone, Salam and Weinberg (1962), Strocchi (1985)]. There are many systems in Nature in which a symmetry is realized in the Nambu–Goldstone mode. One of the most remarkable examples in elementary particle physics is the light π mesons, which are best understood as approximate Nambu–Golstone particles, associated with a “hidden” $SU(2)$ symmetry.

a definite parity. For instance, in the simple one-particle system (or two-particle system reduced to a one-particle problem for the relative motions), the wave function $R(r)Y_{\ell,m}(\theta, \phi)$ is even or odd according to

$$\mathcal{P} = (-)^\ell. \quad (5.7)$$

Such a relation, however, should not obscure the fact that these two symmetries (invariance under three-dimensional rotations and space reflections) are in principle independent concepts. For instance a reflection-invariant potential

$$V(-\mathbf{r}) = V(\mathbf{r}),$$

(such as $V(x^2 + 2y^2 + 7z^2)$) is not necessarily spherically symmetric. Vice versa, there are interactions which are invariant under space rotations but not under parity, such as

$$V = g \mathbf{r} \cdot \mathbf{s},$$

where \mathbf{s} is the spin operator. Within the context of elementary particle physics, the so-called weak interactions are known to violate parity.

Another example which shows that the relation between parity and angular momentum conservation is not always as simple as eqn (5.7) is a system of more than one particle, which do not interact but are all moving under a common, spherically symmetric potential. (In a very crude approximation an atomic system looks like this.)

The wave function is a product of the wave function of the individual particles, each with a definite angular momentum ℓ_i . The total angular momentum L could take one of the possible values appearing in the decomposition

$$\ell_1 \otimes \ell_2 \otimes \ell_3 \cdots = \ell_1 + \ell_2 + \dots \ell_N \oplus \ell_1 + \ell_2 + \dots \ell_N - 1 \oplus \dots,$$

while parity is simply

$$\mathcal{P} = \prod (-)^{\ell_i}.$$

There is no simple relation between L and \mathcal{P} .

Intrinsic parity

An important empirical fact is that each elementary particle carries a definite, intrinsic parity, besides the parity due to the orbital motion. It is a little analogous to the spin of each particle, which is unrelated to its orbital motion. Some of the known elementary particles carry the intrinsic parity

$$\mathcal{P}|\pi\rangle = -|\pi\rangle; \quad \mathcal{P}|K\rangle = -|K\rangle; \quad \mathcal{P}|p\rangle = +|p\rangle;$$

$$\mathcal{P}|n\rangle = +|n\rangle; \quad \mathcal{P}|\bar{p}\rangle = -|\bar{p}\rangle;$$

etc. If a given interaction respects parity, the total parity (the product of the parity of the orbital wave functions and of the intrinsic parities of all particles involved) is conserved in any process.

The spin operator transforms under parity as follows

$$\mathcal{P} \mathbf{s} \mathcal{P}^{-1} = \mathbf{s},$$

i.e., as an orbital angular momentum. The ordinary momentum operator \mathbf{p} transforms like the position operator:

$$\mathcal{P} \mathbf{p} \mathcal{P}^{-1} = -\mathbf{p}.$$

In general, the operators can be classified according to their behavior under parity. The momentum, position, vector potential, etc. are *vectors*; the angular momentum operators (including spin operators) are *axial vectors*. Scalar quantities (invariant under rotations) which change sign under parity are known as *pseudo-scalars*, to be compared to ordinary scalars, which are invariant under parity. *

Parity, in spite of its natural definition, is not an exact symmetry of Nature: it is only an approximate symmetry. As already anticipated above, weak interactions (in more modern terminology, the exchange of W or Z bosons) violate parity. This is a good reminder of the fact that symmetry is, in general, a property of a given type of interaction (force) rather than being some absolute principle. To the best of our knowledge today, the electromagnetic, strong, and gravitational interactions respect parity.

The explicit form of the parity operator \mathcal{P}

It could be of some interest to construct the parity operator in an explicit form, in terms of the operators q and p . Let us first consider a one-dimensional system. For *any* such system, consider the operator

$$A = \frac{p^2}{2} + \frac{q^2}{2} - \frac{\hbar}{2}.$$

It is, apart from an additive constant, just the Hamiltonian of a harmonic oscillator with $m = \omega = 1$. By using the known solution of the Heisenberg equation for such an oscillator, see eqns (7.60) and (7.61), we know that after half the period of the evolution q and p change sign:

$$e^{i\frac{1}{\hbar}A\pi} p e^{-i\frac{1}{\hbar}A\pi} = -p, \quad e^{i\frac{1}{\hbar}A\pi} q e^{-i\frac{1}{\hbar}A\pi} = -q. \quad (5.8)$$

But actually the derivation of eqn (5.8) depends *only* on the canonical commutators between q and p , and hence holds in any system. The parity operator is thus given, *in any system*, by

$$\mathcal{P} = \exp\left(\frac{i}{\hbar} A\pi\right) = \exp\left[\frac{i}{\hbar} \left(\frac{p^2}{2} + \frac{q^2}{2} - \frac{\hbar}{2}\right)\pi\right]. \quad (5.9)$$

This result might be puzzling at first sight: how can one see that operator (5.9) commutes with a Hamiltonian which is even under parity? Also, what is special about the frequency $\omega = 1$ or $m = 1$?

To clarify these points, first observe that the operator A is certainly self-adjoint and admits a complete basis of orthonormal eigenvectors: the standard eigenstates of a harmonic oscillator. On these states \mathcal{P} acts as follows

$$\mathcal{P}|n\rangle = e^{in\pi}|n\rangle = (-1)^n|n\rangle,$$

so \mathcal{P} is in fact the parity operator. As any state of any system can be expanded in terms of $\{|n\rangle\}$,

$$\Psi(x, t) = \sum_n c_n(t) \varphi_n(x), \quad \varphi_n(x) \equiv \langle x|n\rangle, \quad (5.10)$$

it follows that \mathcal{P} always acts as the parity operator.

Let us separate all the even and odd eigenstates of A . Any operator in any system has the form of a matrix in such a basis (ee for even-even, etc.),

$$O = \begin{pmatrix} O_{ee} & O_{eo} \\ O_{oe} & O_{oo} \end{pmatrix};$$

in particular, the operator \mathcal{P} itself will have the form

$$\mathcal{P} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (5.11)$$

The point is that this form remains invariant under any unitary transformations (Chap. 7) which leaves the block diagonal form invariant:

$$S = \begin{pmatrix} S_{ee} & 0 \\ 0 & S_{oo} \end{pmatrix} \Rightarrow S \mathcal{P} S^\dagger = \mathcal{P} \quad (5.12)$$

i.e., under transformations under which even and odd states do not get mixed. Now if H is even, clearly the evolution operator is of eqn (5.12) type, and thus commutes with parity.

What if we change the frequency or mass in the definition of the operator A ? Namely we now consider the operator

$$\mathcal{P}_\omega = \exp \left[\frac{i}{\hbar} \left(\frac{p^2}{2m} + m\omega^2 \frac{q^2}{2} - \frac{\hbar\omega}{2} \right) \frac{\pi}{\omega} \right] \equiv \exp \left(\frac{i\pi A_\omega}{\omega\hbar} \right).$$

Actually, nothing whatsoever changes. In fact, the eigenstates of the new operator A_ω , $|n_\omega\rangle$, can be obtained by the scale transformation D :

$$D : p \rightarrow \frac{p}{\sqrt{m\omega}}, \quad D : q \rightarrow q\sqrt{m\omega}; \quad |n_\omega\rangle = D|n\rangle$$

D obviously has the structure of eqn (5.12). It is evident that in the basis $|n_\omega\rangle$ the operator \mathcal{P}_ω has the form of eqn (5.11), but the point is that it also has the same form in the basis $|n\rangle$; vice versa, the original parity operator \mathcal{P} has the same form in the basis $|n_\omega\rangle$. Indeed, from eqn (5.12) it follows that

$$\langle n_\omega | \mathcal{P} | k_\omega \rangle = \langle n | D^\dagger \mathcal{P} D | k \rangle = \langle n | \mathcal{P} | k \rangle.$$

In other words, in spite of appearances, operators \mathcal{P}_ω and \mathcal{P} are one and the same operator!

The generalization to higher-dimensional systems is straightforward; it suffices to make a product of operators (5.9) for each Cartesian coordinate. Obviously the result of this subsection refers only to “orbital” parity, not to the intrinsic parity carried by elementary particles.

5.2.3 Time reversal

Another important example of a discrete symmetry is time reversal, T . In classical mechanics, Newton's equation for a particle moving under the influence of a conservative force,

$$m \ddot{\mathbf{r}} = -\nabla V,$$

is invariant under time reversal, $t \rightarrow -t$. This means that if a motion from (\mathbf{r}_1, t_1) to (\mathbf{r}_2, t_2) is possible, another motion from $(\mathbf{r}_2, -t_2)$ to $(\mathbf{r}_1, -t_1)$, tracing the same trajectory in the opposite direction, and with $\mathbf{r}(-t) = \mathbf{r}(t)$; $\mathbf{p}(-t) = -\mathbf{p}(t)$, is also a possible solution of the equation of motion. Vice versa, if the force included friction, proportional to velocity, clearly the time-reversed motion would be an impossible motion.

In quantum mechanics, the dynamics is described by the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = H\psi(\mathbf{r}, t). \quad (5.13)$$

For example,

$$H = -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r})$$

for a particle moving in a three-dimensional potential $V(\mathbf{r})$. The transformation $t \rightarrow t' = -t$ gives an equation

$$-i\hbar \frac{\partial}{\partial t'} \psi(\mathbf{r}, -t') = H\psi(\mathbf{r}, -t'),$$

in general having a *different* form from the original Schrödinger equation. It might seem to be hardly possible that the quantum mechanical laws be invariant under the time reversal.

Actually there is no reason that the wave function of the time-reversed motion should be given just by $\psi(\mathbf{r}, -t)$. Indeed, upon taking the complex conjugate of the preceding equation, one finds an equation

$$i\hbar \frac{\partial}{\partial t'} \psi^*(\mathbf{r}, -t') = H^* \psi^*(\mathbf{r}, -t'),$$

which more closely resembles the original equation (5.13). The original Schrödinger equation would then be recovered if an (anti-)unitary operator O exists such that

$$O H^* O^{-1} = H.$$

In such a case, the wave function for the reversed motion can be taken to be

$$\tilde{\psi}(\mathbf{r}, t) = O\psi^*(\mathbf{r}, -t) : \quad (5.14)$$

the new wave function $\tilde{\psi}(\mathbf{r}, t)$ satisfies a Schrödinger equation identical to the original one. The time-reversal motion is indeed a possible time evolution in quantum mechanics, in this case.

An operator O such that for any state vectors ψ, ϕ , the relation

$$\langle O\phi|O\psi\rangle = \langle\psi|\phi\rangle$$

holds (see eqn (5.14)) is known as an *anti-unitary* operator. In contrast, for an ordinary unitary operator U the relation

$$\langle U\phi|U\psi\rangle = \langle\phi|\psi\rangle$$

holds for any pair of state vectors. It is evident that under either unitary or anti-unitary transformations, all physical predictions of the theory remain the same. That these are the only possibilities to realize a symmetry in quantum mechanics is known as

Theorem 5.1. (Wigner's theorem) *Every symmetry transformation in quantum mechanics is realized either by a unitary or by an anti-unitary transformation.*

Again, it should be noted that time-reversal symmetry (T) is a property of the particular kind of interaction, rather than being an absolute law of Nature. Although at a macroscopic level it is easy to think of systems which are not conservative, and hence not invariant under T , it is known that at the level of fundamental interactions, T is an extremely good approximate symmetry. As far as we know, gravitational, electromagnetic, and strong interactions respect T , while a small subset of weak interactions due to the exchange of W bosons violate it. (Actually these are more directly connected to the violation of so-called CP symmetry. However, for any theory described by a local Hermitian Hamiltonian the product CPT is a good symmetry—a result known as the CPT theorem. If CPT is an exact symmetry of Nature, then CP violation implies T violation and vice versa.) For a discussion on CP violation in the K^0 - \bar{K}^0 system, see Supplement Section 22.1.

The great mystery of time-reversal symmetry is that, in spite of the fact that T is almost exactly conserved in fundamental interactions, it is grossly violated in the macroscopic world: it suffices to remember that the second law of thermodynamics—the law of the entropy increase—implies a preferential arrow of time, from the past to the future. It is an extravagant idea to think that the arrow of time is in some way caused by the very tiny amount of T -violating interactions, which are certainly irrelevant to the vast majority of electromagnetic, chemical, and gravitational processes governing the macroscopic world. It is possible that the arrow of time is somehow related to the expansion of the universe. We know that the concept of uniform time evolution itself would have to be modified somehow at the time of the big bang.

5.2.4 The Galilean transformation

Consider two systems of reference, K' and K , moving with respect to each other with a constant relative velocity, \mathbf{V} ,

$$\mathbf{r} = \mathbf{r}' + \mathbf{V}t. \quad (5.15)$$

How is the wave function $\psi'(\mathbf{r}', t)$ in one system related to $\psi(\mathbf{r}, t)$ in the other? To find the transformation law, one may proceed as follows: a plane wave in system K is also seen as a plane wave in system K' . Once we understand how these transform into each other, it must be possible to find out how a generic wave function transforms, as the latter can be composed of plane waves.

The plane waves in the two systems are

$$\psi(\mathbf{r}, t) = \exp \left[\frac{i}{\hbar} (\mathbf{p} \cdot \mathbf{r} - Et) \right]; \quad (5.16)$$

$$\psi'(\mathbf{r}', t) = \exp \left[\frac{i}{\hbar} (\mathbf{p}' \cdot \mathbf{r}' - E't) \right]. \quad (5.17)$$

From classical mechanics we know that the momentum and energy in the two systems are related as follows

$$\mathbf{p} = \mathbf{p}' + m\mathbf{V} \quad E = E' + \mathbf{V} \cdot \mathbf{p}' + \frac{1}{2}m\mathbf{V}^2. \quad (5.18)$$

By substituting eqns (5.15) and (5.18) into eqn (5.16) one finds that

$$e^{\frac{i}{\hbar}(\mathbf{p} \cdot \mathbf{r} - Et)} = e^{\frac{i}{\hbar}(\mathbf{p}' \cdot \mathbf{r}' - E't)} e^{\frac{i}{\hbar}(m\mathbf{V} \cdot \mathbf{r}' + \frac{1}{2}m\mathbf{V}^2 t)}.$$

In the second phase factor on the right-hand side there are no references left to the particular plane wave considered, so the relation should be valid for a generic wave function which can be constructed as a linear combination of the latter:

$$\psi'(\mathbf{r}', t) = e^{-\frac{i}{\hbar}(m\mathbf{V} \cdot \mathbf{r}' + \frac{1}{2}m\mathbf{V}^2 t)} \psi(\mathbf{r}, t). \quad (5.19)$$

In eqn (5.19) it is understood that \mathbf{r} is expressed in terms of \mathbf{r}' and t through eqn (5.15).

In the case of a system of many particles, the phase of eqn (5.19) sums up to give

$$m\mathbf{V} \cdot \mathbf{r}' + \frac{1}{2}m\mathbf{V}^2 t \rightarrow \sum_i m_i \mathbf{V} \cdot \mathbf{r}'_i + \frac{1}{2}m_i \mathbf{V}^2 t = M_{tot} \mathbf{V} \cdot \mathbf{R}_{CM} + \frac{1}{2}M_{tot} \mathbf{V}^2 t.$$

It is thus the center-of-mass coordinate, and the total mass plays the role of the free particle.

Transformation law (5.19) is generally valid, and does not in general imply *invariance* of the dynamical law under Galilean transformations. Of course, we expect that it is the case for the free particles. Let us check that the Schrödinger equation for a free particle indeed remains invariant. The wave function ψ satisfies the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} \psi. \quad (5.20)$$

In evaluating the partial derivative of ψ' with respect to time, we must keep in mind that the right-hand side of eqn (5.19) depend on time both explicitly and implicitly through the relation $\mathbf{r} = \mathbf{r}' + \mathbf{V}t$. Thus

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \psi' &= \left(\frac{1}{2} m V^2 \psi + i\hbar \frac{\partial}{\partial t} \psi + i\hbar \mathbf{V} \cdot \frac{\partial}{\partial \mathbf{r}} \psi \right) e^{-\frac{i}{\hbar} (m \mathbf{V} \cdot \mathbf{r}' + \frac{1}{2} m \mathbf{V}^2 t)} \\ &= \left(\frac{1}{2} m V^2 \psi - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}'^2} \psi + i\hbar \mathbf{V} \cdot \frac{\partial}{\partial \mathbf{r}'} \psi \right) e^{-\frac{i}{\hbar} (m \mathbf{V} \cdot \mathbf{r}' + \frac{1}{2} m \mathbf{V}^2 t)} \\ &= \left(\frac{1}{2} m V^2 \psi - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}'^2} \psi + i\hbar \mathbf{V} \cdot \frac{\partial}{\partial \mathbf{r}'} \psi \right) e^{-\frac{i}{\hbar} (m \mathbf{V} \cdot \mathbf{r}' + \frac{1}{2} m \mathbf{V}^2 t)}. \end{aligned}$$

In the last step use was made of the fact that $\partial/\partial \mathbf{r} = \partial/\partial \mathbf{r}'$.

On the other hand one can evaluate the kinetic term directly for ψ' :

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}'^2} \psi' &= \\ -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial \mathbf{r}'^2} \psi - 2i \frac{1}{\hbar} m \mathbf{V} \cdot \frac{\partial}{\partial \mathbf{r}'} \psi - \frac{m^2}{\hbar^2} \mathbf{V}^2 \right] &e^{-\frac{i}{\hbar} (m \mathbf{V} \cdot \mathbf{r}' + \frac{1}{2} m \mathbf{V}^2 t)}. \end{aligned}$$

Thus one indeed has

$$i\hbar \frac{\partial}{\partial t} \psi' = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}'^2} \psi' ;$$

that is, the evolution equation in system K' is identical to that in system K .

The transformation

$$\mathbf{r} \rightarrow \mathbf{r} + \mathbf{V}t ; \quad \mathbf{p} \rightarrow \mathbf{p} + m\mathbf{V}$$

is generated by the unitary operator

$$U = \exp \left[\frac{i}{\hbar} \mathbf{V}(\mathbf{pt} - m\mathbf{r}) \right].$$

This can be easily checked by considering infinitesimal \mathbf{V} . The generator of the transformation is

$$G = \mathbf{pt} - m\mathbf{r}$$

This operator is time dependent. We have, for a Hamiltonian $\mathbf{p}^2/2m$,

$$i\hbar \frac{\partial G}{\partial t} + [G, H] = i\hbar \mathbf{p} + \left[\mathbf{pt} - m\mathbf{r}, \frac{\mathbf{p}^2}{2m} \right] = 0,$$

in agreement with eqn (5.4).

We leave it as an exercise to prove the converse: if the system is invariant under Galileo transformation, then the dependence of the center-of-mass coordinates in the Hamiltonian is $\mathbf{P}^2/2M$, where \mathbf{P} is the total momentum and M the total mass.

5.2.5 The Wigner–Eckart theorem

A very powerful theorem that illustrates well the use of the symmetry argument is due to Wigner and Eckart. Consider first a spinless particle, described by a wave function of the form $\psi_0(r)$, a function of the radial coordinate only. Clearly it is invariant under three-dimensional rotations: it represents a state with $\ell = 0$. Now consider instead a state

$$\psi_i(r) = \text{const. } \mathbf{r}_i \psi_0(r),$$

obtained from the first by applying the position operator. This is a state with $\ell = 1$, being proportional to some combination of $Y_{1,m}(\theta, \phi)$, $m = 1, 0, -1$. The value of the angular momentum ($\ell = 1$) does not depend on the details of the nature of the operator \mathbf{r}_i ; the same can be said of the state

$$\psi'_i(r) = \text{const. } \mathbf{p}_i \psi_0(r).$$

Under a three-dimensional rotation a generic operator O transforms as follows:

$$O \rightarrow e^{i\omega \cdot \hat{\mathbf{J}}} O e^{-i\omega \cdot \hat{\mathbf{J}}},$$

while a state transforms like this:

$$| \rangle \rightarrow e^{i\omega \cdot \hat{\mathbf{J}}} | \rangle.$$

We have already seen that certain states—those with definite angular momentum (J, M)—transform in a simple, universal way (see eqn (4.38)):

$$| J, M \rangle \rightarrow \sum_{M'} D_{M', M}^J(\omega) | J, M' \rangle.$$

The rotation matrix for spin J is known once and for all: it depends only on J and does not depend on any other attributes of the particular system considered.

Analogously, certain operators transform in simple manner. Operators such as \mathbf{r}^2 , \mathbf{p}^2 , $U(r)$ are all *scalars*: they are invariant under rotations; others, such as \mathbf{r} , \mathbf{p} , \mathbf{e} , \mathbf{J} , are *vectors*. Quantities transforming as products of vectors are generally known as *tensors*.

To study the properties of transformations of operators under rotations, it is convenient to reorganize the components of tensors so as to make them proportional to the components of some spherical harmonics—they are known as *spherical tensors*—rather than using Cartesian components. For instance, a spherical tensor of rank 1 is equivalent to a vector (A_x, A_y, A_z) , but its components are called $T_{1,m}$, $m = 1, 0, -1$, where

$$T_{1,1} = -\frac{A_x + iA_y}{\sqrt{2}}; \quad T_{1,0} = A_z; \quad T_{1,-1} = \frac{A_x - iA_y}{\sqrt{2}}. \quad (5.21)$$

In the particular case of the position vector \mathbf{r} , the corresponding spherical tensor components are:

$$T_{1,1} = -\frac{x + iy}{\sqrt{2}}; \quad T_{1,0} = z; \quad T_{1,-1} = \frac{x - iy}{\sqrt{2}}. \quad (5.22)$$

⁹In the convention used by Landau and Lifshitz eqns (5.21) and (5.22) are multiplied by a factor i .

They are proportional to the spherical harmonics⁹ $Y_{1,1}$, $Y_{1,0}$, e $Y_{1,-1}$. (see eqn (4.20).)

The inverse of eqn (5.22) is

$$A_x = -\frac{T_{1,1} - T_{1,-1}}{\sqrt{2}} ; \quad A_y = -i \frac{T_{1,1} + T_{1,-1}}{\sqrt{2}} ; \quad A_z = T_{1,0} .$$

The components of a spherical tensor of rank 2 (of “spin 2”) are related to those in Cartesian components as follows:

$$\begin{aligned} T_{2,0} &= -\sqrt{\frac{1}{6}}(A_{xx} + A_{yy} - 2A_{zz}) ; \\ T_{2,\pm 1} &= \mp(A_{xz} \pm iA_{yz}) ; \\ T_{2,\pm 2} &= \frac{1}{2}(A_{xx} - A_{yy} \pm 2iA_{xy}) . \end{aligned}$$

By construction the spherical tensor of “spin” p with $2p+1$ components transform as follows:

$$T_q^p \Rightarrow e^{i\omega \cdot \hat{\mathbf{J}}} T_q^p e^{-i\omega \cdot \hat{\mathbf{J}}} = \sum_{q'} D^p{}_{q' q} T_{q'}^p .$$

This means that the action of T_q^p on the state $|j, m; n\rangle$ produces a state

$$T_q^p |j, m; n\rangle ,$$

which transforms exactly as the direct product of two angular momentum eigenstates

$$|p, q\rangle \otimes |j, m\rangle ,$$

i.e.

$$\begin{aligned} T_q^p |j, m; n\rangle &\Rightarrow e^{i\omega \cdot \hat{\mathbf{J}}} T_q^p |j, m; n\rangle = e^{i\omega \cdot \hat{\mathbf{J}}} T_q^p e^{-i\omega \cdot \hat{\mathbf{J}}} e^{i\omega \cdot \hat{\mathbf{J}}} |j, m; n\rangle \\ &= \sum_{q', m'} D^p{}_{q' q} D^j_{m' m} T_{q'}^p |j, m'; n\rangle . \end{aligned}$$

As a consequence, one has the following theorem:

Theorem 5.2. (The Wigner–Eckart theorem) *The matrix element*

$$\langle J, M; n' | T_q^p | j, m; n \rangle ,$$

where n, n' stand for all other quantum numbers (the radial quantum number, type of particle, etc.) are proportional to the Clebsch–Gordan coefficients:

$$\langle J, M; n' | T_q^p | j, m; n \rangle = \langle p, j; J, M | p, q, j, m \rangle \langle J, n' | \mathbf{T}^p | j, n \rangle . \quad (5.23)$$

The proportionality constant, indicated by $\langle J, n' | \mathbf{T}^p | j, n \rangle$, called the *reduced matrix element*, depends only on the absolute magnitude of the angular momenta as well as other quantum numbers, but not on the azimuthal quantum numbers. All the dependence on the latter is in the universal Clebsch–Gordan coefficients. Equation (5.23) provides many

nontrivial relations among those matrix elements which differ only in the azimuthal quantum numbers M, q, m . In particular, it leads to a set of *selection rules*: the only non-vanishing matrix elements are those with nonzero Clebsch–Gordan coefficients. We talk about *allowed transition*, a terminology borrowed from the analysis of electromagnetic transitions (see Section 9.5).

Let us list some examples, which the reader can verify as an exercise:

1. *Scalar*, $p = 0$. Only the transitions

$$j = J \quad m = M$$

are allowed.

2. *Vector*, $p = 1$. The allowed transitions are

$$|J - j| = \pm 1, 0 \quad ((J = 0) - (j = 0) \text{ forbidden}) ; \quad M = m + q .$$

5.3 Identical particles: Bose–Einstein and Fermi–Dirac statistics

Closely related to the general concept of symmetry discussed in the preceding section is that of a *symmetry under exchange of identical particles*. Nature abounds with systems made of more than one particle of the same kind; it suffices to think of an atom (with many electrons), a metal (with many atoms of the same species and with many electrons), and in fact, any constituent of the universe.

In quantum mechanics, the wave function of such systems turns out to obey precise properties under the exchange of identical particles: they must be either totally symmetric (for particles with integer spins, known as *bosons*) or totally antisymmetric (for particles with half-integer spins, known as *fermions*). The wave functions are said to obey *Bose–Einstein* (BE) statistics or *Fermi–Dirac* (FD) statistics, respectively.

The restrictions imposed by BE or FD statistics bring about far-reaching and profound consequences in all applications of quantum mechanics, from atoms to macroscopic systems.

Note that by definition two identical particles cannot be distinguished by their intrinsic properties, such as mass, charge, spin. From this point of view, there is no difference between classical and quantum mechanics. What makes particles distinguishable in all cases in classical mechanics is the existence of a definite trajectory (history) for each particle. This allows the particles to be labeled in a convenient way at any reference time, e.g., by the positions they occupy at that precise moment; each particle will maintain its identity during the subsequent time evolution, however complicated it might be.

In quantum mechanics the situation is very different. Owing to the uncertainty relations, there is no precisely defined trajectory for each particle, and the physical state of a system composed, for example, of

two identical particles is simply described by a wave function with two sets of arguments,

$$\psi(\xi_1, \xi_2), \quad \xi \equiv \{\mathbf{r}, \sigma\}, \quad \sigma = s, s-1, \dots, -s,$$

where σ stands for the third component of the spin. The exchange of the two particles gives rise to the state

$$\psi(\xi_2, \xi_1),$$

which, owing to the identity of the two particles, must represent the same quantum state as $\psi(q_1, q_2)$. According to the principles of quantum mechanics, this implies that

$$\psi(\xi_2, \xi_1) = e^{i\alpha} \psi(\xi_1, \xi_2), \quad (5.24)$$

where α is some phase. By repeating the exchange of the two identical particles twice, one must get back to the original wave function, so that

$$e^{2i\alpha} = 1. \quad (5.25)$$

It follows then that

$$e^{i\alpha} = \pm 1, \quad (5.26)$$

in eqn (5.24). This argument can be generalized to a system consisting of N identical particles. The wave function must be either symmetric or antisymmetric under the exchange of any two identical particles.

Which sign should we choose? As already anticipated, in Nature all particles with integer spins (bosons) are described by wave functions which are totally symmetric, while the wave functions of identical particles with half-integer spins (fermions) are totally antisymmetric, i.e., they change sign under the exchange of any pair of particles. We say that bosons obey **Bose–Einstein statistics**, while fermions satisfy **Fermi–Dirac statistics**. Or simply BE or FD statistics, respectively.

For instance, the wave function of two identical spin- $\frac{1}{2}$ fermions (two electrons, two protons, etc.) has the form

$$\Psi = \frac{1}{\sqrt{2}} (\psi(\xi_1, \xi_2) - \psi(\xi_2, \xi_1)) = \frac{1}{\sqrt{2}} (\psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) - \psi(\mathbf{r}_2, \sigma_2; \mathbf{r}_1, \sigma_1)), \quad (5.27)$$

where $\sigma_{1,2} = \uparrow, \downarrow$.

In the general case, the identity of the particles is formally expressed by the statement that *every* observable $A(\xi_1, \dots, \xi_n)$ is *symmetric* under any permutation of the single particle variables. We note that this is a restriction on the number of physically acceptable observables; as an example, for two particles the operator \mathbf{r}_1 is not an observable, while $\mathbf{r}_1 + \mathbf{r}_2$ is. Following our discussion in Chapter 2 we see that in this case not every self adjoint operator corresponds to an observable.

Remarks

- (i) Within non-relativistic quantum mechanics, the correlation between the spin of the particle and the statistics such a particle obeys (called the spin-statistics relation) is an empirical law. However, it is one of the fundamental results of relativistic quantum mechanics that the spin-statistics correlation follows from the principles of special relativity, of quantum mechanics, and of the positivity of energy. See Section 17.2.3.
- (ii) The rule that *all* particles with half-integer spin (or integer spin) obey Fermi-Dirac (vis à vis Bose-Einstein) statistics, is internally consistent. Consider the nucleon (a collective name for the two constituent particles of atomic nuclei—the proton and neutron) which has spin $\frac{1}{2}$ and is therefore a fermion. Two identical nuclei, composed of n nucleons, would have integer or half-integer spins, according to whether n is even or odd, respectively. But as the exchange of the two identical nuclei is equivalent to the exchange of n pairs of nucleons, it follows that the wave function of the former is either symmetric (n even) or antisymmetric (n odd).
- (iii) From a formal point of view, the wave function of N identical particles can be regarded as a representation of the permutation groups of N objects. The (standard) assumption that the wave function for definite positions and for definite spin components is a well-defined complex number, apart from an arbitrary phase, corresponds to the hypothesis that the wave functions form a one-dimensional representation of the permutation group. Under this condition result (5.25), and hence eqn (5.26), follows inevitably.¹⁰
- (iv) The above consideration hinges upon one more aspect of the physical world: the topological structure of the configuration space. In fact, in order to discuss the meaning of the exchange of the two particles clearly, it is necessary to place the two particles at two distinct points. Say one of the particles is at $\{0\}$ and the other particle is at a generic point $\{x\}$. Clearly the repeated exchange of the two particles is equivalent to the particle at $\{x\}$ going around the point $\{0\}$ and coming back to the original point. The three-dimensional space minus a point, $\mathbf{R}^3/\{0\}$, is simply-connected,¹¹

$$\pi_1(\mathbf{R}^3/\{0\}) = \mathbb{1}.$$

Therefore property (5.25) is necessary for the theory to be consistent: the wave function cannot make a jump as the loop is gradually shrunk to zero.

- (v) The above discussion shows, however, that some two-dimensional systems may admit exceptions to the rule. Indeed a two-dimensional space minus a point is topologically equivalent to a circle, S^1 , and its fundamental group is \mathbb{Z} . In this case a more general statistics is possible. Excitations (called the *anyons*) obeying these more general statistics with a nontrivial phase in eqns (5.25) and (5.26),

¹⁰By losing this assumption, it is logically possible to construct a quantum theory with a more general type of statistics (*parastatistics*). However, no physical particles or systems are known which make use of such unusual kinds of statistics.

¹¹The symbol $\pi_1(M)$ (the fundamental group of the space M) represents the group of equivalent classes of the map from a circle S^1 to the space M . Any space in which a closed loop can be smoothly shrunk to a point is *simply connected*, with the trivial fundamental group, $\pi_1(M) = \mathbb{1}$; a map from a circle to a circle can be classified by positive or negative winding numbers, so $\pi_1(S^1) = \mathbb{Z}$; a torus has $\pi_1(T^1) = \mathbb{Z} \times \mathbb{Z}$, and so on.

known as *the fractional statistics*, are known to play an important role in the physics of the quantum Hall effect, and, perhaps, in high- T superconductors.

The operation of symmetrization or antisymmetrization of the wave function with respect to the exchanges of identical particles can be realized by

$$\mathcal{S} = \frac{1}{N!} \sum_P P; \quad \mathcal{A} = \frac{1}{N!} \sum_P \epsilon_P P, \quad (5.28)$$

¹²Any permutation can be constructed as a product of an even or odd number of exchanges of a pair of objects: even though the way a given permutation can be constructed this way is not unique, the parity of each permutation is well defined.

where P represents all possible permutations of $(12\dots N)$ particles and $\epsilon_P = \pm 1$ according to the whether P is an even or odd permutation.¹² They act as projection operators,

$$\mathcal{S}^2 = \mathcal{S}; \quad \mathcal{A}^2 = \mathcal{A}; \quad \mathcal{S}\mathcal{A} = 0.$$

On the other hand, the Hamiltonian of N identical particles is clearly invariant under the exchange of the operators (momenta, position, spin, etc.) referring to these particles. Therefore the operation of symmetrization or antisymmetrization commutes with the evolution operator,

$$e^{-iHt/\hbar} :$$

the statistics is consistent with and maintained during the time evolution of the system.

As the symmetric states and antisymmetric states are orthogonal,

$$\langle \psi_S | \psi_A \rangle = \langle \psi_S | \mathcal{S}\mathcal{A} | \psi_A \rangle = 0,$$

a given system of N identical particles (with a definite statistics) will never mix with or leak to systems with a “wrong” statistics. This guarantees that all the constructions of quantum mechanics, completeness, unitarity (total probability is equal to unity), etc. remain valid even under the restriction of states with definite statistics.

5.3.1 Identical bosons

Consider now systems of N identical bosons. In the simplest case of two identical particles without spin, interacting with a potential $V(\mathbf{r})$, where $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, the wave function can be factorized as

$$\Psi = \Phi(\mathbf{R})\psi(\mathbf{r}), \quad \mathbf{R} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2},$$

where $\Phi(\mathbf{R})$ describes the center of mass, $\psi(\mathbf{r})$ the relative motion. The condition that Ψ be symmetric under the exchange of the two particles implies that

$$\psi(-\mathbf{r}) = \psi(\mathbf{r}).$$

Thus only those motions with even values of angular momenta $\ell = 0, 2, \dots$ are allowed.

To discuss the more general case, it is often useful to consider as a basis of the states

$$|p_{i_1}\rangle \otimes |p_{i_2}\rangle \dots |p_{i_N}\rangle \equiv |p_{i_1}, p_{i_2}, \dots, p_{i_N}\rangle, \quad (5.29)$$

with reference to the composite system

$$\mathcal{H}^{(N)} = \mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \dots \otimes \mathcal{H}_N. \quad (5.30)$$

Such a description in terms of *single-particle states* $|p_{i_k}\rangle$ ($k = 1, \dots, N$) is particularly useful in the case of N particles weakly interacting (so that in the first approximation they can be considered to be non-interacting). Of course, the states (5.29) form a valid basis of the composite system even when the interactions are important.

For general N the state vector has the form

$$|p_{i_1}, \dots, p_{i_N}\rangle_S = \left(\frac{N_1! N_2! \dots N_r!}{N!} \right)^{1/2} \sum_{P'} P' |p_{i_1}, \dots, p_{i_N}\rangle, \quad (5.31)$$

$$N_1 + N_2 + \dots + N_r = N,$$

where N_i stands for the number of particles which “occupy” the single-particle state, p_i , which labels all the quantum numbers, including spin.

For $N = 2$, and in the coordinate representation, the wave function takes the possible form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \begin{cases} \frac{1}{\sqrt{2}} [\psi_{p_1}(\mathbf{r}_1)\psi_{p_2}(\mathbf{r}_2) + \psi_{p_2}(\mathbf{r}_1)\psi_{p_1}(\mathbf{r}_2)], & (p_1 \neq p_2), \\ \psi_{p_1}(\mathbf{r}_1)\psi_{p_1}(\mathbf{r}_2), & (p_1 = p_2). \end{cases}$$

Note that the probability that the particles occupy the same position $\mathbf{r}_1 \simeq \mathbf{r}_2$ is *twice* what is expected in classical mechanics. An analogous argument can be made in the momentum representation.

A word of caution is appropriate here. The states (5.31) form a basis in the tensor space (5.30). A generic state is described by a linear combination of such vectors. This means that while it is true that any N -boson wave function satisfies the symmetry property

$$\Phi(\xi_1, \xi_2, \dots, \xi_N) = \Phi(\xi_{i_1}, \xi_{i_2}, \dots, \xi_{i_N}),$$

for every permutation $(1, 2, \dots, N) \rightarrow (i_1, i_2, \dots, i_N)$, this does not imply that it can be written as a symmetrization of a product of single particle wave functions.¹³

These properties of the wave functions of the identical bosons, whether they are elementary particles, atoms, or molecules, underlie certain extraordinary phenomena. An example is the phenomenon of Bose-Einstein condensation, in which a macroscopic number of, for example, atoms occupy the same quantum states, behaving as if described by a single wave function. These states are realized in Nature at very low temperatures, near absolute zero, such as liquid helium (*superfluidity*); more recently, BE condensation of gaseous atoms has been realized [Ketterle (2002)] or more recently, even for various molecules. The phenomenon of superconductivity is also related to this.

¹³For example,

$$\psi(x_1, x_2) = e^{-(x_1+x_2)^2}$$

is symmetric but is not a symmetrization of a product. Of course, ψ can be expanded in series of plane waves

$$e^{ik_1 x_1} e^{ik_2 x_2} + e^{ik_2 x_1} e^{ik_1 x_2}$$

of the form (5.31).

5.3.2 Identical fermions and Pauli's exclusion principle

Again let us start with the simplest case of two identical spin- $\frac{1}{2}$ particles (e.g., two protons), described by a wave function of the same form as eqn (5.27). If the two particles interact through a potential depending on the relative position \mathbf{r} only, the wave function can be factorized as

$$\Psi = \Phi(\mathbf{R})\psi(\mathbf{r}), \quad \mathbf{R} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2},$$

where $\Phi(\mathbf{R})$ describes the free motion of the center of mass. The relative wave function now depends on the spin states as well. The spin states of two spin- $\frac{1}{2}$ particles can always be decomposed into states of spin 1 (the spin triplet),

$$|\uparrow\uparrow\rangle, \quad \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}, \quad |\downarrow\downarrow\rangle,$$

and a state of spin 0 (the spin singlet),

$$\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}.$$

The triplet states are symmetric under the exchange of two spins, while the singlet state is antisymmetric. It follows that the corresponding orbital wave function must have the opposite parity,

$$\psi_{1m}(-\mathbf{r}) = -\psi_{1m}(\mathbf{r}), \quad (m = 1, 0, -1), \quad \psi_{00}(-\mathbf{r}) = \psi_{00}(\mathbf{r}).$$

Thus the angular momenta of the relative motion of two identical spin- $\frac{1}{2}$ particles are restricted to odd (total spin 1) or even (total spin 0) values only.

If the basis of direct-product states (5.29) is used, one has, for $N = 2$, a wave function of the form

$$|p_1, p_2\rangle_A = \frac{1}{\sqrt{2}} (|p_1\rangle|p_2\rangle - |p_2\rangle|p_1\rangle). \quad (5.32)$$

More generally, the states of a system composed of N identical fermions can be written as

$$\mathcal{A}|p_1\rangle|p_2\rangle\dots|p_N\rangle = \frac{1}{N!} \sum_P \epsilon_P P|p_1\rangle|p_2\rangle\dots|p_N\rangle,$$

which in the coordinate representation takes the form of the *Slater determinant*

$$\psi_{\{p_i\}}(\xi_1, \xi_2, \dots, \xi_N) = \frac{1}{\sqrt{N!}} \det \begin{vmatrix} \psi_{p_1}(\xi_1) & \psi_{p_1}(\xi_2) & \dots & \psi_{p_1}(\xi_N) \\ \psi_{p_2}(\xi_1) & \psi_{p_2}(\xi_2) & \dots & \psi_{p_2}(\xi_N) \\ \vdots & \ddots & \ddots & \vdots \\ \psi_{p_N}(\xi_1) & \psi_{p_N}(\xi_2) & \dots & \psi_{p_N}(\xi_N) \end{vmatrix}.$$

The ξ s denote both orbital and spin variables.

Thus the wave functions of more than one identical fermion vanish whenever two fermions occupy the same state,

$$\psi_{\{p_i\}}(\xi_1, \xi_2, \dots, \xi_N) = 0, \quad \text{if } p_j = p_k, \quad j \neq k.$$

The rule that the two identical fermions cannot occupy the same quantum state is known as **Pauli's exclusion principle**. Pauli's exclusion principle is absolutely fundamental in all applications of quantum mechanics to systems involving identical fermions, such as atomic nuclei, atoms, molecules, solids, gases and neutron stars.

The Slater determinants can thus be regarded as the *basis* in the Hilbert space of N fermions. A general wave function is given by a linear combination of Slater determinants. For the application of these constructions to atoms, see Chapter 15.

In a more general case, one has, in the presence of identical fermions,

$$\Psi(\xi_1, \xi_2, \dots, \xi_N) = \epsilon_P \Psi(\xi_{i_1}, \xi_{i_2}, \dots, \xi_{i_N})$$

for each permutation $P : (1, 2, \dots, N) \rightarrow (i_1, i_2, \dots, i_N)$. Note that Pauli's principle in the restricted sense stated above refers to those situations in which single-particle quantum numbers give a good description of the system, which is not always the case.

In atoms, the electronic configurations are basically constrained by Pauli's principle because two electrons (in the same spin state) cannot stay in the same atomic orbit. The periodic nature of elements essentially originates from Pauli's principle and the quantization of the atomic orbits. See Chapter 15.

Guide to the Supplements

In Supplement 20.8 we give a brief account of the permutation group S_N and of the Young tableaux. In Supplement 20.9 a practical problem is solved: how to write the matrix elements of operators between multi-particle states. These formulas will be used in the construction of wave functions for heavy atoms.

Supplements 20.10 and 20.11 are a brief introduction

to the Fock representation and to the non-relativistic version of second quantization. These supplements are meant to help in understanding the relation between non-relativistic quantum mechanics and quantum field theory. See Chapter 17 for more about *relativistic* quantum field theories and the theory of elementary particles.

Problems

- (5.1) A particle of spin $J = 1$ and unknown parity decays at rest into two identical spin- $\frac{1}{2}$ particles.

- (a) Compute the orbital angular momentum of the final particles and the total spin.
- (b) Determine the parity of the decaying particle, assuming that in the decay, parity is conserved.
- (c) Let us suppose that the initial particle is in the state $|J, J_z\rangle = |1, 0\rangle$. Write explicitly the final state with an unknown radial function, but with explicit use of spherical harmonics and spin states.

Let us now suppose that one measures the spin projections of the final particles with Stern-Gerlach-type apparatus, for two particles emitted in the directions (θ, φ) and

$$(\pi - \theta, \varphi + \pi).$$

- (d) For fixed values of (θ, φ) , write the normalized spin wave function of the final state.
 - (e) Compute the probability that a particle is emitted in the direction (θ, φ) with $s_z = \frac{1}{2}$.
 - (f) Compute the probability that a simultaneous measurement of $(s_y(1), s_y(2))$ gives $(\frac{1}{2}, \frac{1}{2})$.
- (5.2) A deuteron d is a nucleus with charge +1, composed of a proton (p) and a neutron (n). The deuteron has spin 1 and parity +. A negative pion π^- , with charge -1 and spin 0, can be bound to the deuteron to form a sort of "deuterium atom". Let us suppose that this system is formed in the lowest Bohr orbit.

- (a) Compute the ratio between the Bohr radius of this system and the standard Bohr radius,

and compute the binding energy of the system. Some masses needed for the computation are listed below, in MeV/c^2 :

$$\begin{aligned} M_{\pi^-} &= 139.6; & M_{e^-} &= 0.51; \\ M_d &= 1875.6; & M_p &= 938.3. \end{aligned}$$

- (b) The bound system described above decays with the reaction $\pi^- + d \rightarrow n + n$. Both angular momentum and parity are conserved in the decay. Discuss if one can determine the intrinsic parity of the π^- from these data.
- (c) Compute the angular distribution of neutrons in the final state, knowing that in the initial state $J_z = 0$.
- (d) Explain why the hydrogen atom does not decay via a somewhat analogous process, $e^- + p \rightarrow n + \nu$, where ν is the (electron) neutrino.
- (5.3) Write the explicit form of the completeness relation for a system of two free identical particles.
- (5.4) Write the Hamiltonian and the Heisenberg equations for a system of particles interacting with a potential $U(\mathbf{x}_1, \mathbf{x}_2)$ in the second quantization formalism.
- (5.5) Consider a simplified version of the Young experiment, limiting the dynamics to two single "modes" of the electromagnetic field that describe a photon passing from slit 1 or 2 respectively. Use a Fock formalism to describe the photon's beam, and compute the probability of measuring a photon through slit 1 k times in a single-photon experiment repeated n times. Show that the same probability is obtained by measuring k photons in a single experiment with a beam of n photons. Describe in this model the interference.

Three-dimensional problems

6

In this chapter several simple three-dimensional systems are studied: the free particles, the potential well or barrier, the harmonic oscillator, and the hydrogen atom.

6.1 Simple three-dimensional systems

6.1.1 Reduced mass

The Hamiltonian of a system consisting of two particles with masses m_1 , m_2 which interact with each other through the potential $V(\mathbf{r})$, where

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$$

is the relative position, is given by

$$H = -\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2 + V(\mathbf{r}).$$

Introducing the center of mass

$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2},$$

we have

$$H = -\frac{\hbar^2}{2(m_1 + m_2)}\Delta_R - \frac{\hbar^2}{2\mu}\Delta_r + V(\mathbf{r}),$$

where

$$\mu \equiv \frac{m_1m_2}{m_1 + m_2}$$

is the *reduced mass*. Separating the variables as

$$\psi = \Phi(\mathbf{R})\psi(\mathbf{r}),$$

we find the equation for the relative motion:

$$i\hbar\frac{\partial}{\partial t}\psi = H^{(rel)}\psi = \left(-\frac{\hbar^2}{2\mu}\Delta_r + V(\mathbf{r})\right)\psi,$$

which has the form of the Schrödinger equation for a single particle, with reduced mass, which moves in the potential $V(\mathbf{r})$.

6.1 Simple three-dimensional systems	135
6.2 Bound states in potential wells	140
6.3 The three-dimensional oscillator	141
6.4 The hydrogen atom	143
Guide to the Supplements	148
Problems	149
Numerical analyses	150

6.1.2 Motion in a spherically symmetric potential

When the potential depends only on the absolute value of the position vector $r \equiv |\mathbf{r}|$, the time-independent Schrödinger equation

$$H\psi = \left(-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (6.1)$$

can be solved by separating the variables as follows:

$$\psi(\mathbf{r}) = R(r)\Phi(\theta, \phi).$$

The angular part can be solved by the spherical harmonics

$$\Phi(\theta, \phi) = Y_{\ell,m}(\theta, \phi)$$

while the radial part takes the form

$$\left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{2m}{\hbar^2} (E - V(r)) - \frac{\ell(\ell+1)}{r^2} \right] R(r) = 0.$$

If we set

$$R(r) = \frac{\chi(r)}{r}$$

the equation for χ is

$$\frac{d^2\chi}{dr^2} + \left[\frac{2m}{\hbar^2} (E - V(r)) - \frac{\ell(\ell+1)}{r^2} \right] \chi = 0,$$

but this is formally a one-dimensional Schrödinger equation, with an effective potential

$$V_{\text{eff}}(r) = V(r) + \frac{\ell(\ell+1)\hbar^2}{2mr^2}.$$

Clearly the second term represents the centrifugal force (classically the force is $F \sim mr\dot{\theta}^2 \sim (\mathbf{r} \times \mathbf{p})^2/mr^3$ for circular motion).

The normalization condition is

$$\int_0^\infty dr r^2 |R|^2 = \int_0^\infty dr |\chi|^2 = 1,$$

while the condition of regularity at the origin implies that

$$\chi(0) = 0.$$

The problem is therefore equivalent to that of a particle moving in the half-axis $0 \leq r < \infty$, under the potential $V = V_{\text{eff}}(r)$, $r > 0$; $V(0) = \infty$.

The no-degeneracy theorem for one-dimensional discrete levels (3.2) is also valid in this case: the radial wave function (for each ℓ) is labeled by the single quantum number n , known as the principal quantum number, which determines the energy eigenvalues. It follows that a stationary state in a spherically symmetric potential is uniquely specified by three quantum numbers, (n, ℓ, m) , associated with the maximal set of observables (E, L^2, L_z) . For historical reasons the states with various orbital quantum numbers ℓ are known as $S, P, D, F, G, H, I, K, \dots$ waves, respectively, for $\ell = 0, 1, 2, 3, 4, 5, 6, 7, \dots$

6.1.3 Spherical waves

Let us first consider a free particle, $V = 0$. The Schrödinger equation in this case can be easily solved by using the momentum eigenstates (plane waves); however, solutions corresponding to definite values of angular momentum are needed in scattering problems.

The radial equation for a given ℓ is

$$\left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + k^2 - \frac{\ell(\ell+1)}{r^2} \right] R_{k,\ell}(r) = 0, \quad (6.2)$$

where $k^2 = \frac{2m}{\hbar^2} E$, or

$$R'' + \frac{2}{r} R' + \left(k^2 - \frac{\ell(\ell+1)}{r^2} \right) R = 0. \quad (6.3)$$

For $\ell = 0$, eqn (6.2) simplifies to

$$R'' + \frac{2}{r} R' + k^2 R = 0$$

or

$$(rR)'' + k^2(rR) = 0.$$

The regular solution at $r = 0$ is

$$R = A \frac{\sin kr}{r}$$

while the singular solution is

$$R = A' \frac{\cos kr}{r}.$$

The normalization constant A can be fixed by the condition

$$\int_0^\infty dr r^2 R_{k',\ell} R_{k,\ell} = 2\pi\delta(k' - k);$$

$$\begin{aligned} A^2 \int_0^\infty dr \sin kr \sin k'r &= -\frac{A^2}{4} \int_{-\infty}^\infty dr e^{ikr} (e^{ik'r} - e^{-ik'r}) \\ &= \frac{\pi A^2}{2} \delta(k - k'), \end{aligned}$$

so that $A = 2$.

The solutions for $\ell \neq 0$ can be found as follows. If we set $R_\ell = r^\ell \eta_\ell$, the equation for η_ℓ is

$$\eta_\ell'' + \frac{2(\ell+1)}{r} \eta_\ell' + k^2 \eta_\ell = 0.$$

Differentiating this with r , one has

$$\eta_\ell''' + \frac{2(\ell+1)}{r} \eta_\ell'' + \left(k^2 - \frac{2(\ell+1)}{r^2} \right) \eta_\ell' = 0.$$

But with the substitution $\eta'_\ell = r\zeta_\ell$ this becomes

$$\zeta''_\ell + \frac{2(\ell+2)}{r}\zeta'_\ell + k^2\zeta_\ell = 0,$$

which is just the equation for $\eta_{\ell+1}$. This implies that $\zeta_\ell = \eta_{\ell+1}$, i.e.,

$$\eta'_\ell = r\eta_{\ell+1},$$

i.e. we have found a recursion relation. Starting from $\chi_0 = R_0$ one can find all other radial wave functions. The regular solutions are

$$R_\ell = N_\ell r^\ell \left(\frac{1}{r} \frac{d}{dr} \right)^\ell \frac{\sin kr}{r},$$

while the singular solutions at the origin are given by

$$Q_\ell = N_\ell r^\ell \left(\frac{1}{r} \frac{d}{dr} \right)^\ell \frac{\cos kr}{r}.$$

The normalization constants can be determined appropriately, e.g., $N_\ell = (-)^\ell 2/k^\ell$ (see [Landau and Lifshitz (1976 c)]).

The behavior of R_ℓ near the origin $r = 0$ can be easily determined by introducing the variable $\xi \equiv r^2$:

$$\left(\frac{1}{r} \frac{d}{dr} \right)^\ell \frac{\sin kr}{r} = \left(2 \frac{d}{d\xi} \right)^\ell \sum_{n=0}^{\infty} \frac{(-)^n}{(2n+1)!} k^{2n+1} \xi^n = \frac{k^{2\ell+1} (-)^\ell}{(2\ell+1)!!} + O(r^2),$$

where $(2\ell+1)!! \equiv (2\ell+1)(2\ell-1)(2\ell-3)\dots 5 \times 3 \times 1$, so that

$$R_\ell \simeq \frac{2k^{\ell+1} r^\ell}{(2\ell+1)!!} \{1 + O(r^2)\}.$$

The free spherical waves can be expressed by the *spherical Bessel functions* j_ℓ, n_ℓ , which are *Bessel functions* of half-integer orders:

$$R_{k,\ell}(r) = \sqrt{\frac{2\pi k}{r}} J_{\ell+\frac{1}{2}}(kr) = 2k j_\ell(kr),$$

$$Q_{k,\ell}(r) = \sqrt{\frac{2\pi k}{r}} N_{\ell+\frac{1}{2}}(kr) = 2k n_\ell(kr).$$

$J_\nu(z), N_\nu(z)$ are the two independent solutions of the Bessel equation,

$$\frac{d^2}{dz^2} Z_\nu + \frac{1}{z} \frac{d}{dz} Z_\nu + \left(1 - \frac{\nu^2}{z^2} \right) Z_\nu = 0,$$

of which $J_\nu(z)$ is the regular solution at $z = 0$ (see, for instance, [Gradshteyn and Ryzhik (1965)]).

The spherical Bessel functions are elementary functions:

$$j_\ell(x) = (-)^\ell x^\ell \left(\frac{1}{x} \frac{d}{dx} \right)^\ell \frac{\sin x}{x}; \quad n_\ell(x) = -(-)^\ell x^\ell \left(\frac{1}{x} \frac{d}{dx} \right)^\ell \frac{\cos x}{x}.$$

Some examples are:

$$\begin{aligned} j_0(x) &= \frac{\sin x}{x}, & n_0(x) &= -\frac{\cos x}{x}; \\ j_1(x) &= \frac{\sin x}{x^2} - \frac{\cos x}{x}, & n_1(x) &= -\frac{\cos x}{x^2} - \frac{\sin x}{x}; \\ j_2(x) &= \left(\frac{3}{x^3} - \frac{1}{x}\right) \sin x - \frac{3 \cos x}{x^2}, & n_2(x) &= -\left(\frac{3}{x^3} - \frac{1}{x}\right) \cos x - \frac{3 \sin x}{x^2}; \end{aligned}$$

etc. The behavior near $x = 0$ is known:

$$j_\ell(x) \sim \frac{x^\ell}{(2\ell+1)!!}, \quad n_\ell(x) \sim \frac{(2\ell-1)!!}{x^{\ell+1}}, \quad (6.4)$$

while the asymptotic behavior at $x \rightarrow \infty$ is

$$j_\ell(x) \sim \frac{1}{x} \cos\left(x - \frac{(\ell+1)\pi}{2}\right), \quad n_\ell(x) \sim \frac{1}{x} \sin\left(x - \frac{(\ell+1)\pi}{2}\right). \quad (6.5)$$

It is sometimes useful to introduce other combinations, the so-called spherical Hankel functions (of the first and second kinds),

$$h_\ell^{(1)}(x) \equiv j_\ell(x) + i n_\ell(x), \quad h_\ell^{(2)}(x) \equiv j_\ell(x) - i n_\ell(x).$$

Their asymptotic behaviors are

$$h_\ell^{(1)}(x) \sim \frac{1}{x} e^{i(x - \frac{(\ell+1)\pi}{2})}, \quad h_\ell^{(2)}(x) \sim \frac{1}{x} e^{-i(x - \frac{(\ell+1)\pi}{2})}. \quad (6.6)$$

(Note that, apart from the factor $1/x$, the Hankel functions are analogous to the exponential functions $\exp \pm ix$, with respect to the real functions $\sin x, \cos x$.) The corresponding radial functions are

$$R_{k,\ell}^{(1)} = 2k h_\ell^{(1)}(kr), \quad R_{k,\ell}^{(2)} = 2k h_\ell^{(2)}(kr).$$

Which of the solutions are to be used depends on the physical problem considered (boundary condition, regularity at the origin, etc.). The asymptotic behaviors of the four solutions are:

$$\begin{aligned} R_{k,\ell}(r) &\sim \frac{2}{r} \cos\left(kr - \frac{(\ell+1)\pi}{2}\right), & Q_{k,\ell}(r) &\sim \frac{2}{r} \sin\left(kr - \frac{(\ell+1)\pi}{2}\right) \\ R_{k,\ell}^{(1)} &\sim \frac{2}{r} e^{i(kr - \frac{(\ell+1)\pi}{2})}, & R_{k,\ell}^{(2)} &\sim \frac{2}{r} e^{-i(kr - \frac{(\ell+1)\pi}{2})}. \end{aligned}$$

The last two represent an expanding ($R^{(1)}$) or contracting ($R^{(2)}$) spherical wave.

Both plane waves and spherical waves represent a complete set of solutions of the free Schrödinger equation: one can be expanded in terms of the other. For instance, a free plane wave can be expanded as

$$e^{ikz} = e^{ikr \cos \theta} = \sum_{\ell=0}^{\infty} (2\ell+1) i^\ell j_\ell(kr) P_\ell(\cos \theta). \quad (6.7)$$

This formula can be verified by comparing the coefficients of $(r \cos \theta)^n$ on both sides. It can be rewritten in a coordinate-independent fashion:

$$e^{ik \cdot r} = 4\pi \sum_{\ell=0}^{\infty} i^\ell j_\ell(kr) \sum_{m=-\ell}^{\ell} Y_{\ell m}(\Omega_1) Y_{\ell m}^*(\Omega_2), \quad (6.8)$$

where Ω_1 and Ω_2 indicate the angular variables corresponding to \mathbf{k} and \mathbf{r} .

6.2 Bound states in potential wells

The potential

$$V(r) = \begin{cases} -V_0 & \text{if } r < a \\ 0 & \text{if } r > a \end{cases} \quad (6.9)$$

describes a rudimentary model of atomic *nuclei*: the nuclear force has a finite and well-defined range. This is in contrast to the Coulomb force, which has an infinite range of action.

The radial Schrödinger equation outside the potential well is the free one

$$R'' + \frac{2}{r} R' + \left(k^2 - \frac{\ell(\ell+1)}{r^2} \right) R = 0, \quad r > a,$$

where $k^2 = 2mE/\hbar^2 < 0$ (k pure imaginary), while

$$R'' + \frac{2}{r} R' + \left(k'^2 - \frac{\ell(\ell+1)}{r^2} \right) R = 0, \quad r < a,$$

where $k'^2 = 2m(E + V_0)/\hbar^2 > 0$ (k' real), for energy in the range $-V_0 < E < 0$. The radial equation has the form of the free Schrödinger equation in the both domains, therefore the solution is given by an appropriate combination of the spherical Bessel functions, j_ℓ and n_ℓ , or equivalently, $h_\ell^{(1)}$ and $h_\ell^{(2)}$.

For the internal region ($r < a$) the condition of regularity at the origin uniquely selects the solution

$$R_\ell^{(int)} = A j_\ell(k'r) \quad (6.10)$$

(A is a constant). On the other hand, the external solution must be such that the wave function is normalizable. From the asymptotic behaviors (6.5) and (6.6), we see that for

$$k = i\sqrt{-2mE}/\hbar \equiv i\kappa, \quad \kappa = \sqrt{-2mE}/\hbar$$

($\kappa > 0$) and for $r \rightarrow \infty$,

$$j_\ell, n_\ell, h_\ell^{(2)} \sim \frac{1}{r} e^{i\kappa r}; \quad h_\ell^{(1)} \sim \frac{1}{r} e^{-i\kappa r},$$

so that only the function $h_\ell^{(1)}(i\kappa r)$ is compatible with the normalizability. One then has

$$R_\ell^{(ext)} = B h_\ell^{(1)}(i\kappa r). \quad (6.11)$$

The internal solution (6.10) and external one (6.11) must be connected smoothly at $r = a$. It follows that the condition

$$\frac{i\kappa h_\ell^{(1)'}(i\kappa a)}{h_\ell^{(1)}(i\kappa a)} = \frac{k' j_\ell'(k'a)}{j_\ell(k'a)}$$

determines the energy eigenvalues.

For instance, for $\ell = 0$ we find that $j_0(k'r) = \frac{\sin k'r}{k'r}$, $h_0^{(1)}(i\kappa r) = -\frac{e^{-\kappa r}}{\kappa r}$, and the condition becomes, after the change of variables $\xi \equiv k'a$; $\eta \equiv \kappa a$,

$$\xi \cot \xi = -\eta. \quad (6.12)$$

The variables ξ and η are constrained by the relation

$$\xi^2 + \eta^2 = \frac{2mV_0a^2}{\hbar^2}. \quad (6.13)$$

The system of equations found here is the same as the one (cf. eqn (3.23)) encountered in the problem of the one-dimensional symmetric potential well. More precisely here we find only one type of solution, corresponding to the odd solutions, owing to the condition of regularity at the origin $\chi(0) = 0$. From the graphs representing curves (6.12) and (6.13) in the first quadrant, $\xi > 0$, $\eta > 0$ (Fig. 6.1), it can be observed that:

- (1) For $\sqrt{2mV_0a^2/\hbar^2} \leq \pi/2$, no solutions exist: there are no bound states.
- (2) For $\pi/2 < \sqrt{2mV_0a^2/\hbar^2} \leq 3\pi/2$ there is only one solution (one bound state).
- (3) In the range of parameters $3\pi/2 < \sqrt{2mV_0a^2/\hbar^2} \leq 5\pi/2$ there are two bound states.

And so on.

In contrast to the case of the one-dimensional potential well, therefore, there is a minimum width/depth of the potential well ($\sqrt{2mV_0a^2/\hbar^2} = \pi/2$) below which the well cannot support a bound state¹.

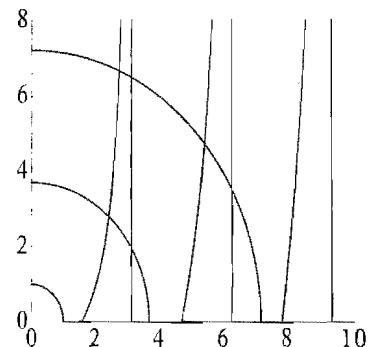


Fig. 6.1 Graphical solution for the 3D potential well

6.3 The three-dimensional oscillator

As the next simplest example, consider the three-dimensional oscillator,

$$H = \frac{\mathbf{p}^2}{2m} + \frac{1}{2}m\omega^2\mathbf{r}^2. \quad (6.14)$$

This problem can be easily solved by separating the variables in Cartesian coordinates,

$$\Psi(\mathbf{r}) = \psi(x)\phi(y)\chi(z),$$

and the problem is reduced to the one-dimensional oscillator discussed earlier. The energy levels are given by

$$E_{n_1, n_2, n_3} = \omega\hbar(n_1 + n_2 + n_3 + \frac{3}{2}), \quad (6.15)$$

¹A possible interpretation is that the minimum momentum fluctuations implied by the uncertainty relations has a larger effect the higher the dimension of the system is.

where $n_1, n_2, n_3 = 0, 1, 2, \dots$. The associated eigenfunctions are

$$\Psi_{n_1, n_2, n_3} = \psi_{n_1}(x) \psi_{n_2}(y) \psi_{n_3}(z),$$

where $\psi_n(x)$ is the n th normalized eigenfunction of the one-dimensional oscillator, (3.33),

$$\psi_n(x) = C_n H_n(\alpha x) e^{-\frac{1}{2}\alpha^2 x^2} = C_n H_n\left(\sqrt{\frac{m\omega}{\hbar}} x\right) e^{-\frac{m\omega}{2\hbar} x^2},$$

where

$$C_n = \left(\frac{\alpha}{\pi^{1/2} 2^n n!}\right)^{1/2}, \quad \alpha \equiv \sqrt{\frac{m\omega}{\hbar}}.$$

The case of an anisotropic oscillator can be solved with a minor change.

Let us concentrate on the isotropic oscillator, (6.14), however. The spectrum, eqn (6.15), shows a characteristic degeneracy of excited levels, $d(1) = 3, d(2) = 6, d(3) = 10$, etc., and

$$d(n) = \frac{(n+2)(n+1)}{2} \quad (6.16)$$

for the n th level. This degeneracy can be understood by the fact that the n -th energy eigenstates contain the momentum eigenstates up to $\ell = n$, and furthermore the given level has a definite parity (even or odd, according to whether n is even or odd, respectively). Summing the multiplicity $2\ell + 1$ over $\ell = 0, 1, 2, \dots, n$ (n even) or $\ell = 1, 2, \dots, n$ (n odd), one finds the degeneracy, (6.16).

This being so, what is the physical reason for eqn (6.16)? Is there any *symmetry* behind such a degeneracy? The origin of this particular degeneracy can be seen by going to the formalism of the creation and annihilation operators.² Following the discussion of Section 3.4.2 and introducing creation and annihilation operators for each oscillator, one arrives at the Hamiltonian

$$H = \frac{\omega\hbar}{2} \sum_{i=1}^3 (a_i a_i^\dagger + a_i^\dagger a_i) = \omega\hbar \sum_{i=1}^3 \left(a_i^\dagger a_i + \frac{3}{2}\right). \quad (6.17)$$

It is obvious that this Hamiltonian is invariant under the three-dimensional rotations under which (a_1, a_2, a_3) transform as a vector, the ordinary rotation matrices being real. This of course explains the $(2\ell + 1)$ -tuple degeneracy among states with definite ℓ , as we know. However, the invariance group of eqn (6.17) is actually *larger* than $SO(3)$. It is in fact invariant under the transformations of the *special unitary group* $SU(3)$ among the three operators a_i . Just as the orthogonal group is defined as the group which leaves the scalar product $\mathbf{a} \cdot \mathbf{a}$ invariant for any vector \mathbf{a} , the $SU(3)$ group is a group which leaves the product

$$\sum_{i=1}^3 z_i^* z_i$$

²Various $SU(n)$ groups appear in the theory of fundamental interactions and elementary particles, such as the "color" $SU(3)$ gauge group of strong interactions and the Weinberg-Salam $SU(2) \times U(1)$ group of electroweak interactions. The reason for the appearance of the special unitary groups is always the same: it can be traced to the fact that the Hamiltonian or Lagrangian of n types of oscillators in quantum mechanical systems is automatically invariant under an $SU(n)$ group, as in the three-dimensional harmonic oscillator.

invariant, where (z_1, z_2, z_3) is any complex three-dimensional vector. We shall not go further into the details of the general properties of the unitary groups here: there is some discussion of the special unitary groups $SU(n)$ in Supplement 20.6. It suffices for present purposes to note that *totally symmetric* irreducible representations (multiplets) of the $SU(3)$ group are characterized by the horizontal Young tableaux (see Supplement 20.8)

$$(\cdot), \quad \square, \quad \square\square, \quad \square\square\square, \quad \square\square\square\square, \quad \text{etc.},$$

where the first indicates the singlet (trivial) representation. The *dimension* (multiplicity) of these symmetric representations is known to be given precisely by

$$\frac{(n+2)(n+1)}{2}, \quad n = 0, 1, 2, 3, \dots$$

6.4 The hydrogen atom

The hydrogen atom is a bound state of a proton and an electron, owing to the static Coulomb potential

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}. \quad (6.18)$$

This is the simplest of all possible atoms and is exactly soluble. The reduced mass is equal to $m = m_e m_P / (m_e + m_P) \simeq 0.995 m_e$ and in a first approximation can be identified with the electron mass. The radial equation takes the form

$$\frac{d^2}{dr^2}R + \frac{2}{r}\frac{d}{dr}R - \frac{\ell(\ell+1)}{r^2}R + \frac{2m}{\hbar^2}\left(E + \frac{e^2}{r}\right)R = 0. \quad (6.19)$$

The effective potential

$$V_{\text{eff}}(r) = -\frac{e^2}{r} + \frac{\ell(\ell+1)\hbar^2}{2mr^2}$$

tends to zero at $r \rightarrow \infty$. Bound states are possible only for the negative values of the energy.

We shall set

$$\tilde{E} \equiv \frac{mE}{\hbar^2} = [\text{cm}^{-2}] \quad (6.20)$$

and choose the unit of length

$$\frac{\hbar^2}{me^2} \equiv r_B = 1.$$

$r_B \simeq 0.5 \times 10^{-8}$ cm is known as the Bohr radius, and as we shall see, it sets the scale of the problem: the wave function of the hydrogen atom will have an extension of this order, and the energy levels are characterized by the Coulomb energy at this distance. It can be reinstated

without difficulty after the calculations by a simple dimensional consideration. The equation

$$\frac{d^2}{dr^2}R + \frac{2}{r}\frac{d}{dr}R - \frac{\ell(\ell+1)}{r^2}R + 2\left(\tilde{E} + \frac{1}{r}\right)R = 0 \quad (6.21)$$

can be further simplified by introducing the dimensionless variable ρ ,

$$\rho \equiv \frac{2r}{\lambda}, \quad \lambda \equiv \frac{1}{\sqrt{-2\tilde{E}}}. \quad (6.22)$$

Equation (6.21) now takes the form

$$R'' + \frac{2}{\rho}R' + \left[-\frac{1}{4} + \frac{\lambda}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right]R = 0,$$

where $R' \equiv (d/d\rho)R$.

At small ρ the centrifugal term dominates in the square bracket and gives rise to the behavior

$$R_\ell \sim \rho^\ell,$$

whereas at large ρ the equation becomes approximately $R'' - (1/4)R \approx 0$, implying the asymptotic behavior

$$R_\ell \sim e^{\pm\rho/2}. \quad (6.23)$$

Obviously we have to choose the solution with negative exponent, $e^{-\rho/2}$, to ensure normalizability. Let us then set

$$R \equiv \rho^\ell e^{-\rho/2} w_\ell.$$

The equation for w_ℓ is

$$\rho w'' + (2\ell + 2 - \rho)w' + (\lambda - \ell - 1)w = 0. \quad (6.24)$$

We need a solution such that $w(0) = \text{const.} (\neq 0)$ $w(\rho) < \rho^A$, $\rho \rightarrow \infty$. The problem can be solved by the power series expansion method. Substitution of

$$w(\rho) = \sum_{k=0}^{\infty} a_k \rho^k, \quad a_0 \neq 0 \quad (6.25)$$

in eqn (6.24) gives the relations

$$(2\ell + 2)a_1 + (\lambda - \ell - 1)a_0 = 0,$$

$$2a_2 - a_1 + 2(2\ell + 2)a_2 + (\lambda - \ell - 1)a_1 = 0,$$

...

$$(k+1)ka_{k+1} - ka_k + (k+1)(2\ell + 2)a_{k+1} + (\lambda - \ell - 1)a_k = 0,$$

etc, which amount to a simple recursion relation

$$(k+1)(2\ell + 2 + k)a_{k+1} + (\lambda - \ell - k - 1)a_k = 0, \quad k \geq 1. \quad (6.26)$$

If the series, eqn (6.25), terminates, w is a polynomial; otherwise it is an infinite series. In the latter case, the asymptotic behavior of $w(\rho)$ can be easily found from the large-order terms of the series, which approximately satisfy

$$a_{k+1} = \frac{a_k}{k} = \frac{a_{k-1}}{k(k-1)} = \dots = \text{const. } \frac{1}{k!},$$

and thus

$$w(\rho) \sim e^\rho, \quad \rho \rightarrow \infty.$$

Such behavior, leading to the “wrong” solution of eqn (6.23), is clearly incompatible with the requirement of normalizability. We must require the series to terminate.

From the recursion relation, eqn (6.26), it follows that the condition for termination of the series is that the constant λ is such that

$$\lambda - \ell - k - 1 = 0 \quad (6.27)$$

for a non-negative integer k . Since ℓ is also an integer, it follows that λ must be a positive integer,

$$\lambda = n \quad (n = 1, 2, 3, \dots).$$

Recalling definition (6.22) and (6.20), we see that this determines the quantized energy of the hydrogen atom,

$$E_n = -\frac{\hbar^2}{2mn^2}.$$

By reinstating a factor r_B^{-2} to get the correct dimension of energy, one finds that

$E_n = -\frac{m e^4}{2\hbar^2 n^2} = -\frac{e^2}{2n^2 r_B}, \quad r_B = \frac{\hbar^2}{m e^2} \quad (n = 1, 2, 3, \dots),$

(6.28)

which are the celebrated Bohr levels.

For each value of n , the angular momentum ℓ takes values

$$\ell = 0, 1, 2, \dots, n-1$$

(see eqn (6.27)). Since the energy does not depend on the angular momentum ℓ , and as there are $2\ell + 1$ states for each ℓ , the n th energy level is

$$\sum_{\ell=0}^{n-1} (2\ell + 1) = n^2$$

(6.29)

times degenerate. Such degeneracy is specific to the Coulomb bound states.³

³As in the isotropic 3D oscillator case, the origin of this characteristic degeneracy lies in a symmetry—an $SO(4)$ group—present in the Coulomb bound state Hamiltonian. See Problem 6.3.

The recursion formulas above can be used to construct the associated wave functions as well. However, the generating function method, similar to that used for the one-dimensional harmonic oscillator, is more powerful and better suited to studying the general eigenfunctions of the hydrogen atom. The equation satisfied by $w(\rho)$ for $\lambda = n$ (a positive integer),

$$\rho w'' + (2\ell + 2 - \rho)w' + (n - \ell - 1)w = 0, \quad (6.30)$$

has a regular solution known as the *associated Laguerre polynomials*

$$w_{n,\ell} = L_{n+\ell}^{2\ell+1}(\rho). \quad (6.31)$$

To start with, the *Laguerre polynomials* are generated by the generating function

$$U(\rho, s) = \frac{e^{-\rho s/(1-s)}}{1-s} = \sum_{k=0}^{\infty} \frac{L_k(\rho)}{k!} s^k \quad (6.32)$$

($s < 1$). As in the case of the Legendre or Hermite polynomials, we consider the derivatives with respect to the variable ρ on both sides of eqn (6.32) to get

$$L'_k - kL'_{k-1} = -kL_{k-1};$$

on the other hand, consideration of the derivative d/ds gives

$$L_{k+1} = (2k + 1 - \rho)L_k - k^2 L_{k-1}.$$

Combining the two, one finds the differential equation

$$\rho L''_k + (1 - \rho)L'_k + kL_k = 0.$$

This resembles eqn (6.30) but is not exactly the same.

However, if one now introduces the associated Laguerre polynomials by

$$L_k^p(\rho) \equiv \frac{d^p}{d\rho^p} L_k(\rho),$$

then the equation satisfied by them is

$$\rho L''_k + (p + 1 - \rho)L'_k + (k - p)L_k^p = 0,$$

which is indeed identical to eqn (6.30), with parameters identified appropriately. The associated Laguerre polynomials are generated by

$$U_p(\rho, s) = \frac{(-)^p e^{-\rho s/(1-s)}}{(1-s)^{p+1}} = \sum_{k=0}^{\infty} \frac{L_k^p(\rho)}{k!} s^k. \quad (6.33)$$

In conclusion, the radial wave function of the n th Bohr level is

$$R_{n,\ell} = \rho^\ell e^{-\rho/2} w(\rho) = C_{n,\ell} \rho^\ell e^{-\rho/2} L_{n+\ell}^{2\ell+1}(\rho), \quad (6.34)$$

$$\rho \equiv \frac{2r}{n} = \frac{me^2}{\hbar^2} \frac{2r}{n} = \frac{2r}{nr^B}; \quad r_B \equiv \frac{\hbar^2}{me^2}.$$

The Bohr radius, $r_B \simeq 5.291 \times 10^{-9}$ cm determines the spatial extension of the ground state wave function. The normalization constant is

$$C_{n,\ell} = -\frac{2}{n^2} r_B^{-3/2} \sqrt{\frac{(n-\ell-1)!}{[(n+\ell)!]^3}}.$$

The first couple of radial eigenfunctions can be easily found by using eqn (6.33). The ground state ($n = 1, \ell = 0$) and the first excited state ($n = 2, \ell = 0, 1$) radial functions are:

$$\begin{aligned} R_{1,0}(r) &= 2r_B^{-3/2} e^{-r/r_B}, \\ R_{2,0}(r) &= \frac{1}{2\sqrt{2}} r_B^{-3/2} \left(2 - \frac{r}{r_B} \right) e^{-r/2r_B}, \\ R_{2,1}(r) &= \frac{1}{2\sqrt{6}} r_B^{-3/2} \frac{r}{r_B} e^{-r/2r_B}. \end{aligned}$$

The wave function of the generic (n, ℓ, m) state is

$$\psi_{(n,\ell,m)} = R_{n,\ell}(r) Y_{\ell,m}(\theta, \phi).$$

For the reader's convenience we recall the spherical harmonics (4.20) relevant for a few lowest levels:

$$\begin{aligned} Y_{0,0} &= \frac{1}{\sqrt{4\pi}}, \\ Y_{1,0} &= \sqrt{\frac{3}{4\pi}} \cos\theta, & Y_{2,0} &= \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1), \\ Y_{1,\pm 1} &= \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi}, & Y_{2,\pm 1} &= \mp \sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta e^{\pm i\phi}, \\ && Y_{2,\pm 2} &= \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{\pm 2i\phi}. \end{aligned}$$

In **Mathematica**, the radial function $R_{n,L}(r)$, eqn (6.34), can be obtained by writing

$$R[r_-, n_-, L_-] := \frac{2}{n^2} \sqrt{\frac{(n-L-1)!}{(n+L)^2}} \left(\frac{2r}{n} \right)^L e^{-\frac{r}{n}} \text{LaguerreL}\left[n-L-1, 2L+1, \frac{2r}{n}\right]$$

Note the way the indices of the associated Laguerre polynomials are defined in **Mathematica** compared with the standard quantum mechanical textbooks (eqn (6.34)).

Observations

- (1) Quantum mechanics thus exactly reproduces the energy levels obtained by Bohr, in good agreement with the experimental line spectra data, although the degeneracy result can only follow from a quantum mechanical treatment of the problem, as here.

- (2) The spatial extension of the ground state wave function is given by $r \simeq r_B \simeq 5.291 \times 10^{-9} \text{ cm}$ and can be regarded as the “size” of the hydrogen atom.
- (3) The formulas for the energy and wave function obtained here are valid for any hydrogenlike atom, i.e., an atom with an electron and a nucleus of electric charge $Z|e|$, upon a simple substitution $e^2 \rightarrow Ze^2$.
- (4) The expectation value of the momentum $\sqrt{\langle p^2 \rangle}$ is of the order of me^2/\hbar . This can also be obtained by extending the electron distribution to the order of r_B and from Heisenberg’s uncertainty relation. The average “velocity” of the electron is then

$$v \sim p/m \simeq e^2/\hbar = \alpha c \simeq c/137 \ll c,$$

where $\alpha \equiv e^2/\hbar c \simeq 1/137$ is the so-called *fine-structure constant*. The motion of the electron is thus non-relativistic, which *a posteriori* justifies the use of an approximate Hamiltonian, eqn (6.18). At the same time one must expect corrections of the order of 10^{-2} .

- (5) The ionization energy is equal to the energy required to liberate the bound electron, and is equal to

$$e^2/2r_B \sim 14 \text{ eV},$$

which is known as the *Rydberg energy*.

- (6) The principal series of the hydrogen spectrum are shown in Table 6.1. Each series is named after its discoverer.

Lyman series	$n_2 = 1$	$\nu = (E_n - E_1)/\hbar$,	$n = 2, 3, \dots$	ultraviolet
Balmer series	$n_2 = 2$	$\nu = (E_n - E_2)/\hbar$,	$n = 3, 4, \dots$	visible
Paschen series	$n_2 = 3$	$\nu = (E_n - E_3)/\hbar$,	$n = 4, 5, \dots$	infrared
Brackett series	$n_2 = 4$	$\nu = (E_n - E_4)/\hbar$,	$n = 5, 6, \dots$	infrared
Pfund series	$n_2 = 5$	$\nu = (E_n - E_5)/\hbar$,	$n = 6, 7, \dots$	infrared

Table 6.1 Spectral series of the hydrogen atom

Guide to the Supplements

Analyze the bound state energy levels of a particle moving in a three- or two-dimensional delta function potential,

$$H = \frac{\mathbf{p}^2}{2m} - g \delta^D(\mathbf{r}), \quad D = 2, 3.$$

This is an example of a problem in which the standard quantum mechanical approach does not give the correct answer. In order to get a physically meaningful system, the interaction constant g must be appropriately *renormalized*—a well-known procedure in rela-

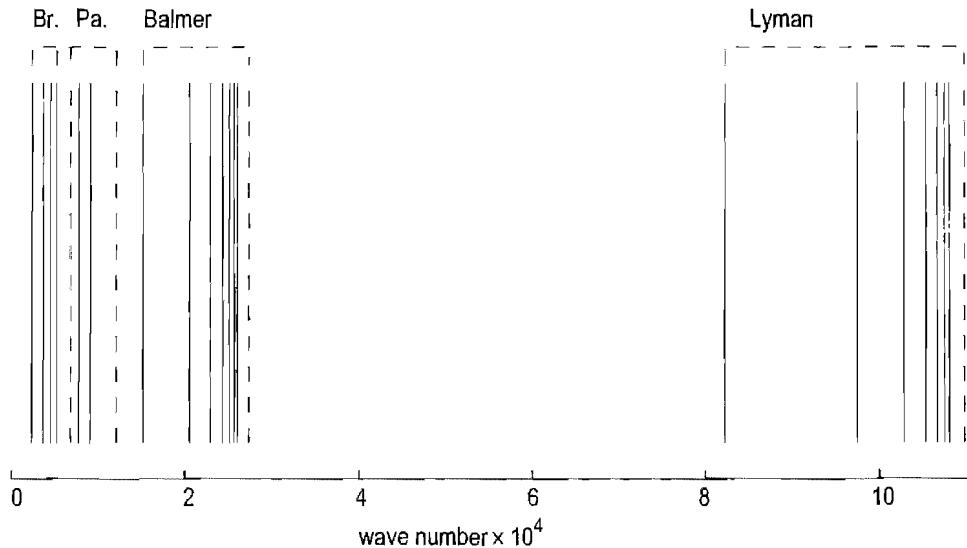


Fig. 6.2 Schematic diagram of some of the spectral lines of the hydrogen atom. The abscissas are the wave numbers $1/\lambda$. The vertical dashed lines indicate the points where the various series end. Four series are shown, from the Lyman to the Brackett. Note the partial overlap between some of them, in the diagram between the Brackett and the Ritz-Paschen series.

tivistic quantum field theories in four dimensions—or put in another more mathematical way, one must make a self-adjoint extension of the free Hamiltonian defined in $\mathbf{R}^D/\{0\}$. Either way, one finds a simple system with one bound state, whose energy cannot be calculated (an experimental input), but with the wave function and scattering amplitude determined uniquely in terms of it. This

system is discussed in Supplement 20.13. The same potential is considered from a slightly different point of view in Problem 6.5. In Problem 6.3 the origin of the n^2 degeneracy of Bohr's levels of the hydrogen atom is discussed.

In another Supplement, 20.12, quantum mechanical systems with supersymmetry are briefly discussed.

Problems

- (6.1) A particle of mass m moves in a radial potential,

$$V(\mathbf{r}) = V(r) = \begin{cases} \infty & r < R, \\ 0 & R \leq r \leq R + a, \\ \infty & r > R + a, \end{cases}$$

We wish to study the spectrum of the system.

- (a) Show that the stationary solutions can be separated in spherical coordinates and write the correct boundary conditions for the radial part of the wave function.

- (b) Find the condition which determines the energy levels at fixed L (angular momentum).

- (c) Solve the equation for part (b) for $L = 0$.

- (d) Show that for $a \ll R$ the first excited state has energy $\Delta E = \hbar^2/mR^2$ above the ground state. Explain this result on physical grounds.

- (6.2) Compute the limit of radial hydrogen wave functions as $n \rightarrow \infty$.
- (6.3) Explain the n^2 degeneracy of the hydrogen energy levels, by making use of the fact that the Lenz vec-

tor

$$\mathbf{A} = \frac{\mathbf{r}}{r} - \frac{1}{2Z}(\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p})$$

commutes with H .

- (6.4) Solve the Coulomb problem in parabolic coordinates

(ξ, η, φ) defined by

$$x = \sqrt{\xi, \eta} \cos \varphi; \quad y = \sqrt{\xi, \eta} \sin \varphi; \quad z = \frac{1}{2}(\xi - \eta).$$

- (6.5) A particle of mass m moves in a radial potential $v \delta(r - R)/4\pi R^2$. Compute for small R the continuum eigenstates and the possible bound states.

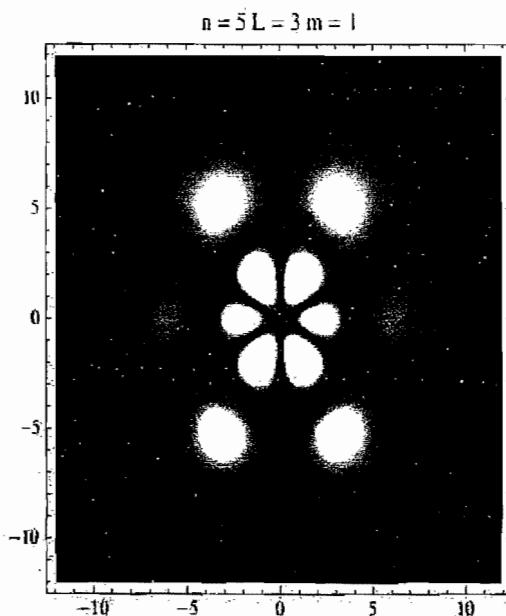


Fig. 6.3 Density plots in two and three dimensions for the states $(n, l, m) = (5, 3, 1)$ and $(4, 2, 0)$.

Numerical analyses

- (6.1) Plot the radial wave functions for hydrogen. Draw two- and three-dimensional plots for the electron density (see Figure 6.3).
 (6.2) Plot the first few free spherical waves j_ℓ , n_ℓ graphically. Check how the goodness of the expansion

$$e^{ikz} = e^{ikr \cos \theta} = \sum_{\ell=0}^{\infty} (2\ell + 1) i^\ell j_\ell(kr) P_\ell(\cos \theta)$$

depends on the number of terms kept.

- (6.3) Find numerically the energy levels and angular momentum quantum numbers of all bound states for

the potential well

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}), \quad V(\mathbf{r}) = \begin{cases} -V_0, & r < a; \\ 0, & r > a, \end{cases}$$

by taking as the parameters

$$V_0 = 300 \text{ MeV}; \quad a = 3 \text{ fm}; \quad \mu = 940 \text{ MeV}/c^2.$$

Note that $1 \text{ fm} = 10^{-13} \text{ cm}$; use $\hbar c \simeq 200 \text{ MeV fm}$.

- (6.4) Check in Mathematica the solution in parabolic coordinates for the hydrogen atom obtained in problem 6.4.

Some finer points of quantum mechanics

7

In this chapter, central concepts in quantum mechanics such as states and operators are reconsidered and defined more carefully. This reveals a large arbitrariness in the choice of representations for states and operators, related to each other by unitary transformations. Even the way in which the time evolution of the systems is described can be changed so that, for example, the time dependence is carried by operators (the Heisenberg picture) rather than by state vectors (the Schrödinger picture). Also, an important generalization of the concept of the quantum state itself is introduced, which allows us to describe more general physical situations where a complete quantum-mechanical description is unavailable. The “state” in such a case is known as a *mixed state* and is described by a *density matrix*, as compared to a *pure state* represented by a wave function.

7.1 Representations	151
7.2 States and operators	155
7.3 Unbounded operators	158
7.4 Unitary transformations	167
7.5 The Heisenberg picture	169
7.6 The uncertainty principle	172
7.7 Mixed states and the density matrix	173
7.8 Quantization in general coordinates	178
Further reading	182
Guide to the Supplements	182
Problems	182

7.1 Representations

There is a wide freedom in the way states and dynamical variables are described in quantum mechanics; the physical results must be independent of the particular language used, called the *representation*. A somewhat similar arbitrariness in the choice of language also exists in classical mechanics, such as the wide class of possible choices of canonical variables, which are related to each other by canonical transformations. However, the possibility of using different representations according to the problem considered appears to have much more profound consequences and implications in quantum mechanics.

Such a freedom of choice of language means that central concepts such as states and operators, time evolution of the system, etc., must be defined in a more general and abstract way than has been done so far in this book (the so-called Schrödinger representation). Different descriptions are usually related by a *unitary transformation*. The theory of unitary transformations, besides providing us with a conceptual clarification of the whole construction of quantum mechanics, often offers a powerful method of solution.

The principles of quantum mechanics developed so far may be summarized as follows:

P1 A separable Hilbert space \mathcal{H} is associated with each quantum-

mechanical system. A quantum state is described by the ray in this space, i.e., by a unit-norm vector (wave function), modulo the phase.

P2 A Hermitian (self-adjoint) operator A in \mathcal{H} is associated with each observable \mathcal{A} .

P3 The expectation value of an observable \mathcal{A} in a state is given by $\langle \psi | A | \psi \rangle$. If a_k stands for an eigenvalue of A and $|k, \alpha\rangle$ the corresponding eigenvector (the index α labels possible degenerate states), the probability of finding the value a_k in a measurement of \mathcal{A} in the state $|\psi\rangle$ is given by $\sum_{\alpha} |\langle k, \alpha | \psi \rangle|^2$.

P4 There exists a Hermitian (self-adjoint) operator H , the Hamiltonian, which determines the time evolution according to the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H|\psi\rangle.$$

P5 Quantum operators Q, P are associated with the classical canonical variables q, p in any cartesian coordinates. They obey Heisenberg's commutation relation,

$$[Q, P] = i\hbar.$$

The aim of this chapter is to make these rules more precise, qualifying them a little more carefully. Another, important issue in this chapter is the *generalization* of the notion of the quantum state itself, point [P1] above, to include the cases of mixed states.

7.1.1 Coordinate and momentum representations

We begin with an example of the change of representation, which will illustrate well the points made in the introduction to this chapter.

In Schrödinger's approach the wave function $\psi(x, t)$ represents a quantum state. Here x plays the role of the *parameter*, in the sense that it helps us to specify the probability amplitude of finding the particle at various spatial points, but the *state* is really represented by the whole function ψ . But x plays also another role: it is the (improper) eigenvalue of the position operator \hat{q} defined by

$$\hat{q}\psi(q) = q\psi(q).$$

This operator has the eigenfunctions $f_q(x) = \delta(q - x)$

$$f_q(x) = \delta(q - x), \quad \hat{q}\delta(q - x) = x\delta(q - x) = q\delta(q - x),$$

as we have seen already.

It helps perhaps to draw an analogy with vectors in a finite-dimensional space: the components v_i of a vector can be defined, in terms of an orthonormal basis of unit vectors e_i , as various projections $v_i = (e_i, v)$ (here $(*, *)$ stands for the scalar product between two vectors), but naturally the vector v has a well-defined meaning independently of how they are expressed, using components referring to a particular basis.

The idea is similar here: we should really consider the “state vector” ψ or the scalar product of two of state vectors independent of the particular basis chosen. Just as the scalar product

$$(a, b) = a_i b_i$$

between two finite-dimensional vectors

$$(a, b) = a_i b_i$$

has a basis-independent meaning, the quantum-mechanical state vectors and their Hermitian scalar products are independent of the particular basis chosen.

Thus one can write

$$\psi(x) = \int dx' \delta(x' - x) \psi(x') = \int dx' f_x^*(x') \psi(x') \quad (7.1)$$

and interpret (7.1) as a scalar product

$$\langle x | \psi \rangle,$$

having defined the scalar product as

$$\int dx' \phi^*(x') \chi(x') = \langle \phi | \chi \rangle, \quad (7.2)$$

where a notation due to Dirac has been introduced in eqn (7.2).

The state vector $|q\rangle$, the position eigenvector, plays the role of the basis of abstract vectors, whose components are $\langle x | q \rangle = f_q(x) = \delta(x - q)$. In order to have a complete analogy with finite-dimensional vectors, it is necessary that the basis vectors form an orthonormal and complete set (so that *any* state can be expressed in terms of their linear combination). The latter is just the eqn (7.1), while the first is

$$\langle q | q' \rangle = \int dx f_q^*(x) f_{q'}(x) = \int dx \delta(q - x) \delta(q' - x) = \delta(q - q'),$$

which is similar to $(e_i, e_j) = \delta_{ij}$.

The idea is then that the construction can be done by using a different variable than q (which is the case for the Schrödinger representation, or *coordinate representation*). In *momentum representation*, we first consider the eigenvectors of \hat{p} in the x representation,

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}, \quad (7.3)$$

which satisfy the orthonormality condition

$$\langle p | p' \rangle = \delta(p - p'). \quad (7.4)$$

The abstract state vector (or “ket”) $|p\rangle$ can be defined such that $\hat{p}|p\rangle = p|p\rangle$, whose x representation is given by eqn (7.3).

A generic state $|\psi\rangle$ can be written in the momentum representation as

$$\tilde{\psi}(p) = \langle p|\psi\rangle = \int dx f_p(x)^* \psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int dx e^{-ipx/\hbar} \psi(x).$$

The “wave function” in the p representation is nothing but a Fourier component of the usual wave function. Going to the p representation from the x representation thus amounts to the Fourier transform. In particular, the position eigenstate, with eigenvalue x' , is given in the p representation by

$$\langle p|x\rangle = \int dx' f_p^*(x') \delta(x - x') = f_p^*(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{-ipx/\hbar} \quad (7.5)$$

and, by virtue of the property of a Hermitian scalar product, $\langle p|x\rangle = \langle x|p\rangle^*$.

As another example, consider the n -th energy eigenstate of a harmonic oscillator in the two representations. In the x representation we obtained earlier,

$$\langle x|n\rangle = \psi_n(x) = C_n H_n(\alpha x) e^{-\alpha^2 x^2/2} \quad (7.6)$$

(see Chap. 3). The same state is described in the p representation by the wave function

$$\psi(p) = \langle p|n\rangle = \int dx \langle p|x\rangle \langle x|n\rangle = \frac{C_n}{\alpha \hbar^{1/2}} (-i)^n H_n\left(\frac{p}{\alpha \hbar}\right) e^{-p^2/2\alpha^2 \hbar^2}, \quad (7.7)$$

which is the Fourier transform of (7.6).

The effect of the change of basis can also be seen on operators. In the momentum representation, the momentum is represented by a multiplicative operator, $\hat{p} = p$, whereas the position operator becomes a differential operator

$$\hat{x} = i\hbar \frac{\partial}{\partial p}.$$

Note the (crucial) difference in the sign with respect to the more familiar expression $\hat{p} = -i\hbar \frac{\partial}{\partial x}$ of the momentum in the x representation. This is necessary so that the fundamental commutation relation

$$[\hat{x}, \hat{p}] = i\hbar$$

is valid in any representation.

We see that in particular the harmonic oscillator Hamiltonian in the p representation takes the form

$$H = -\frac{1}{2}m\omega^2\hbar^2 \frac{\partial^2}{\partial p^2} + \frac{p^2}{2m},$$

which has the same form as the standard one in the x representation, after the replacement,

$$m \rightarrow M = \frac{1}{m\omega^2}, \quad \omega \rightarrow \omega,$$

and this explains the simple result (7.7): it could have been obtained just by inspection, without really performing any Fourier transformation, from eqn (7.6)!

7.2 States and operators

7.2.1 Bra and ket; abstract Hilbert space

The preceding discussion clearly highlights a fact which is conceptually important: a quantum state is described by (the ray of) an abstract vector, called a *ket*,

$$|\psi\rangle.$$

It is also convenient to introduce a kind of conjugate, $\langle\psi|$, called the *bra* vector. These terminologies were introduced by Dirac from the English word “bracket”. The description of “ ψ ” in terms of a complex function (e.g., of x) is just a possible representation. The operators, the equation of motion, etc., must be defined in the space of such abstract state vectors. We shall study first the properties of this space, leaving the study of relations among different representations (unitary transformations) to subsequent sections.

The required properties of the space \mathcal{H} of vectors representing possible quantum states of a system are:

- [1] \mathcal{H} is a vector space.
- [2] A scalar product $\langle\chi|\phi\rangle$, which is a complex number, is defined for each pair of vectors in \mathcal{H} .
- [3] \mathcal{H} is complete.
- [4] \mathcal{H} is separable.

A space with these properties is known as a (separable) *Hilbert space*.¹

[1] \mathcal{H} is a vector space

This property means that, given two vectors $|\psi\rangle$, $|\phi\rangle$ in \mathcal{H} , any combination

$$c\psi + d\phi \in \mathcal{H}, \quad c, d \in \mathbb{C} \quad (7.8)$$

belongs to \mathcal{H} also. In other words, in \mathcal{H} the sum among vectors and multiplication with complex numbers are defined, with the standard rules:

$$\begin{aligned} \psi + \phi &= \phi + \psi; & (\psi + \phi) + \chi &= \psi + (\phi + \chi); \\ c(\psi + \phi) &= c\psi + c\phi; & (cd)\psi &= c(d\psi); \\ 0 \cdot \psi &= 0; & 1 \cdot \psi &= \psi. \end{aligned}$$

Note in particular that a null vector $\psi - \psi = 0$ exists in \mathcal{H} . The vectors $\psi_1, \psi_2, \dots, \psi_k$ are *linearly independent* if

$$c_1\psi_1 + c_2\psi_2 + \dots + c_k\psi_k = 0, \quad (7.9)$$

¹ The concept of a Hilbert space was introduced by D. Hilbert (~ 1910), as generalizations of the finite-dimensional Euclidean space R^n (with elements (x_1, x_2, \dots, x_n)) in the $n \rightarrow \infty$ limit. A Hilbert space inherits many of its properties from the latter, in a natural fashion.

implies

$$c_1 = c_2 = \dots = c_k = 0.$$

The maximum number of linearly independent vectors is the *dimension* of \mathcal{H} .

[2] A scalar product $\langle \chi | \phi \rangle$ is defined for each pair of vectors in \mathcal{H}

For each pair of vectors in \mathcal{H} , ψ , and ϕ , a (Hermitian) scalar product $\langle \phi | \psi \rangle \in \mathbb{C}$ (a complex number) is defined such that

$$\begin{aligned} \langle \phi | c_1 \psi_1 + c_2 \psi_2 \rangle &= c_1 \langle \phi | \psi_1 \rangle + c_2 \langle \phi | \psi_2 \rangle; \\ \langle \phi | \psi \rangle^* &= \langle \psi | \phi \rangle; \\ \langle \psi | \psi \rangle &\geq 0, \quad (= 0, \quad \text{if and only if} \quad |\psi\rangle = 0). \end{aligned} \quad (7.10)$$

²Sometimes different notations are used in the literature, e.g. (ϕ, ψ) or (ψ, ϕ) , instead of $\langle \phi | \psi \rangle$.

The first two relations imply that²

$$\langle c_1 \psi_1 + c_2 \psi_2 | \phi \rangle = c_1^* \langle \psi_1 | \phi \rangle + c_2^* \langle \psi_2 | \phi \rangle.$$

In coordinate representation the scalar product can be written explicitly as:

$$\langle \phi | \psi \rangle = \int dq \phi^*(q) \psi(q),$$

where $dq \equiv d^n x$ if the coordinate degrees of freedom is n . For instance $n = 6$ for a two-particle system in three dimensions.

The positivity of the scalar product (7.10) allows us to introduce the *norm* of a state vector by

$$\|\psi\| \equiv \sqrt{\langle \psi | \psi \rangle}.$$

The introduction of the norm—the length of each vector—in \mathcal{H} implies that the “distance” between any pair of states can be defined naturally as

$$\|\psi - \phi\| = \sqrt{\langle \psi - \phi | \psi - \phi \rangle}. \quad (7.11)$$

\mathcal{H} is thus a *metric space*. In such a space one can introduce the concept of the limit of a sequence, $\{\psi_n\} = \psi_1, \psi_2, \dots$, by Cauchy’s criterion:

$$\lim_{n \rightarrow \infty} \psi_n = \psi \quad \text{exists if} \quad \forall \epsilon > 0, \exists N > 0 : \quad \forall n > N, \quad \|\psi_n - \psi\| < \epsilon.$$

Any acceptable definition of a distance must be such that for any three points (chosen here as 0 , ψ , and ϕ) the relation

$$\|\psi - \phi\| \leq \|\psi\| + \|\phi\| \quad (7.12)$$

holds (the triangular inequality). Equation (7.12) can also be written as (ϕ to $-\phi$):

$$\|\psi + \phi\| \leq \|\psi\| + \|\phi\|. \quad (7.13)$$

It is not difficult to show that eqn (7.13) is satisfied by definition (7.11). Note first that

$$\langle \psi + \phi | \psi + \phi \rangle = \|\psi\|^2 + \|\phi\|^2 + 2\operatorname{Re}\langle \phi | \psi \rangle.$$

But for any complex number the relation

$$\operatorname{Re}\langle \phi | \psi \rangle \leq |\langle \phi | \psi \rangle|$$

holds, so we need only to demonstrate that

$$|\langle \phi | \psi \rangle| \leq \|\phi\| \|\psi\|. \quad (7.14)$$

(the Schwarz inequality).

To show eqn (7.14), it suffices to consider a vector

$$\tilde{\phi} \equiv \phi - \psi \cdot \sqrt{\langle \psi | \phi \rangle} \|\psi\|^2.$$

Equation (7.14) is a simple consequence of the fact that $\tilde{\phi}$ is semi-positive definite. Note also that the equality holds if and only if $c_1\psi = c_2\phi$, $c_1, c_2 \in \mathbb{C}$.

[3] \mathcal{H} is complete

A Cauchy sequence is

$$\forall \epsilon > 0, \exists N : \forall n, m > N, \|\psi_n - \psi_m\| < \epsilon.$$

The space \mathcal{H} is complete if each Cauchy sequence converges in \mathcal{H} .

An example of a space which is not complete is the set of rational numbers \mathbb{Q} which is a subspace of the real numbers \mathbb{R} .

A useful property of a complete space is that each closed subspace is complete. Recall that a closed space contains all the limit points. Then a closed vector subspace of \mathcal{H} is complete, and is itself a Hilbert space.

[4] \mathcal{H} is separable

That is, there is a countable subensemble (base) $S \subset \mathcal{H}$, dense everywhere in \mathcal{H} . In other words, each vector $\psi \in \mathcal{H}$ is a limit of a sequence $\{\phi_n\}$ in S . (The set of rational numbers forms a numerable base and is dense everywhere in the space of real numbers, therefore \mathbb{R} is separable.)

The most important consequence of [1]–[4] is the existence of a complete and orthonormal system of vectors in \mathcal{H} , $\{\psi_n\}$. Any vector in \mathcal{H} can be written as

$$\psi = \lim_{N \rightarrow \infty} \sum_{n=0}^N c_n \psi_n \equiv \sum c_n \psi_n \quad \text{where } \langle \psi_i | \psi_j \rangle = \delta_{ij}. \quad (7.15)$$

The expansion coefficients c_n are given by

$$c_n = \langle \psi_n | \psi \rangle,$$

that is, for each vector the relation

$$|\psi\rangle = \sum_n |\psi_n\rangle \langle\psi_n| \psi\rangle$$

holds. This can be written symbolically as

$$\sum_n |\psi_n\rangle \langle\psi_n| = 1,$$

which is the completeness relation seen already in Section 2.6.

We emphasize that not all linear combinations (7.15) define a vector in \mathcal{H} . The requirement of finite norm implies, by virtue of the orthogonality, that

$$\langle\psi|\psi\rangle = \sum_i |c_i|^2 < \infty.$$

In a Hilbert space of finite dimensions properties [3] and [4] are automatically satisfied. Vice versa, for infinite-dimensional Hilbert spaces these requirements are of fundamental importance.

7.3 Unbounded operators

The observables are described by operators acting in the abstract Hilbert space

$$A : \mathcal{H} \rightarrow \mathcal{H}. \quad (7.16)$$

We want the action of an operator to preserve the linear structure, so require it to be *linear*

$$A(\alpha_1|\varphi_1\rangle + \alpha_2|\varphi_2\rangle) = \alpha_1 A|\varphi_1\rangle + \alpha_2 A|\varphi_2\rangle.$$

If there exists a real positive number C such that

$$\|A\psi\| \leq C\|\psi\|, \quad \forall \psi \in \mathcal{H}, \quad (7.17)$$

the operator is said to be *bounded*; otherwise it is unbounded. The *norm* of the operator A , denoted as $\|A\|$, is defined as the lower limit of the constant C satisfying eqn (7.17), i.e.,

$$\|A\| = \sup_{\psi \neq 0} \|A\psi\|/\|\psi\|; \quad \text{or} \quad \|A\| = \sup_{\|\psi\|=1} \|A\psi\|. \quad (7.18)$$

In other words, the operator is bounded if $\|A\| < \infty$. It is easy to convince oneself that an operator A is continuous if and only if it is bounded. In a finite-dimensional Hilbert space all operators are bounded; in an infinite-dimensional space it is not the case.

We note that for linear operators the notion of continuity is global: if an operator is continuous in a point it is so everywhere in the Hilbert space. Vice versa, if it is unbounded it is discontinuous everywhere. This can be understood, simplifying a little, by noting that the condition of continuity at ψ , given by

$$\forall \epsilon > 0, \exists \delta > 0 : \quad \forall \varphi : \|\varphi - \psi\| < \delta \Rightarrow \|A\varphi - A\psi\| < \epsilon$$

can be translated into a statement about the origin 0, by writing it as $f = \varphi - \psi$ and $A(\psi) - A(\varphi) = A(\psi - \varphi) = A(f)$.

The fundamental commutation relation

$$[Q, P] = i\hbar \quad (7.19)$$

explains why unbounded operators occur as a rule in quantum mechanics. In fact, it follows from eqn (7.19) that

$$PQ^n - Q^n P = -in\hbar Q^{n-1}, \quad (7.20)$$

and therefore

$$n\hbar ||Q^{n-1}|| \leq 2||PQ^n|| \leq 2||P|| ||Q|| ||Q^{n-1}||,$$

where we used

$$||AB|| \leq ||A|| ||B||, \quad ||A+B|| \leq ||A|| + ||B||,$$

valid for any pair of operators. Thus

$$2||P|| ||Q|| \geq n\hbar.$$

As the inequality is valid for any n , at least one of the operators P, Q must be unbounded.

Other common examples of unbounded operators are:

(i) The energy operator of a harmonic oscillator,

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2,$$

is unbounded as there are states ψ_n such that $H\psi^{(n)} = E_n\psi^{(n)}$, $||\psi_n|| = 1$, with an arbitrarily large value of E_n .

(ii) The position operator x : for instance the states $\psi^{(n)} = \frac{e^{-x^2/2n^2}}{\pi^{1/4}n^{1/2}}$, are normalized but

$$||x\psi^{(n)}||^2 = \frac{n^2}{2}$$

can be arbitrarily large.

(iii) In one dimension $\psi(x) = \sqrt{\frac{a}{\pi}} \frac{1}{\sqrt{x^2+a^2}} \in \mathcal{H}$ but $x\psi \notin \mathcal{H}$.

As is clear from these examples, sometimes the action of an operator on a vector in \mathcal{H} is not defined (i.e., does not generate a state in \mathcal{H}). It is therefore necessary to define the *domain* of an operator A , $\mathcal{D}(A)$, a subspace of \mathcal{H} upon which A acts:

$$\psi \in \mathcal{D}(A) \subset \mathcal{H}, \quad \text{if } A\psi \in \mathcal{H}. \quad (7.21)$$

Definition (7.21) is flexible enough to allow for possible extension of the domain. One can define an *extension* of an operator A, B by

$$\mathcal{D}(A) \subset \mathcal{D}(B) \quad \text{e} \quad \forall |f\rangle \in \mathcal{D}(A) : A|f\rangle = B|f\rangle.$$

The necessity of dealing with unbounded operators renders it indispensable to require a more precise condition on the operators to be associated with dynamical variables.

First of all, recall the reasoning of the Subsection 2.3.2. An operator A is called *Hermitian* or *symmetric* if

$$\forall f, g \in \mathcal{D}(A) \quad \langle Af | g \rangle = \langle f | Ag \rangle. \quad (7.22)$$

The expectation value of a dynamical variable must be real in any state. The necessary and sufficient condition for this is that A be Hermitian.

In a finite-dimensional (N) space, this requirement is equivalent to the condition that the matrix representing the operator in a given basis is Hermitian. Let $\{|e_i\rangle\}$ be an orthonormal basis, and define the matrix as

$$A|e_i\rangle = \sum_{j=1}^N A_{ji} e_j. \quad (7.23)$$

From eqn (7.22) it follows immediately that $A_{ij} = A_{ji}^*$ e $A(\sum_i c_i |e_i\rangle) = (\sum_{ij} (A_{ij} c_j) |e_i\rangle)$.

An important theorem in this context (known as the Hellinger–Toeplitz theorem) asserts that an operator defined everywhere in \mathcal{H} , with the property

$$\langle A\phi|\psi\rangle = \langle\phi|A\psi\rangle,$$

is necessarily bounded. It follows that for an unbounded operator the definition of “reality” requires more careful study.

7.3.1 Self-adjoint operators

If for any given vector $\psi \in \mathcal{H}$, another vector $\eta \in \mathcal{H}$ exists such that

$$\langle A\phi|\psi\rangle = \langle\phi|\eta\rangle, \quad \forall\phi \in \mathcal{D}(A),$$

then we define

$$A^\dagger|\psi\rangle \equiv |\eta\rangle.$$

The existence of such a vector η defines $\mathcal{D}(A^\dagger)$. The operator A^\dagger is called the *adjoint* of the operator A . This definition makes sense only if A is defined densely, that is, $\overline{\mathcal{D}(A)} = \mathcal{H}$. For otherwise let v be an element orthogonal to $\overline{\mathcal{D}(A)}$. We would have $\langle\phi|\eta\rangle = \langle\phi|\eta+v\rangle$, and thus the definition of η is not well defined.

Let us note that

$$\langle A\phi|\psi\rangle = \langle\phi|A^\dagger|\psi\rangle;$$

it follows from the definition of the scalar product that

$$\langle\phi|A^\dagger|\psi\rangle = (\langle\psi|A|\phi\rangle)^*.$$

In particular, if a matrix representation for A exists, one has $(A^\dagger)_{ij} = A_{ji}^*$, i.e., a Hermitian conjugate (adjoint) of A , known from linear algebra in finite-dimensional spaces. For a symmetric operator,

$$\langle A\varphi|\psi\rangle = \langle\varphi|A\psi\rangle \quad \text{for any vector } \varphi, \psi \in \mathcal{D}(A) :$$

thus if $\varphi \in \mathcal{D}(A)$ holds, so does $\varphi \in \mathcal{D}(A^+)$. In other words, an operator is symmetric if

$$A^\dagger \psi = A\psi, \quad \forall \psi \in \mathcal{D}(A), \quad \mathcal{D}(A) \subset \mathcal{D}(A^\dagger). \quad (7.24)$$

If furthermore the condition

$$\mathcal{D}(A^\dagger) = \mathcal{D}(A) \quad (7.25)$$

is satisfied, the operator is said to be *self-adjoint*.

For any self-adjoint operator, the relation

$$\langle \psi | A | \psi \rangle = \langle \psi | A | \psi \rangle^*, \quad \forall \psi \in \mathcal{D}(A), \quad (7.26)$$

holds: i.e., its expectation value in any state (hence any of its eigenvalues) is real. By postulate,

Any dynamical variable is represented by a self-adjoint operator.

Such a requirement might appear at first sight somewhat arbitrary. Is the distinction between Hermitian operators and self-adjoint operators a physically irrelevant mathematical sophistication? Actually, apart from various mathematical requirements of consistency, this specification is physically based. Consider for instance an observable \mathcal{A} represented by an operator A . A very reasonable physical requirement is that, whatever the correspondence between them, an observable which is a function $f(\mathcal{A})$ of \mathcal{A} be associated with an *operator*, $f(A)$. It is precisely the self-adjoint operators among the symmetric operators which satisfy this requirement.

In most cases treated in this book we shall deal with a symmetric operator which is automatically also self-adjoint. Usually the question of the domains $\mathcal{D}(A) \subset \mathcal{D}(A^\dagger)$ arises in problems with nontrivial boundary conditions, and in these cases one must be careful how to extend the symmetric operator to a self-adjoint one. Sometimes the extension is not unique: we may find that there correspond more than one physically distinct quantum operators correspond to a given classical operator. See some examples discussed in the Supplement on Hilbert space.

The importance of having self-adjoint operators can be appreciated from the following two theorems, which we quote here without proof. The definition of unitary operators will be given below, in the Section 7.4.

Theorem 7.1 *Let A be a self-adjoint operator and*

$$U(t) \equiv e^{itA} \quad (7.27)$$

with $t \in \mathbb{R}$ a continuous parameter. It follows then that

- (a) *For t, s real, $U^\dagger(t)U(t) = \mathbf{1}$, $U(t+s) = U(t)U(s)$.*
- (b) *For any $\phi \in \mathcal{H}$ and for $t \rightarrow t_0$ $U(t)\phi \rightarrow U(t_0)\phi$ holds.*
- (c) *For any $\psi \in \mathcal{D}(A)$ $\frac{U(t)\psi - \psi}{t} \xrightarrow{t \rightarrow 0} iA\psi$ holds.*

(d) If $\lim_{t \rightarrow 0} \frac{U(t)\psi - \psi}{t}$ exists, then $\psi \in \mathcal{D}(A)$.

Theorem 7.2. (Stone's theorem) If $U(t)$ is a unitary operator in \mathcal{H} and strongly continuous in t (i.e., satisfies the properties (a) and (b) above), then there exists a self-adjoint operator A in \mathcal{H} such that

$$U(t) = e^{itA}. \quad (7.28)$$

The operators $U(t)$ described above are unitary, and the family of operators obtained by varying t is a one-parameter group of unitary operators. Stone's theorem shows the close connection between one-parameter groups of unitary operators and self-adjoint operators. The operator A in Stone's theorem is usually called *infinitesimal generator* of the transformation. The reader will recognize in these statements a natural generalization of analogous properties of transformation groups in finite-dimensional spaces; it can be said that the self-adjoint operators are those operators for which many of the properties of Hermitian matrices continue to hold. A simple but important property of a self-adjoint operator is that if B is self-adjoint and if $A = B^\dagger B$, then A is semi-positive definite:

$$\langle \psi | B^\dagger B | \psi \rangle \geq 0, \quad (7.29)$$

with the equality holding if and only if $B |\psi\rangle = 0$.

Our starting point in the analysis of the Schrödinger equation was the study of its eigenvalues, which also determines the results of possible energy measurements. It is here that the importance of self-adjoint operators makes its appearance.

In finite-dimensional spaces it is well known that a Hermitian matrix can be diagonalized by a unitary transformation. In such a basis the matrix takes the form

$$\begin{pmatrix} \lambda_1 & 0 & 0 & \dots \\ 0 & \lambda_2 & 0 & \vdots \\ 0 & 0 & \ddots & \vdots \\ \vdots & \dots & \dots & \lambda_k \end{pmatrix} \quad (7.30)$$

Each eigenvalue λ_i might appear with a certain multiplicity n_i . An important point is that the decomposition (7.30) can be expressed in a form independent of the basis chosen. In fact, within each block of dimension $n_i \times n_i$ the matrix is a multiple of identity, and this is nothing but the projection onto the subspace associated with the eigenvalue λ_i . If the eigenvectors corresponding to the first eigenvalue λ_1 are $e_1^{(a)}, e_1^{(b)}, \dots$, then the first part of the above matrix is

$$\lambda_1 \left(|e_1^{(a)}\rangle\langle e_1^{(a)}| + |e_1^{(b)}\rangle\langle e_1^{(b)}| + \dots \right) = \lambda_1 \Pi_1,$$

where Π_1 is the projection operator onto the subspace, span by $e_1^{(a)}, e_1^{(b)}, \dots$. In general, one has a decomposition

$$A = \sum_i \lambda_i \Pi_i \quad (7.31)$$

known as the *spectral decomposition* of the matrix A . Note that the projection operators are mutually orthogonal and the identity

$$\mathbb{I}_{N \times N} = \sum_i \Pi_i$$

holds ($\mathbb{I}_{N \times N}$ is the identity matrix), which expresses the *completeness* of the basis of eigenvectors.

The spectrum of self-adjoint operators

For self-adjoint operators it is possible to write an analogue of eqn (7.31). The *spectrum* of a self-adjoint operator A is the ensemble of its proper eigenvalues (discrete eigenvalues) and improper eigenvalues (continuous eigenvalues). The first, the discrete eigenvalues, correspond to the values of λ such that

$$(A - \lambda_m)|\psi_m\rangle = 0; \quad \|\psi_m\| = 1, \quad m = 0, 1, 2, \dots \quad (7.32)$$

as is well known.

For operators (and the systems) possessing a continuous spectrum, however, the criterion for deciding whether a value belongs to its spectrum must be expressed in a more general manner. Let us define the **resolvent set** of an operator A as the ensemble of the points $x \in \rho(A) \subset \mathbb{R}$ for which $A - x \mathbf{1}$ has a bounded inverse,

$$R(x) = (A - x \mathbf{1})^{-1}, \quad \|R\| < \infty$$

(known as the resolvent operator of A). It is physically clear that the spectrum of the operator A is the complement of $\rho(A)$, $\sigma(A)$, which by definition is the set of all $x \notin \rho(A)$. The resolvent set is obviously an open set; it follows that the spectrum $\sigma(A)$ forms a closed set.

These conditions can be expressed in a form similar to eqn (7.32), known as

Weyl's criterion:

A value λ belongs to the spectrum of a self-adjoint operator A if and only if there exists a sequence ψ_N , such that

$$\lim_{N \rightarrow \infty} \|A\psi_N - \lambda\psi_N\| = 0, \quad \|\psi_N\| = 1. \quad (7.33)$$

In other words, the (continuous or improper) eigenvalues of an operator are those values for which there exist functions in \mathcal{H} , *arbitrarily close to the concept of the eigenfunction* (see eqn (7.32)), even if the limit of such a sequence might not be a normalizable function. Obviously, a discrete eigenvalue λ_m satisfies Weyl's criterion trivially, with $\psi_N = \psi_m, \forall N$.

For example, in the case of the momentum operator, the existence of the sequence

$$\psi_N = \frac{1}{\pi^{1/4} N^{1/2}} e^{ipx/\hbar} e^{-x^2/2N^2}, \quad N = 1, 2, \dots \quad (7.34)$$

shows that all real values belong to the spectrum of $p = -i\hbar(d/dx)$. Analogously, for the position operator one finds that

$$\lim_{N \rightarrow \infty} \|(x - x_0)\psi_N\| = 0, \quad (7.35)$$

³**Exercise.** Show that eqn (7.33) is satisfied by the operator $\hat{p} = -i\hbar(d/dx)$ with sequence (7.34) and with $\lambda = p$. Verify eqn (7.35).

for the sequence³

$$\psi_N = \left(\frac{2N}{\pi}\right)^{1/4} e^{-N(x-x_0)^2}, \quad N = 1, 2, \dots \quad (7.36)$$

The foremost consequence of the requirement of the self-adjointness of an operator A is the existence of the set of real (proper and improper) eigenvalues $\{\lambda_n, \lambda\}$ and a *family of projection operators* (assuming a continuous spectrum $[\lambda_0, \infty)$):

$$\mathcal{P}_c(\lambda) = \int_{\lambda_0}^{\lambda} d\lambda' \sum_{\alpha} |\lambda', \alpha\rangle \langle \lambda', \alpha|, \quad \mathcal{P}_n = \sum_{\alpha} |n, \alpha\rangle \langle n, \alpha|. \quad (7.37)$$

The index α runs over the possible degenerate sets. For simplicity we use Dirac's notation with the normalization

$$\langle \lambda, \alpha | \lambda', \beta \rangle = \delta_{\alpha\beta} \delta(\lambda - \lambda').$$

If the degeneracy were of continuous type, an obvious change of notation would be needed for the sum over α . The existence of the projection operators does not depend on the basis chosen. In the following the formulas will be given both in terms of the projection operators and in a base of improper eigenvectors.

It is convenient to unify the two terms in eqn (7.37), by using

$$\begin{aligned} \mathcal{P}(\lambda) &= \int_{\lambda_0}^{\lambda} d\lambda' \left[\sum_{\alpha} |\lambda', \alpha\rangle \langle \lambda', \alpha| + \sum_n \delta(\lambda' - \lambda_n) \sum_{\alpha} |n, \alpha\rangle \langle n, \alpha| \right] = \\ &= \int_{\lambda_0}^{\lambda} d\mathcal{P}(\lambda'). \end{aligned}$$

The function $\mathcal{P}(\lambda)$ is discontinuous at the points corresponding to a discrete spectrum: i.e., has a jump at such points, and is understood continuous on the right of these point:

$$\begin{aligned} \lim_{\lambda \rightarrow \lambda_n^+} \mathcal{P}(\lambda) &= \mathcal{P}(\lambda_n) = \int_{\lambda_0}^{\lambda_n} d\lambda' \sum_{\alpha} |\lambda', \alpha\rangle \langle \lambda', \alpha| + \sum_{\lambda_k \leq \lambda_n} \sum_{\alpha} |k, \alpha\rangle \langle k, \alpha| \\ \lim_{\lambda \rightarrow \lambda_n^-} \mathcal{P}(\lambda) &= \mathcal{P}(\lambda_n) = \int_{\lambda_0}^{\lambda_n} d\lambda' \sum_{\alpha} |\lambda', \alpha\rangle \langle \lambda', \alpha| + \sum_{\lambda_k < \lambda_n} \sum_{\alpha} |k, \alpha\rangle \langle k, \alpha|. \end{aligned}$$

The operators \mathcal{P} are the (sum of orthogonal projection operators) and satisfy

$$\lambda_1 < \lambda_2 \Rightarrow \mathcal{P}(\lambda_1)\mathcal{P}(\lambda_2) = \mathcal{P}(\lambda_1), \quad (7.38)$$

which is a natural generalization of the familiar property of projection operators in the case of a discrete spectrum:

$$\mathcal{P}_n^2 = \mathcal{P}_n, \quad \mathcal{P}_n \mathcal{P}_m = 0, \quad m \neq n.$$

The operators \mathcal{P} satisfy (*the spectral theorem*):

$$\mathbf{1} = \int d\mathcal{P}(\lambda) = \int d\mathcal{P}_c(\lambda) + \sum_n \mathcal{P}_n; \quad (7.39a)$$

$$|\psi\rangle = \int d\mathcal{P}(\lambda) |\psi\rangle = \int d\mathcal{P}_c(\lambda) |\psi\rangle + \sum_n \mathcal{P}_n |\psi\rangle, \quad \forall \psi \in \mathcal{H}; \quad (7.39b)$$

$$A = \int \lambda d\mathcal{P}(\lambda) = \int \lambda d\mathcal{P}_c(\lambda) + \sum_n \lambda_n \mathcal{P}_n. \quad (7.39c)$$

In particular, as $A|\psi\rangle$ must belong to the Hilbert space, one has

$$\langle A\psi|A\psi\rangle = \langle\psi|A^2\psi\rangle < \infty \quad (7.40)$$

and thus the dispersion of \mathcal{A} is finite. More explicitly,

$$\begin{aligned} \langle\psi|A^2\psi\rangle &= \int \lambda^2 d\|\mathcal{P}(\lambda)\psi\|^2 = \int \lambda^2 d\|\mathcal{P}_c(\lambda)\psi\|^2 + \sum_n \lambda_n^2 \|\mathcal{P}_n\psi\|^2 \\ &\equiv \int d\lambda \lambda^2 \sum_\alpha |\langle\lambda, \alpha|\psi\rangle|^2 + \sum_n \lambda_n^2 \sum_\alpha |\langle n, \alpha|\psi\rangle|^2. \end{aligned}$$

The spectral theorem allows us to define the operator $f(\mathcal{A})$, given the operator representing an observable A , where $f(x)$ is any function of x , as

$$f(A) = \int f(\lambda) d\mathcal{P}(\lambda) = \int f(\lambda) d\mathcal{P}_c(\lambda) + \sum_n f(\lambda_n) \mathcal{P}_n. \quad (7.41)$$

For instance its mean value is then given by

$$\begin{aligned} \langle\psi|f(A)|\psi\rangle &= \int f(\lambda) d\|\mathcal{P}(\lambda)\psi\|^2 = \int f(\lambda) d\|\mathcal{P}_c(\lambda)\psi\|^2 + \sum_n f(\lambda_n) \|\mathcal{P}_n\psi\|^2 \\ &\equiv \int d\lambda f(\lambda) \sum_\alpha |\langle\lambda, \alpha|\psi\rangle|^2 + \sum_n f(\lambda_n) \sum_\alpha |\langle\lambda_n, \alpha|\psi\rangle|^2. \end{aligned} \quad (7.42)$$

We recognize in eqn (7.39a,b) the completeness relation. These relations in fact guarantee the consistency of the rules of quantum mechanics, in particular, postulates P3, P4. If the mean value of the observable \mathcal{A} is given by the expectation value of the operator A in a given state, one finds that

$$\begin{aligned} \langle\psi|A|\psi\rangle &= \int \lambda d\|\mathcal{P}(\lambda)\psi\|^2 = \int \lambda d\|\mathcal{P}_c(\lambda)\psi\|^2 + \sum_n \lambda_n \|\mathcal{P}_n\psi\|^2 \\ &\equiv \int d\lambda \lambda \sum_\alpha |\langle\lambda, \alpha|\psi\rangle|^2 + \sum_n \lambda_n \sum_\alpha |\langle\lambda_n, \alpha|\psi\rangle|^2. \end{aligned} \quad (7.43)$$

In writing eqn (7.43) we have used the fact that the operators $\mathcal{P}(\lambda)$ are projection operators, so that

$$\langle\psi|d\mathcal{P}(\lambda)|\psi\rangle = d\langle\psi|\mathcal{P}(\lambda)\psi\rangle = d\langle\mathcal{P}(\lambda)\psi|\mathcal{P}(\lambda)\psi\rangle = d\|\mathcal{P}(\lambda)\psi\|^2.$$

Equation (7.43) allows us to interpret (see also Section 2.3)

$$\rho(\lambda) d\lambda = \int \sum_{\alpha} |\langle \lambda, \alpha | \psi \rangle|^2 d\lambda; \quad P_n = \sum_{\alpha} |\langle n, \alpha | \psi \rangle|^2, \quad (7.44)$$

respectively, as the *probability* of observing a value contained in the range $[\lambda, \lambda + d\lambda]$ for the observable \mathcal{A} (ρ is the probability density) or as the probability that \mathcal{A} takes the value λ_n . Let us note, in particular, that the total probability is given by

$$\int \rho(\lambda) d\lambda + \sum_n P_n = \langle \psi | \left\{ \int dP_c(\lambda) + \sum_n P_n \right\} | \psi \rangle = \langle \psi | \psi \rangle = 1. \quad (7.45)$$

⁴Consider two state vectors $f + g$ and $f + ig$, then

$$\begin{aligned} \langle f + g | A | f + g \rangle &= \\ \langle f | A | f \rangle + \langle g | A | g \rangle + 2 \operatorname{Re}[\langle g | A | f \rangle] &; \\ \langle f + i g | A | f + ig \rangle &= \\ \langle f | A | f \rangle + \langle g | A | g \rangle + 2 \operatorname{Im}[\langle g | A | f \rangle]. & \end{aligned}$$

$\operatorname{Re}[\langle g | A | f \rangle]$ and $\operatorname{Im}[\langle g | A | f \rangle]$ are thus determined by the expectation values of A .

Expectation values of a self-adjoint operator

We have already seen that the expectation value of a self-adjoint operator on any state is real. A remarkable property of a self-adjoint operator is that it is possible to reconstruct the operator itself from its expectation values;⁴ for instance, two operators having the same expectation values in all states are equal.

Theorem 7.3 *If two (maximally extended) self-adjoint operators A, B are such that*

$$\forall \psi \quad \langle \psi | A | \psi \rangle = \langle \psi | B | \psi \rangle,$$

then $A = B$.

Commuting operators

We have already noted that, in order for two observables \mathcal{A}, \mathcal{B} to be measurable simultaneously, the corresponding operators A, B must commute (see page 33). A useful theorem in this connection is the following

Theorem 7.4. (von Neumann's theorem) *Given two (maximally extended) self-adjoint and commuting operators A, B there exists an operator R of which A and B are functions, i.e., $A = F(R)$, $B = G(R)$.*

Let us give an idea of the proof by considering operators having only discrete spectra. As we have already seen, if two operators A, B commute, it is possible to choose a base of common eigenvectors

$$A|n\rangle = \lambda_n |n\rangle, \quad B|n\rangle = \mu_n |n\rangle.$$

Let us consider now some sequence x_n and construct a self-adjoint operator R defined by

$$R = \sum_n x_n |n\rangle \langle n|, \quad R|n\rangle = x_n |n\rangle.$$

One can always choose two functions F, G such that $F(x_n) = \lambda_n$, $G(x_n) = \mu_n$ hold for each n . Then by using the spectral decomposition of R ,

$$F(R) = \sum_n F(x_n) |n\rangle \langle n| = \sum_n \lambda_n |n\rangle \langle n| = A$$

$$G(R) = \sum_n G(x_n) |n\rangle \langle n| = \sum_n \mu_n |n\rangle \langle n| = B.$$

7.4 Unitary transformations

Physical quantities in quantum mechanics are associated with the matrix elements of various operators

$$\langle \phi | O | \psi \rangle, \quad (7.46)$$

or, $O|\psi\rangle$ being a vector itself, to various scalar products

$$\langle f | g \rangle. \quad (7.47)$$

It is natural to ask for which sort of change of basis, $f \rightarrow Uf$, $\forall f$, does the physics remain the same. In other words, for which kind of operators U does the relation

$$\langle Uf | Ug \rangle = \langle f | g \rangle \quad (7.48)$$

hold for all f, g ? A “change of basis” of this sort will leave all physical predictions of the theory invariant, though each state, operator, etc., is described differently.⁵ If a transformation of this sort leaves the *form* of the Hamiltonian invariant, then one is dealing actually with a *symmetry* (see Section 5.1); the notion of allowed base transformations we are considering here, is, however, a more general one.

As we wish to perform the same transformation on every vector of the system, it must be that $\mathcal{D}(U) = \mathcal{H}$; furthermore, as one is simply changing representation, the role of the original and the new one must be interchangeable: the image of U must also be \mathcal{H} . We thus arrive at the following

Definition An operator U with domain \mathcal{H} and image \mathcal{H} is said to be *unitary* if

$$\boxed{\forall x, y \in \mathcal{H} : \langle Ux, Uy \rangle = \langle x, y \rangle.} \quad (7.49)$$

Note that no requirement of linearity has been made; we have only required the definability on the entire Hilbert space and that its action on \mathcal{H} is surjective. One can show immediately that U has an inverse, that is, if $Uf = Ug$ then $f = g$:

$$\begin{aligned} 0 &= (Uf - Ug, Uf - Ug) = (Uf, Uf) - (Uf, Ug) - (Ug, Uf) + (Ug, Ug) \\ &= (f, f) - (f, g) - (g, f) + (g, g) = (f - g, f - g) \Rightarrow f = g \end{aligned}$$

Clearly U^{-1} is unitary also. Let us write $f = \alpha_1 x + \alpha_2 y$ and use the existence of the inverse,

$$\begin{aligned} (g, Uf) &= (U^{-1}g, f) = (U^{-1}g, \alpha_1 x + \alpha_2 y) = \alpha_1 (U^{-1}g, x) + \alpha_2 (U^{-1}g, y) \\ &= \alpha_1 (g, Ux) + \alpha_2 (g, Uy); g \text{ arbitrary} \Rightarrow U(\alpha_1 x + \alpha_2 y) = \alpha_1 Ux + \alpha_2 Uy. \end{aligned}$$

Therefore a unitary operator is also *linear*. From the preceding relations it follows that $U^\dagger = U^{-1}$. From the relation $(Uf, Uf) = |Uf|^2 = |f|^2$ it follows that $\|U\| = 1$ hence U is a linear bounded operator, and hence continuous.

⁵To be precise, a transformation in which a relation $\langle Vf | Vg \rangle = (\langle f | g \rangle)^*$ holds for all states—known as anti-unitary transformations—is also allowed, as has been already noted in connection with the time reversal symmetry in Section 5.1.

Recapitulating,

$$U^\dagger U = U U^\dagger = \mathbf{1}; \quad U^\dagger = U^{-1}. \quad (7.50)$$

The transformation law of the *operators* under a unitary transformation follows from eqn (7.50): let us rewrite eqn (7.46) twice inserting the identity operator $\mathbf{1} = U^\dagger U$:

$$\langle \phi | O | \psi \rangle = \langle \phi | U^\dagger U O U^\dagger U | \psi \rangle = \langle \tilde{\phi} | \tilde{O} | \tilde{\psi} \rangle, \quad (7.51)$$

where

$$|\tilde{\psi}\rangle \equiv U|\psi\rangle; \quad |\tilde{\phi}\rangle \equiv U|\phi\rangle; \quad \tilde{O} \equiv U O U^\dagger. \quad (7.52)$$

Note that the norm of the states remains, as it should, invariant:

$$\langle \tilde{\psi} | \tilde{\psi} \rangle = \langle \psi | U^\dagger U | \psi \rangle = \langle \psi | \psi \rangle.$$

The transformation of the state vectors and the operators given by eqns (7.51, 7.52) is known as a *unitary transformation*. As all the quantities dealt with in quantum mechanics reduce to some combinations of the matrix elements of type (7.47), it follows that the theory is invariant under unitary transformations. But this means that

**the states and operators in quantum mechanics are defined
up to unitary transformations.**

For the eigenvalues of the unitary operator U we have the following obvious properties:

- The eigenvalues of a unitary operator have a norm 1, $|\lambda| = 1$.
- The eigenvectors relative to two distinct eigenvalues are orthogonal.

In fact, $\langle \psi | \psi \rangle = \langle U\psi | U\psi \rangle = |\lambda|^2 \langle \psi | \psi \rangle$. For two eigenvectors belonging to different eigenvalues,

$$\langle \psi_1 | \psi_2 \rangle = \langle U\psi_1 | U\psi_2 \rangle = \lambda_1^* \lambda_2 \langle \psi_1 | \psi_2 \rangle.$$

As $\lambda_1^* \lambda_2 \neq 1$ (as $\lambda_1 \neq \lambda_2$ and because they have the absolute value 1), it follows that $\langle \psi_1 | \psi_2 \rangle = 0$.

Also for the unitary operators it is possible to write a spectral representation, in a form analogous to eqn (7.39):

$$\mathbf{1} = \int_0^{2\pi} dP(\lambda) = \int_0^{2\pi} dP_c(\lambda) + \sum_n P_n; \quad (7.53a)$$

$$|\psi\rangle = \int_0^{2\pi} dP(\lambda) |\psi\rangle = \int_0^{2\pi} dP_c(\lambda) |\psi\rangle + \sum_n P_n |\psi\rangle, \quad \forall \psi \in \mathcal{H}; \quad (7.53b)$$

$$U = \int_0^{2\pi} e^{i\lambda} dP(\lambda) = \int_0^{2\pi} e^{i\lambda} dP_c(\lambda) + \sum_n e^{i\lambda_n} P_n. \quad (7.53c)$$

Remark. It is possible to generalize eqn (7.48)—and it is sometimes useful to do so—to the cases in which U is an operator transforming the states of a Hilbert space to those in another Hilbert space, $U : \mathcal{H} \rightarrow \mathcal{H}'$; in these cases, the transformations are often termed *isometries*.

7.5 The Heisenberg picture

A significant result in classical mechanics (see Supplement 20.1) is that the time evolution $q(t), p(t) \rightarrow q(t+dt), p(t+dt)$ is a succession of infinitesimal canonical transformations, with the Hamiltonian playing the role of their generator. Analogously, in quantum mechanics, the time evolution of the system is described as a unitary transformation,

$$|\psi(t)\rangle = e^{-iHt/\hbar} |\psi(0)\rangle. \quad (7.54)$$

with the Hamiltonian operator playing the role of infinitesimal generator of time evolution. Indeed, eqn (7.54) is the formal solution of the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H |\psi(t)\rangle, \quad |\psi(t)\rangle|_{t=0} = |\psi(0)\rangle,$$

and as H is self-adjoint (which is always assumed to be the case) the operator $\exp(-iHt/\hbar)$ is unitary (see Theorem 7.2 on page 162).

The discussion of the previous section allows us to study the time evolution in quantum mechanics from a new point of view. Let us consider a particular, time-dependent unitary transformation

$$U(t) = e^{iHt/\hbar}.$$

The states and generic operators of the system transform according to eqn (7.52):

$$|\psi_H\rangle = U(t)|\psi(t)\rangle = e^{iHt/\hbar} |\psi(t)\rangle = |\psi(0)\rangle; \quad (7.55)$$

$$O_H(t) = U(t) O U(t)^\dagger = e^{iHt/\hbar} O e^{-iHt/\hbar}. \quad (7.56)$$

All the matrix elements are invariant under such transformations,

$$\langle \psi(t) | O | \psi(t) \rangle = \langle \psi_H | O_H(t) | \psi_H \rangle,$$

but now the time evolution of the systems is no longer described by the Schrödinger equation; it resides in a nontrivial time dependence of the operators!

The equation of motion of a generic operator O follows from eqn (7.56); it is given by⁶

$$i\hbar \frac{dO_H}{dt} = i\hbar \frac{\partial O_H}{\partial t} + [O_H, H], \quad (7.57)$$

where the first term is present if the operator explicitly depends on time. Equation (7.57) is known as the *Heisenberg equation*.

⁶Note the resemblance of this formula to the classical equation of motion expressed in terms of Poisson's brackets:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \{H, f\}.$$

The description of the time evolution in quantum mechanics in terms of eqns (7.55), (7.56), (7.57) is known as the **Heisenberg picture** or Heisenberg representation, as opposed to the **Schrödinger picture** or Schrödinger representation, in which the state vectors evolve with time. At an instant (e.g., at $t = 0$) the two pictures coincide:

$$O_H(0) = O; \quad |\psi_H\rangle = |\psi(0)\rangle.$$

It is of crucial importance that the fundamental commutators *at equal time* have the same form at any instant and independently of the Hamiltonian,

$$[q_{iH}(t), p_{jH}(t)] = i\hbar\delta_{ij}, \quad [q_{iH}(t), q_{jH}(t)] = [p_{iH}(t), p_{jH}(t)] = 0. \quad (7.58)$$

For instance,

$$\begin{aligned} [q_{iH}(t), p_{jH}(t)] &= [e^{iHt/\hbar} q_i e^{-iHt/\hbar}, e^{iHt/\hbar} p_j e^{-iHt/\hbar}] \\ &= e^{iHt/\hbar} [q_i, p_j] e^{-iHt/\hbar} = i\hbar\delta_{ij}. \end{aligned}$$

⁷We are here assuming the standard properties of the physical world, where time is homogeneous and the total energy conservation holds to a very high precision. Near the initial Big Bang singularity of the expansion of the Universe, when quantum gravity effects become important and spacetime highly curved, the whole concept of quantum mechanics itself might require some drastic revisions.

The usual commutators in the Schrödinger picture can, in fact, be seen as a particular case (for $t = 0$) of the more general result (7.58). The fact that the fundamental commutators have the same form at any time and hold independently of the particular Hamiltonian (details of dynamics) is essential for the consistency of the entire structure of quantum mechanics, as there is no privileged instant of time.⁷

Vice versa, the commutators at two different times

$$[q_{iH}(t), p_{jH}(t')], \quad [q_{iH}(t), q_{jH}(t')], \quad [p_{iH}(t), p_{jH}(t')]$$

contain dynamical information and depend on the system considered.

Let us note that each operator $f(q, p)$ in the Schrödinger picture becomes $f(q_H, p_H)$ in the Heisenberg picture. It is easy to verify this by expanding in powers of q and p , and inserting $U^{-1}U$ for each monomial, for instance:

$$\begin{aligned} Uq^k p^n U^{-1} &= Uq \dots qp \dots p U^{-1} = Uq U^{-1} Uq U^{-1} U \dots Up U^{-1} \dots \\ &= (Uq U^{-1})^k (Up U^{-1})^n = q_H^k p_H^n. \end{aligned}$$

The problem of time evolution is thus reduced to solving the Heisenberg equations for q_H, p_H .⁸

$$\frac{d}{dt}q_H = -\frac{i}{\hbar}[q_H, H]; \quad \frac{d}{dt}p_H = -\frac{i}{\hbar}[p_H, H]. \quad (7.59)$$

The time-dependent operators which are solutions of the above must satisfy constraint (7.58). The invariance of the latter during the time evolution guarantees that if the constraint is satisfied at the initial time, it will be satisfied at later times as well.

⁸**Exercise.** Solve the Heisenberg equation for a *free* particle of mass m moving in one dimension. Evaluate the commutator $[q_H(t), q_H(0)]$ at $t \neq 0$. (Answer: $[q_H(t), q_H(0)] = -i\hbar t/m$.)

7.5.1 The harmonic oscillator in the Heisenberg picture

Consider the linear oscillator

$$H = \frac{p^2}{2m} + \frac{m\omega^2}{2} x^2.$$

The Hamiltonian in the Heisenberg picture is

$$H_H = U H(x, p) U^\dagger = H(UxU^\dagger, UpU^\dagger) = \frac{p_H^2}{2m} + \frac{m\omega^2}{2} x_H^2.$$

The Heisenberg equations are (7.59)

$$m\dot{x}_H = p_H; \quad \dot{p}_H = -m\omega^2 x_H.$$

The solution has a form identical to that in classical mechanics,

$$x_H(t) = x \cos \omega t + \frac{1}{m\omega} p \sin \omega t; \quad (7.60)$$

$$p_H(t) = p \cos \omega t - m\omega x \sin \omega t. \quad (7.61)$$

In terms of the creation and annihilation operators (3.34), (3.35),

$$a = \sqrt{\frac{m\omega}{2\hbar}} x + i\sqrt{\frac{1}{2m\omega\hbar}} p = \sqrt{\frac{m\omega}{2\hbar}} \left(x + i\frac{p}{m\omega} \right),$$

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}} x - i\sqrt{\frac{1}{2m\omega\hbar}} p = \sqrt{\frac{m\omega}{2\hbar}} \left(x - i\frac{p}{m\omega} \right),$$

one finds from eqn (7.61) that

$$a_H(t) = \sqrt{\frac{m\omega}{2\hbar}} \left[x \cos \omega t + i\frac{p}{m\omega} \sin \omega t + i\frac{p}{m\omega} \cos \omega t - ix \sin \omega t \right] = a_H(0) e^{-i\omega t}$$

and, analogously,

$$a_H^\dagger(t) = a_H^\dagger(0) e^{i\omega t}.$$

Thus

$$a_H(t) = a e^{-i\omega t}; \quad a_H^\dagger(t) = a^\dagger e^{i\omega t} \Rightarrow \dot{a}_H = -i\omega a_H; \quad \dot{a}_H^\dagger = +i\omega a_H.$$

These solutions can naturally be found directly by using the Heisenberg form of the Hamiltonian in terms of the creation and annihilation operators

$$H = \frac{\omega\hbar}{2}(aa^\dagger + a^\dagger a) = \omega\hbar \left(a^\dagger a + \frac{1}{2} \right)$$

and using the commutation relation

$$[a, a^\dagger] = 1.$$

As an example of the use of the Heisenberg picture, let us consider a linear oscillator, described by a *real* wave packet $\psi_0(x)$ at $t = 0$. Suppose

that the expectation values $\langle \psi_0 | p^2 | \psi_0 \rangle \equiv p_0^2$ and $\langle \psi_0 | x^2 | \psi_0 \rangle \equiv x_0^2$ are known, and we want to determine $\langle \psi(t) | p^2 | \psi(t) \rangle$. In the Schrödinger picture one has to solve the Schrödinger equation to find $|\psi(t)\rangle$, and then compute the expectation value of p^2 . In the Heisenberg picture the problem is easily solved by

$$\langle \psi(t) | p^2 | \psi(t) \rangle = \langle \psi_0 | U(t) p^2 U^{-1}(t) | \psi_0 \rangle = \langle \psi_0 | p_H(t)^2 | \psi_0 \rangle.$$

But

$$p_H(t)^2 = p^2 \cos^2 \omega t + m^2 \omega^2 x^2 \sin^2 \omega t - m\omega (xp + px) \cos \omega t \sin \omega t,$$

where use was made of eqn (7.61); furthermore note that

$$\langle \psi_0 | xp + px | \psi_0 \rangle = 0$$

(the left-hand side must be real, being the expectation value of a Hermitian operator, but it is also purely imaginary for any real wave function). It follows then that

$$\langle \psi(t) | p^2 | \psi(t) \rangle = p_0^2 \cos^2 \omega t + m^2 \omega^2 x_0^2 \sin^2 \omega t.$$

Analogously one finds that

$$\langle \psi(t) | x^2 | \psi(t) \rangle = x_0^2 \cos^2 \omega t + \frac{1}{m^2 \omega^2} p_0^2 \sin^2 \omega t.$$

For non-real initial wave functions (moving wave packets) the expectation value of the operator $xp + px$ at $t = 0$ must also be taken into account.

7.6 The uncertainty principle

The connection between the mathematical structure of the abstract Hilbert space and physics is made upon the association, in the Schrödinger picture, between the dynamical variables q, p and the operators Q, P :

$$q \rightarrow Q, \quad Q\psi(x) = x\psi(x); \quad p \rightarrow P, \quad P\psi(x) = \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x)$$

it is the mathematical realization of de Broglie's hypothesis. This leads to

$$[Q, P] = i\hbar, \quad (7.62)$$

which has been stated as one of the postulate, P5.

It is invariant under unitary transformations: indeed if $\tilde{Q} = UQU^{-1}$, $\tilde{P} = UPU^{-1}$ one has

$$[\tilde{Q}, \tilde{P}] = UQU^{-1}UPU^{-1} - UPU^{-1}UQU^{-1} = U[Q, P]U^{-1} = i\hbar :$$

it is valid in the abstract Hilbert space.

A useful generalization of eqn (7.20) is

$$Pf(Q) - f(Q)P = -i\hbar f'(Q).$$

In fact,

$$\begin{aligned} Pf(Q)\psi(x) &= -i\hbar \frac{\partial}{\partial x} (f(x)\psi(x)) = -i\hbar f'(x)\psi(x) + f(x)\psi'(x) = \\ &= -i\hbar f'(Q)\psi(x) + f(Q)(P\psi(x)). \end{aligned}$$

Let us now come back to the uncertainty relation. Let \mathcal{A} be an observable, associated with the operator A . It will have an expectation value $\overline{A}_\psi = \langle \psi | A | \psi \rangle$ in a state ψ . Define the dispersion by

$$(\Delta A)^2 = \langle \psi | A^2 | \psi \rangle - (\langle \psi | A | \psi \rangle)^2 \equiv \langle \psi | (A - \overline{A}_\psi)^2 | \psi \rangle.$$

Consider now, two non-commuting self-adjoint operators A, B :

$$[A, B] = AB - BA = i\hbar C, \quad (7.63)$$

C is Hermitian. In each state in which the expectation value of the both sides of eqn (7.63) can be defined one finds the uncertainty relation

$$\Delta A \cdot \Delta B \geq \frac{\hbar}{2} |\langle \psi | C | \psi \rangle|. \quad (7.64)$$

The proof is the repetition of the one given in Section 2.3.4. Define operators

$$\tilde{A} = A - \overline{A}_\psi; \quad \tilde{B} = B - \overline{B}_\psi; \quad [\tilde{A}, \tilde{B}] = i\hbar C; \quad O = \tilde{A} + i\alpha \tilde{B}.$$

It follows from the positivity $\langle O\psi | O\psi \rangle \geq 0$ that

$$\begin{aligned} 0 \leq \langle O\psi | O\psi \rangle &= \langle \tilde{A}\psi | \tilde{A}\psi \rangle + \alpha^2 \langle \tilde{B}\psi | \tilde{B}\psi \rangle + i\alpha \langle \psi | (\tilde{A}\tilde{B} - \tilde{B}\tilde{A}) | \psi \rangle = \\ &= \langle \tilde{A}\psi | \tilde{A}\psi \rangle + \alpha^2 \langle \tilde{B}\psi | \tilde{B}\psi \rangle - \alpha \hbar \psi | C | \psi \rangle. \end{aligned}$$

Imposing the condition that the discriminant of the quadratic form in α be negative, one finds eqn (7.64).

In particular, by applying the above to the canonical commutation relation we recover the Heisenberg's relation

$$\Delta P \cdot \Delta Q \geq \frac{\hbar}{2}$$

as discussed earlier.

7.7 Mixed states and the density matrix

The description of a physical state of a given system in terms of a state vector (wave function) in a Hilbert space, is the most detailed description in quantum mechanics.⁹ There are many situations (strictly speaking, practically always), however, in which such a "complete" description is

⁹The idea that the probabilistic interpretation of quantum mechanics is to be attributed to an unknown distribution of certain inaccessible but classical variables goes under the generic name of "hidden-variable theories". Einstein famously argued for the incompleteness of quantum mechanics, in favor of these alternative theories. That no such theory can actually reproduce fully the content of quantum mechanics, hence can be experimentally distinguished from the latter (and indeed discarded), was shown in a milestone paper by J.S. Bell in 1960. These questions will be discussed in Chapters 18 and 19.

either impossible or unnecessary. It suffices to consider the case in which we deal with a subsystem of a larger, closed system: having access only to variables belonging to the subsystem, there is no hope of describing it in terms of a wave function. Another important class of cases are systems of many degrees of freedom (macroscopic systems, solid, gas, etc.). In these cases it is obviously impossible to have a complete knowledge of the wave function of, e.g., 10^{23} molecules: we must work with average quantities, defined in various ways. Still other cases concern either unpolarized or partially polarized beams of particles in a scattering problem. Again an incomplete knowledge of the spin state of the particles in the beam makes the description in terms of a wave function unavailable.

In all these cases we are dealing with **mixed states**; in contrast, states described by wave functions are **pure states**. In the case of a mixed state the role of the wave function is taken by a **density matrix**. A mixed state is characterized by various degrees of incomplete (or lack of) information.

Consider for concreteness the case of the first type: a subsystem S of a larger, closed system Σ . We have access, by assumption, to the variables $\{x\}$ in S only. Even though the total system Σ can have a wave function $\psi(q, x)$, it is not in general factorized:

$$\Psi(q, x) \neq \psi_S(x)\psi_{\Sigma/S}(q);$$

the subsystem in itself does not have a wave function. How can one calculate the expectation value of an operator \hat{f}_x which acts only on the variables $\{x\}$ of the subsystem?

By denoting an arbitrarily chosen orthonormal basis for each system S and Σ/S as $|j\rangle$ and $|\alpha\rangle$, respectively, a generic state is described by

$$|\Psi\rangle = \sum_{j,\alpha} c_{j,\alpha} |j\rangle \otimes |\alpha\rangle. \quad (7.65)$$

The expectation value of \hat{f} in this state is

$$\langle \Psi | \hat{f} | \Psi \rangle = \sum_{j,k} \sum_{\alpha} c_{k,\alpha} c_{j,\alpha}^* \langle j | \hat{f} | k \rangle = \text{Tr}(\mathbf{f}\rho),$$

where

$$\rho_{jk} \equiv \sum_{\alpha} c_{j,\alpha} c_{k,\alpha}^*, \quad \mathbf{f}_{jk} = \langle j | \hat{f} | k \rangle.$$

The *density matrix* ρ has the following general properties:

$$\text{Tr } \rho = 1; \quad (7.66a)$$

$$\rho^{\dagger} = \rho; \quad (\text{Hermiticity}) \quad (7.66b)$$

$$0 \leq \rho_{jj} \leq 1; \quad (7.66c)$$

$$|\rho_{jk}|^2 \leq \rho_{jj} \rho_{kk}. \quad (7.66d)$$

Equations (7.66a)–(7.66c) are obvious. The last one can be shown di-

rectly:

$$\begin{aligned} \rho_{jj} \rho_{kk} - \rho_{jk} \rho_{kj} &= \sum_{\alpha, \beta} [c_{j,\alpha} c_{j,\alpha}^* c_{k,\beta} c_{k,\beta}^* - c_{j,\alpha} c_{k,\alpha}^* c_{k,\beta} c_{j,\beta}^*] \\ &= \frac{1}{2} \sum_{\alpha, \beta} [c_{j,\alpha} c_{k,\beta} - c_{k,\alpha} c_{j,\beta}] [c_{j,\alpha} c_{k,\beta} - c_{k,\alpha} c_{j,\beta}]^* \geq 0. \end{aligned}$$

In the case of a pure state, with the wave function (i.e., no sum over α)

$$|\psi\rangle = \sum_j c_j |j\rangle,$$

the density matrix is simply

$$\rho_{jk} = c_j c_k^*.$$

The density matrix of a pure state thus satisfies the characteristic property

$$\rho^2 = \rho,$$

as can be proven easily by using $\sum_\ell c_\ell^* c_\ell = 1$.

Clearly, the concept of a mixed state is a more general one than that of a pure state. A pure state can always be regarded as a special type of mixed state, but not all mixed states are pure.

An important class of applications of the density matrix formalism concerns statistical physics. There the enormous number of the degrees of freedom forces us to appeal to a statistical treatment (Boltzmann). The density matrix $\rho_{jk} = w_{jk}$ is known as a *statistical matrix* in these cases. Let W_n be the probability that one of the microscopic systems (for example, an atom) is in the n -th energy eigenstate

$$|\psi^{(n)}(t)\rangle = \sum_j a_j^n(t) |\psi_j\rangle,$$

where $\{\psi_j\}$ is a generic orthonormal basis (e.g., eigenstates of some operator). For instance, in a canonical ensemble at temperature T the energy distribution is given by Boltzmann's formula

$$W_n = e^{-E_n/kT}/\mathcal{N}, \quad \sum_n W_n = 1,$$

where \mathcal{N} is the partition function $\mathcal{N} = \sum_n e^{-E_n/kT}$. The discussion below is, however, valid in any type of statistical ensemble.

The expectation value of an operator f is thus given by

$$\langle f \rangle = \sum_n W_n \langle \psi^{(n)} | f | \psi^{(n)} \rangle = \sum_n \sum_{j,k} W_n a_j^{(n)*} a_k^{(n)} f_{jk} = \text{Tr}(\rho f),$$

where we have introduced the density (or statistical) matrix

$$\rho_{jk} = \sum_n W_n a_k^{(n)*} a_j^{(n)}. \quad (7.67)$$

Note that, thanks to the positivity of the classical probability $W_n \geq 0$, the density matrix defined here satisfies the same defining properties (7.66a)–(7.66d) introduced before. In both cases the density matrix reflects our ignorance about the system.

The time evolution of the density matrix follows from the fact that $|\psi^{(i)}(t)\rangle$ obeys the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi^{(i)}(t)\rangle = H |\psi^{(i)}(t)\rangle.$$

As

$$a_n^{(i)}(t) = \langle \psi_n | \psi^{(i)}(t) \rangle,$$

one has

$$i\hbar \dot{a}_n^{(i)}(t) = \langle \psi_n | H | \psi^{(i)}(t) \rangle = \sum_k a_k^{(i)} H_{nk}.$$

Analogously

$$-i\hbar \dot{a}_m^{(i)*}(t) = \langle \psi^{(i)}(t) | H | \psi_m \rangle = \sum_k a_k^{(i)*} H_{km}.$$

One thus finds that

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \rho_{nm} &= \sum_i W_i \sum_k (a_m^{(i)*} H_{nk} a_k^{(i)} - a_k^{(i)*} H_{km} a_n^{(i)}) \\ &= \sum_k (H_{nk} \rho_{km} - \rho_{nk} H_{km}) = [\mathbf{H}, \rho]_{nm}. \end{aligned} \quad (7.68)$$

¹⁰ Equation (7.68) formally resembles the Heisenberg equation; note, however, the curious (but well-known) sign difference in the two equations.

This equation substitutes, for a mixed state, the Schrödinger equation or Heisenberg equation for a pure state.¹⁰

7.7.1 Photon polarization

Let us illustrate the use of the density matrix, by taking the example of the polarization of a photon. As discussed in Section 2.1.2, the state of a photon, all other attributes such as the energy, momentum (the wavelength and the direction of propagation) being neglected, is described as a typical two-level system (or a *q-bit*), with the base states $|1\rangle$ and $|2\rangle$. $|1\rangle$ and $|2\rangle$ can be taken as the states of linear (and orthogonal) polarizations, as the two independent circular polarization states, and so on. A pure state is described by a wave function

$$|\psi\rangle = c_1|1\rangle + c_2|2\rangle \equiv \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}, \quad (7.69)$$

where

$$|1\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad |2\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}; \quad \langle 1 | = (1, 0); \quad \langle 2 | = (0, 1), \quad (7.70)$$

c_1, c_2 are arbitrary complex numbers such that

$$|c_1|^2 + |c_2|^2 = 1.$$

The two base states are taken to be orthonormal:

$$\langle 1|1\rangle = \langle 2|2\rangle = 1; \quad \langle 1|2\rangle = \langle 2|1\rangle = 0.$$

The operators which correspond to the measurement of the photon polarizations 1 and 2 act as

$$P_1|1\rangle = |1\rangle; \quad P_1|2\rangle = 0; \quad P_2|2\rangle = |2\rangle; \quad P_2|1\rangle = 0;$$

that is

$$P_1 = |1\rangle\langle 1| = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}; \quad P_2 = |2\rangle\langle 2| = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}; \quad (7.71)$$

they are the projection operators on the states $|1\rangle$ and $|2\rangle$, respectively.

The density matrix for the pure state (7.69) is simply

$$\rho = \begin{pmatrix} |c_1|^2 & c_1 c_2^* \\ c_1^* c_2 & |c_2|^2 \end{pmatrix}.$$

A beam of partially polarized or unpolarized light, is described as a mixed state. A photon in an unpolarized beam is described by the density matrix

$$\rho = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad (7.72)$$

in fact, the mean value of the polarization in directions 1 or 2 is

$$\langle P_1 \rangle = \text{Tr}(P_1 \rho) = \frac{1}{2}; \quad \langle P_2 \rangle = \text{Tr}(P_2 \rho) = \frac{1}{2}, \quad (7.73)$$

respectively. It is not difficult to check that the mean value of the polarization in *any* polarization, in state (7.72), is given by $\frac{1}{2}$.

The state of partial polarization has a general representation of the form

$$\rho = \frac{1}{2} \begin{pmatrix} 1 + \xi_3 & \xi_1 - i\xi_2 \\ \xi_1 + i\xi_2 & 1 - \xi_3 \end{pmatrix} = \frac{1}{2}(\mathbf{1} + \sigma_i \xi_i),$$

where

$$\xi_1^2 + \xi_2^2 + \xi_3^2 \leq 1,$$

and

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

are the Pauli matrices. The three numbers ξ_1, ξ_2, ξ_3 (real) are known as the Stokes parameters. It can be easily seen that

$$\rho^2 = \rho,$$

if and only if

$$\xi^2 \equiv \xi_1^2 + \xi_2^2 + \xi_3^2 = 1:$$

in this case the system is pure. $1 - \xi^2$ thus can be seen as a measure of our ignorance of the state of polarization. ξ_3 describes the degree of polarization in directions 1 or 2, for instance

$$\langle P_1 \rangle = \text{Tr} P_1 \rho = \frac{1 + \xi_3}{2} = \begin{cases} 1 & \text{if } \xi_3 = 1, \\ 0 & \text{if } \xi_3 = -1. \end{cases}$$

Analogously ξ_1 is the measure of the linear polarization in the direction which makes an angle $\pm\frac{\pi}{4}$ with 1 and 2, as can be verified by constructing the projection operator

$$P'_1 = |1'\rangle \langle 1'|, \quad P'_2 = |2'\rangle \langle 2'|, \quad |1'\rangle = \frac{|1\rangle + |2\rangle}{\sqrt{2}}, \quad |2'\rangle = \frac{|1\rangle - |2\rangle}{\sqrt{2}},$$

and evaluating $\langle P'_1 \rangle$, etc. Finally, ξ_2 corresponds to the measure of circular polarizations.

$$|+\rangle = \frac{1}{\sqrt{2}}(|1\rangle + i|2\rangle); \quad |-\rangle = \frac{1}{\sqrt{2}}(|1\rangle - i|2\rangle).$$

7.8 Quantization in general coordinates

The rule for the quantum Hamiltonian introduced in eqns (2.29)–(2.30)

$$\hat{H}(\{\hat{q}_i\}, \{\hat{p}_i\}; t) = H_{\text{clas}}(\{q_i\}, \{p_i\}; t)|_{q_i \rightarrow \hat{q}_i, p_i \rightarrow \hat{p}_i = -i\hbar \frac{\partial}{\partial q_i}} \quad (7.74)$$

looks straightforward, but a little thought shows that it is far from being trivial. Let us discuss some of the questions involved.

In order not to mix up physically distinct problems, let us separate the following two questions:

- (i) quantization of a “simple” class of systems, i.e., in a flat space, with the standard quadratic kinetic term, which has the form

$$\sum_i \sum_{\alpha=x,y,z} \frac{p_{i,\alpha}^2}{2m_i}$$

in cartesian coordinates, with the potential V depending only on $\{q_{i,\alpha}\}$, and

- (ii) quantization of physical systems of more general type, such as particles moving in a curved space or in a topologically nontrivial space, for instance, with nontrivial periodicity (defects), or particles moving in a momentum-dependent potential (e.g., a charged particle moving in an external electromagnetic field \mathbf{A}_i with minimal interactions).

Consider the first class of systems, to start with. Is the quantization procedure (7.74) valid in generic curvilinear coordinates? One could consider any generalized coordinates, construct the canonically conjugate momenta $p_i \equiv \frac{\partial L}{\partial \dot{q}_i}$, and then make the replacement

$$p_i \rightarrow -i\hbar \frac{\partial}{\partial q_i} \quad (7.75)$$

in the Hamiltonian, expressed in terms of the coordinates (q_i, p_i) . It turns out that this procedure in general leads to a quantum Hamiltonian operator different from what is obtained in cartesian coordinates. For

instance, in spherical coordinates $q_i = (r, \theta, \phi)$, the kinetic term is given by

$$L = \frac{m}{2} \left(\dot{r}^2 + r^2 \dot{\theta}^2 + r^2 \sin^2 \theta \dot{\phi}^2 \right),$$

and the canonical momenta are

$$p_r = m \dot{r}; \quad p_\theta = m r^2 \dot{\theta}; \quad p_\phi = m r^2 \sin^2 \theta \dot{\phi}.$$

The kinetic term of the Hamiltonian takes the form

$$H_{\text{kin}} = \frac{p_r^2}{2m} + \frac{p_\theta^2}{2mr^2} + \frac{p_\phi^2}{2mr^2 \sin^2 \theta}.$$

The replacement rule (7.75) yields an operator

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right).$$

It can be seen immediately that such a procedure misses the terms

$$-\frac{\hbar^2}{2m} \left(\frac{2}{r} \frac{\partial}{\partial r} + \frac{\cos \theta}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \right)$$

present in the standard quantum Hamiltonian, *written* in spherical coordinates, see eqns (4.1), (4.2).

Analogously, a free particle moving in a plane

$$H = \frac{1}{2m} (p_x^2 + p_y^2),$$

has the form

$$H = \frac{1}{2m} \left(p_r^2 + \frac{1}{r^2} p_\phi^2 \right).$$

in polar coordinates. The substitution

$$p_r \rightarrow -i\hbar \frac{\partial}{\partial r}, \quad p_\phi \rightarrow -i\hbar \frac{\partial}{\partial \phi}$$

in the second Hamiltonian would yield an operator which differs [Messiah (2000)] from the standard operator obtained in cartesian coordinates, by

$$-\frac{\hbar^2}{2mr} \frac{\partial}{\partial r}.$$

The problem can actually look even more serious if we note that in general curvilinear coordinates procedure (7.74) is not even well defined, due to the well-known “operator ordering problem”. Indeed, if g_{ij} is the metric, the kinetic term in the Lagrangian has the form $L_{(\text{kin})} = (m/2)g_{ij}(q)\dot{q}^i\dot{q}^j$. Furthermore, define g^{ij} as the inverse of the metric g_{ij} and $g \equiv \det g = \det g_{ij}$. In the passage from classical to quantum mechanics, however, there is a fatal arbitrariness in writing the kinetic term as

$$\frac{1}{2m} g^{ij}(q) p_i p_j, \quad \frac{1}{2m} p_i g^{ij}(q) p_j, \quad \frac{1}{2m} \sqrt{g} p_j (\sqrt{g} g^{jk}(q) p_k),$$

or something else. This would appear to irreparably compromise the uniqueness of the quantum Hamiltonian. Note that the requirement of Hermiticity is not sufficient to eliminate this ambiguity.

In systems of the first type (i) there is actually no ambiguity whatsoever. A unique quantum operator corresponds to the classical Hamiltonian. It is an empirical law that the correct quantum Hamiltonian is given by rule (7.74), when one works in cartesian coordinates.¹¹ The replacement rule (7.75) must be applied on the classical Hamiltonian, written in cartesian coordinates and similarly for systems with more than one particle. As long as cartesian coordinates are used, the result does not depend on the particular choice of coordinates.

This does not preclude of course that, once the quantum Hamiltonian is correctly identified, *any* other coordinate system can be used by a *simple change of variables*. The general rule of quantization at the end of this section ultimately reduces to this prescription. (See also the books [Brillouin (1938)], [Kemble (1937)].)

The situation concerning systems of more general types (ii) is subtler. In the cases of minimal coupling, describing the interactions of a charged particle with an electromagnetic potential (for instance), the procedure

$$p_i = \frac{\partial L}{\partial \dot{q}_i} = m \dot{q}_i + \frac{e}{c} A_i(q), \quad p_i \rightarrow \hat{p}_i = -i \hbar \frac{\partial}{\partial q_i}$$

(in cartesian coordinates) gives the correct result: eqns (14.8) and (14.12).

In general, the requirement that the quantum Hamiltonian be self-adjoint (though necessary) is not sufficient to determine uniquely the quantum Hamiltonian. In the case of a particle moving on a circle (or equivalently, a particle moving on a periodic lattice), it is possible to define an infinite number of distinct quantum systems.

An important point, which sometimes risks being overlooked behind the mathematical armor of these considerations, is the fact that in certain systems physical parameters appear that characterize each quantum system. Even though the physical significance of these parameters is often quite clear, the way they characterize the quantum systems is quite remarkable, and unfamiliar from the classical point of view. For instance the θ parameter which characterizes the particle moving on a circle (Subsection 3.2.2) might be related to the magnetic flux flowing through the area encircled (in the physical example of a toroidal superconductor), or to the lattice momentum in the case of a particle moving through a periodic potential (see Subsection 3.6.1).

In the case of a particle moving in a general curved space, the classical Hamiltonian

$$H = \frac{1}{2m} g^{ij}(q) p_i p_j$$

corresponds to the quantum Hamiltonian [DeWitt (1957)]

$$\hat{H} = \frac{1}{2m} g^{-1/4} \hat{p}_i g^{1/2} g^{ij} \hat{p}_j g^{-1/4} + C \hbar^2 R,$$

$$g^{1/4} \hat{p}_j g^{-1/4} = -i \hbar \frac{\partial}{\partial q^j},$$

where the constant C in front of the term of order \hbar^2 and proportional to the scalar curvature R of the space—and only this term—remains undetermined. On the other hand, it is quite understandable that, given the classical system (for which $\hbar = 0$ hence C has no meaning), there can be no *a priori* reason to privilege one particular value or another for C . This arbitrariness is known as DeWitt's ambiguity. In spite of the name, it must be regarded as signaling the presence of a physical parameter which characterizes each quantum system of this kind (which must be determined from experiments), and *not* as a sort of inconsistency or as a genuine ambiguity.

Let us come back now to particles moving in flat space ($R = 0$), a system of the first kind. From what has been just said it follows that the quantization procedure in a general curvilinear coordinate system is given by

$$H \rightarrow \hat{H} = \frac{1}{2m} g^{-1/4} \hat{p}_i g^{1/2} g^{ij} \hat{p}_j g^{-1/4} + V(q), \quad (7.76)$$

$$\hat{p}_i = g^{-1/4} \cdot \left(-i\hbar \frac{\partial}{\partial q^i} \right) \cdot g^{1/4}. \quad (7.77)$$

Rule (7.77) can be rewritten as a sort of covariant derivative. The correctness of this procedure is guaranteed by the fact that the differential operator which follows from eqns (7.76), (7.77) is precisely the Laplace–Beltrami operator

$$\frac{1}{\sqrt{g}} \frac{\partial}{\partial q^i} \left(\sqrt{g} g^{ij} \frac{\partial}{\partial q^j} \right),$$

which is *invariant* under general coordinate transformations, and by the fact that in cartesian coordinate it reduces to the empirically correct prescription, (7.74). Thus in general coordinates neither the substitution rule $p_i \rightarrow \hat{p}_i = -i\hbar \frac{\partial}{\partial q_i}$ nor the canonical commutation rule $[q_i, p_j] = i\hbar \delta_{ij}$ are valid. These must be replaced by (7.77) and by the commutation relations which follow from it.

Further reading

The reader interested in the mathematical aspects of the theory can read the book [von Neumann (1932)]. A proof of Stone's theorem and von Neumann's theorems can be

found in Vol. 1 of the book [Reed and Simon (1980a)], Chap.8. A pedagogical introduction to self-adjoint extensions is in [Bonneau, Faraut, and Valent (2001)].

Guide to the Supplements

One of the main postulates of quantum mechanics is that each physical state corresponds to a ray in the Hilbert space (P_1) (see Section 7.1). Does the inverse statement, “each vector in the Hilbert space describes a physical state”, hold true as well? The question puts the superposition principle under scrutiny: given two physical states $|\alpha\rangle, |\beta\rangle$, is the state $|\alpha\rangle + |\beta\rangle$ also a physical state, for whatever choice of $|\alpha\rangle$ and $|\beta\rangle$? Supplement 20.14 is dedicated to the discussion of this subtle issue. The conclusion will be that the superposition principle actually admits exceptions. A well-known example is related to the exactly conserved electric charge. Only superposi-

tions among the states with the same electric charge are allowed. An analogous restriction holds for the fermion number. Superposition of states with different fermion numbers is unphysical. These restrictions are known as *superselection rules*.

In a second Supplement some details of the von Neumann theorem are given. The theorem basically ensures the uniqueness of the Schrödinger representation for the Heisenberg commutation relations. Related questions on the relevance of canonical transformations in quantum mechanics and the problem of self-adjoint extensions of the operators are briefly addressed.

Problems

- (7.1) Solve the Heisenberg equations of motion for a free particle and for a particle in an external uniform field.
- (7.2) Solve the Heisenberg equations of motion for a harmonic oscillator in a uniform constant external field. Generalize the solution for a uniform time dependent force $F(t)$.
- (7.3) Suppose that the system described by the wave function $\psi_S(x)$ at the instant $t = 0$ is an eigenstate of the operator f , with eigenvalue, f_0 . Show that the wave function at time t is an eigenstate of the Heisenberg operator $\hat{f}_H(-t)$, with the same eigenvalue. (This technique is used in the book [Kogan and Galitsky (1963)] to compute the Green functions of several simple models).

8

Path integrals

An elegant alternative formalism of quantum mechanics was given by R. P. Feynman in 1948. The importance of this formalism, known as the path integral, functional integral, etc. approach, first of all lies in its vivid, intuitive description of quantum fluctuations. At the same time, it provides us with a formidable tool of calculus, of both perturbative effects (Feynman diagrams) and non-perturbative effects (e.g., tunnel effects, instantons).

8.1 Green functions	183
8.2 Path integrals	186
Chapter summary	201
Further reading	201
Numerical analyses	202

8.1 Green functions

An important concept in quantum mechanics is that of the (probability) amplitude for two successive events; in particular, the (probability) amplitude for finding a particle at the point x at time t , *knowing* that the particle was at $x = x_0$ at some earlier instant $t = t_0$. This amplitude is called the *Green function*, and as will be seen below, it is precisely this quantity the path integral is concerned with. Let us therefore review a few elementary aspects of Green functions, before discussing the path integral itself. In the cases in which the Hamiltonian is independent of time, the Green function is given by

$$G(x, x_0; t, t_0) = \langle x | e^{-iH(t-t_0)/\hbar} | x_0 \rangle. \quad (8.1)$$

In other words the Green function is the time evolution operator, written in the x representation.

From the very definition it follows immediately that the Green function possesses a fundamental property, i.e. the property of convolution,

$$G(x, x_0; t, t_0) = \int dx_1 G(x, x_1; t, t_1) G(x_1, x_0; t_1, t_0), \quad (8.2)$$

where x_1 is the position occupied by the particle at *any fixed* intermediate time t_1 (Fig. 8.1). As G represents the amplitude for the two successive events, the *probability* of $(x_0; t_0) \rightarrow (x; t)$ is the square of $G(x, x_0; t, t_0)$, and from eqn (8.2) we see that it contains various interference terms coming from the contributions of different “paths”, $x_0 \rightarrow x_1 \rightarrow x$, with all possible intermediate positions, x_1 .

The concept of the Green function is closely related to that of the wave function. G can be interpreted as the wave function with the special initial condition that the particle was a position eigenstate at

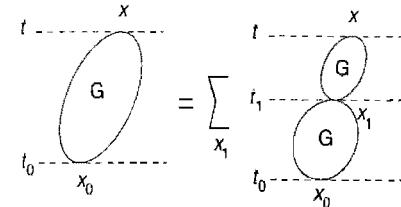


Fig. 8.1

the initial time: $\psi(x, t_0) = \delta(x - x_0)$. Indeed,

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} G(x, x_0; t, t_0) &= i\hbar \frac{\partial}{\partial t} \langle x | e^{-iH(t-t_0)/\hbar} | x_0 \rangle = \langle x | H e^{-iH(t-t_0)/\hbar} | x_0 \rangle \\ &= H_{\text{Sch}} \langle x | e^{-iH(t-t_0)/\hbar} | x_0 \rangle = H_{\text{Sch}} G(x, x_0; t, t_0). \end{aligned}$$

The probability of finding the particle in the interval $(x, x + dx)$ at time t is then given by $|G(x, x_0; t, t_0)|^2 dx$.

For simplicity we briefly review the properties of the Green function in one-dimensional systems. By definition the Green function G gives the solution of the general problem of time evolution in a given system, in the sense that the solution of Schrödinger's equation for *any* initial condition

$$\psi(x, t)|_{t=t_0} = \psi_0(x, t_0),$$

is given by

$$\psi(x, t) = \int dx' G(x, x'; t, t_0) \psi_0(x', t_0), \quad (8.3)$$

¹**Exercise.** Show that $\psi(x, t)$ in eqn (8.3) indeed satisfies both Schrödinger's equation and the initial condition.

in terms of the Green function.¹

The Green function (8.1) can be written, by inserting the completeness relation in terms of the energy eigenstates,

$$\mathbb{1} = \sum_n |\psi_n\rangle \langle \psi_n|$$

as

$$G(x, x_0; t, t_0) = \sum_n e^{-iE_n(t-t_0)/\hbar} \psi_n(x) \psi_n^*(x_0). \quad (8.4)$$

²**Exercise.** Show that the integral in the last factor in eqn (8.5) can be brought to the form of the ordinary gaussian integration over the real axis, by using Cauchy's theorem.

23

In some simple cases the Green function can be evaluated explicitly. For a free particle, by substituting

$$E_n \rightarrow \frac{p^2}{2m}; \quad \psi_n(x) \rightarrow \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}; \quad \sum_n \rightarrow \int_{-\infty}^{\infty} dp$$

into (8.4), one finds that

$$\begin{aligned} G(x, x_0; t, t_0) &= \int_{-\infty}^{\infty} \frac{dp}{2\pi\hbar} e^{-ip^2(t-t_0)/2m\hbar} e^{ip(x-x_0)/\hbar} \\ &= e^{im(x-x_0)^2/2\hbar(t-t_0)} \int_{-\infty}^{\infty} \frac{dp}{2\pi\hbar} \exp \left[-\left(\frac{i(t-t_0)}{2m\hbar} \left(p - \frac{m(x-x_0)}{t-t_0} \right) \right)^2 \right] \\ &= \frac{1}{2\pi\hbar} \sqrt{\frac{2m\hbar}{i(t-t_0)}} e^{im(x-x_0)^2/2\hbar(t-t_0)} \left(\int_C d\xi e^{-\xi^2} \right), \end{aligned} \quad (8.5)$$

where the contour of integration C in ξ is along the straight line $(1+i)\alpha$; $\alpha = -\infty \rightarrow \infty$. The integral is equal to $\sqrt{\pi}$, so the result is

$$G(x, x_0; t, t_0) = \sqrt{\frac{m}{2i\hbar\pi(t-t_0)}} e^{im(x-x_0)^2/2\hbar(t-t_0)}. \quad (8.6)$$

The harmonic oscillator

The harmonic oscillator

$$H = \frac{P^2}{2m} + \frac{1}{2} m \omega^2 Q^2$$

is another system in which the Green function is known explicitly. It can be explicitly evaluated by the path integral method; here we derive the same result by making use of a theorem proposed as a problem in Chapter 7. The Green function $G(q, q_0; t, 0) = \langle q | e^{-iHt/\hbar} | q_0 \rangle$ is equal to the wave function $\psi(q, t)$ with a particular boundary condition

$$\psi(q, 0) = \delta(q - q_0), \quad \therefore Q\psi(q, 0) = q_0 \psi(q, 0). \quad (8.7)$$

According to the theorem mentioned, $\psi(q, t)$ satisfies the equation

$$Q(-t)\psi(q, t) = \left(Q \cos \omega t - \frac{P}{m\omega} \sin \omega t \right) \psi(q, t) = q_0 \psi(q, t),$$

where $Q(t)$ is the Heisenberg position operator at time t ; $Q = Q(0)$, $P = P(0)$ are the ordinary Schrödinger operators, and the known solution of Heisenberg's equations for $Q(t)$ has been used. Thus

$$\frac{i\hbar}{m\omega} \sin \omega t \frac{\partial}{\partial q} \psi(q, t) = (-q \cos \omega t + q_0) \psi(q, t) :$$

and its solution is

$$\psi(q, t) = \exp \left[\frac{im\omega(q \cos \omega t - q_0)^2}{\hbar \sin 2\omega t} + c(t) \right],$$

where $c(t)$ is an integration constant, independent of q . To determine it, we impose the condition

$$\left(i\hbar \frac{\partial}{\partial t} - H \right) \psi(q, t) = 0,$$

which yields a differential equation for \dot{c} :

$$\dot{c}(t) = -\frac{\omega}{2} \cot \omega t - \frac{im\omega^2}{2\hbar} \frac{q_0^2}{\cos^2 \omega t};$$

integrating it, one finds that

$$c(t) = -\frac{1}{2} \log(\sin \omega t) - \frac{im\omega}{2\hbar} q_0^2 \tan \omega t + \text{const.},$$

where the constant depends neither on t nor on q . Collecting the factors and fixing the constant with boundary condition (8.7), we find that

$$\begin{aligned} & G^{HO}(q, q_0; t, t_0) \\ &= \sqrt{\frac{m\omega}{2\pi i\hbar \sin \omega(t-t_0)}} \exp \left[\frac{im\omega}{\hbar} \frac{(q^2 + q_0^2) \cos \omega(t-t_0) - 2q_0 q}{2 \sin \omega(t-t_0)} \right]. \end{aligned} \quad (8.8)$$

8.2 Path integrals

In the path integral formulation the Green function

$$\langle q_1 | e^{-iH(T_1-T_0)/\hbar} | q_0 \rangle$$

is given by the expression

$$\int_{q(T_0)=q_0}^{q(T_1)=q_1} [\mathcal{D}q] e^{\frac{i}{\hbar}S}, \quad S = \int_{T_0}^{T_1} dt L(q, \dot{q}), \quad (8.9)$$

⁴This formula contains in one all of the three melodies of theoretical physics of the 20th century: quantization, symmetry and phase factor”, C. N. Yang. Int. Conf. of Theoretical Physics. TH2002, Paris (2002).

where $L(q, \dot{q})$ is the Lagrangian (S is the classical action).⁴ The symbol $\int [\mathcal{D}q] \dots$ will be defined in the following: its meaning is however quite clear: the Green function is given by the sum over all possible paths connecting the initial point $q(T_0) = q_0$ to the final point $q(T_1) = q_1$, each weighed with the factor $e^{iS/\hbar}$, where S is the classical action corresponding to each path (see Fig. 8.9). Without entering into the details, one notes several salient features:

- The “virtual paths” introduced in the Lagrangian formalism of classical mechanics with the minimal action principle appear here as real paths: in quantum mechanics all trajectories—whether or not they satisfy the classical equation of motion—contribute, each with weight $e^{iS/\hbar}$. The fact that the electron “sees” both of the double slits (see Chapter 1) simultaneously, a rather counterintuitive fact, is here expressed in a very natural way.
- The sum over different paths is in the amplitude; contributions from different paths interfere nontrivially in the probability for a given event. This is of course a well-known, characteristic aspect of quantum mechanics.
- In the limit $\hbar \rightarrow 0$, only the stationary path for which $\delta S = 0$ contributes: the contributions of non-stationary paths cancel out due to the rapid phase oscillations. We thus recover the minimal principle of classical mechanics in the limit $\hbar \rightarrow 0$, as required.

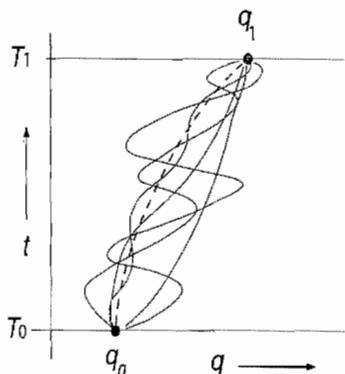


Fig. 8.2

8.2.1 Derivation

To derive eqn (8.9), we start by dividing the time interval $[T_1, T_0]$ into many tiny segments:

$$t_N = T_1 > t_{N-1} > t_{N-2} > \dots > t_2 > t_1 > t_0 = T_0,$$

$$t_i - t_{i-1} = \epsilon, \quad N \epsilon = T_1 - T_0.$$

The evolution operator can be factorized as

$$e^{-iH(T_1-T_0)/\hbar} = e^{-iH\epsilon/\hbar} e^{-iH\epsilon/\hbar} \dots e^{-iH\epsilon/\hbar}.$$

Inserting the completeness relation

$$\sum_{q_i} |q_i\rangle \langle q_i| = 1$$

into each time slice, one gets

$$G(q, q_0; T_1, T_0) = \int \prod_i dq_i \prod_i G_{i+1,i}(q_{i+1}, q_i; t_{i+1}, t_i),$$

where

$$G_{i+1,i} = \langle q_{i+1} | e^{-iH\epsilon/\hbar} | q_i \rangle \simeq \langle q_{i+1} | 1 - iH\epsilon/\hbar + \dots | q_i \rangle.$$

For a Hamiltonian of the form, $H = \frac{p^2}{2m} + V(q)$, it follows that

$$\begin{aligned} \langle q_{i+1} | H | q_i \rangle &= \langle q_{i+1} | \frac{p^2}{2m} + V(q) | q_i \rangle = \int dp \langle q_{i+1} | p \rangle \langle p | \frac{p^2}{2m} + V(q) | q_i \rangle \\ &= \int \frac{dp}{2\pi\hbar} e^{ip(q_{i+1}-q_i)/\hbar} \left(\frac{p^2}{2m} + V(q_i) \right) = \int \frac{dp}{2\pi\hbar} e^{ip\Delta q/\hbar} \left(\frac{p^2}{2m} + V(q_i) \right). \end{aligned}$$

Thus

$$G_{i+1,i} \simeq \int \frac{dp}{2\pi\hbar} e^{ip\Delta q/\hbar} \left(1 - i \frac{H(p, q_i)\epsilon}{\hbar} + \dots \right) = \int \frac{dp}{2\pi\hbar} e^{ip\Delta q/\hbar - i\epsilon H/\hbar}.$$

Collecting the factors one finds that⁵

$$G(q, q_0; T_1, T_0) = \lim_{N \rightarrow \infty} \int \prod \frac{dq_i dp_i}{2\pi\hbar} e^{i \sum_i \left[\frac{p_i(q_{i+1}-q_i)}{\hbar} - H(p_i, q_i) \right]}.$$

Finally, performing the integration over p_i ,

$$\begin{aligned} G_{i+1,i} &= \int \frac{dp}{2\pi\hbar} e^{ip\Delta q/\hbar - i\epsilon p^2/2m\hbar - i\epsilon V(q_i)/\hbar} \\ &= \text{const. } e^{i\epsilon m(\Delta q/\epsilon)^2/2 - i\epsilon V(q_i)/\hbar} = e^{i\epsilon L(q_i, \dot{q}_i)/\hbar}, \end{aligned}$$

where we have written

$$L(q_i, \dot{q}_i) = \frac{m}{2} \left(\frac{\Delta q}{\epsilon} \right)^2 - V(q_i) \simeq \frac{m(\dot{q})^2}{2} - V(q_i).$$

Thus

$$G(q, q_0; T_1, T_0) = \lim_{N \rightarrow \infty; \epsilon \rightarrow 0} \int \prod dq_i e^{i \sum_i \epsilon L(q_i, \dot{q}_i)/\hbar} \equiv \int [\mathcal{D}q] e^{iS/\hbar}.$$

Remarks. The reader with a tendency for mathematical rigor might be appalled to see the omnipresent symbol \simeq and the limit with infinite-dimensional integrals taken with nonchalance. Actually, the derivation can be made rigorous. First of all, we consider the Euclidean time, i.e., a continuation $t = -it_E$, which makes all the integrals of Gaussian type,

$$iS \rightarrow -S_E, \quad S_E = \int dt_E \left[\left(\frac{dq(t_E)}{dt_E} \right)^2 + V(q(t_E)) \right].$$

As for the infinite product, the convergence of the limit (Trotter's formula)

$$\lim_{N \rightarrow \infty} \left(e^{-(T+V)/N} \right)^N = \lim_{N \rightarrow \infty} \left(e^{-T/N} e^{-V/N} \right)^N$$

can be proved for any *self-adjoint* operators (see Section 7.3.1) T, V .

⁵Feynman's inspiration came from some observations made by Dirac. In fact all the basic ideas about the path integral can be already found in a somewhat mysterious §32 of Dirac's book [Dirac (1958)].

The convolution property of the path integral

$$\int_{q(T_0)=q_0}^{q(T_1)=q_1} [\mathcal{D}q] e^{\frac{i}{\hbar} S} = \int dq \left[\int_{q(t)=q}^{q(T_1)=q_1} [\mathcal{D}q] e^{\frac{i}{\hbar} S} \right] \left[\int_{q(T_0)=q_0}^{q(t)=q} [\mathcal{D}q] e^{\frac{i}{\hbar} S} \right]$$

(valid for any fixed t , $T_1 > t > T_0$) follows immediately from the very definition of the path integral. In agreement with the general principles of quantum mechanics, the amplitude for the particle at q_0 initially ($t = T_0$) to travel to q_1 at time $t = T_1$, is a coherent sum of the amplitudes for the particle traveling first from q_0 to q , then from q to q_1 , summed over the intermediate position q .

The amplitude studied above can also be written as a matrix element between two Heisenberg states,

$$G(q_1, q_0; T_1, T_0) =_H \langle q_1, T_1 | q_0, T_0 \rangle_H.$$

⁶As this point might be confusing, let us remind the reader that the state $|q_1, t\rangle_H$ is *not* the same as the Schrödinger state at time t , which is $e^{-iHt/\hbar}|q_1\rangle$; the latter is certainly not an eigenstate of any position operator. On the contrary, $|q_1, t\rangle_H$ is an eigenstate of $Q_H(t)$ with eigenvalue q_1 .

where $|q_1, t\rangle_H = e^{iHt/\hbar}|q_1\rangle$ is an eigenstate of the Heisenberg operator⁶

$$Q_H(t) = e^{iHt} Q e^{-iHt}, \quad Q_H(t)|q_1, t\rangle_H = q_1 |q_1, t\rangle_H.$$

The states without suffix H stands for the position eigenstates of the standard Schrödinger operator Q . Let us now consider a matrix element,

$$\begin{aligned} {}_H\langle q_1, T_1 | Q_H(t) | q_0, T_0 \rangle_H &= \langle q_1 | e^{-iH(T_1-t)/\hbar} Q e^{-iH(t-T_0)/\hbar} | q_0 \rangle \\ &= \int dq \langle q_1 | e^{-iH(T_1-t)/\hbar} | q \rangle q \langle q | e^{-iH(t-T_0)/\hbar} | q_0 \rangle; \end{aligned}$$

calculating it between the time intervals $[T_1, t]$ and $[t, T_0]$ as above, one finds that

$${}_H\langle q_1, T_1 | Q_H(t) | q_0, T_0 \rangle_H = \int [\mathcal{D}q] q(t) e^{\frac{i}{\hbar} \int_{T_0}^{T_1} L};$$

analogously, one finds for $t_1 > t_2$

$${}_H\langle q_1, T_1 | Q_H(t_1) Q_H(t_2) | q_0, T_0 \rangle_H = \int [\mathcal{D}q] q(t_1) q(t_2) e^{\frac{i}{\hbar} \int_{T_0}^{T_1} L};$$

and so on. In general, we find a remarkable result,

$$\begin{aligned} &\int [\mathcal{D}q] q(t_1) q(t_2) \dots q(t_n) e^{\frac{i}{\hbar} \int_{T_0}^{T_1} L} \\ &= {}_H\langle q_1, T_1 | T\{Q_H(t_1) Q_H(t_2) \dots Q_H(t_n)\} | q_0, T_0 \rangle_H, \end{aligned}$$

where the chronological product $T\{\dots\}$ is defined as

$$T\{Q_H(t_1) Q_H(t_2) Q_H(t_3)\} = \begin{cases} Q_H(t_1) Q_H(t_2) Q_H(t_3) & \text{if } t_1 > t_2 > t_3; \\ Q_H(t_2) Q_H(t_3) Q_H(t_1) & \text{if } t_2 > t_3 > t_1; \end{cases}, \quad (8.10)$$

etc.

We further modify the Lagrangian by introducing a “source term” $J(t)$, as

$$L \rightarrow L + J(t) q(t).$$

If one assumes that the source is non-vanishing only during the time interval between t and t' ,

$$T_1 > t' > t > T_0,$$

then the Green function (path integral) in the presence of such a source term

$$W^{(J)} = \int [Dq] e^{\frac{i}{\hbar} \int (L + J q)}$$

is equal to

$${}_H\langle q_1, T_1 | q_0, T_0 \rangle_H^{(J)} = \int dq' dq_H \langle q_1, T_1 | q', t' \rangle_H H(q', t') \langle q', t' | q, t \rangle_H^{(J)} H(q, t | q_0, T_0 \rangle_H.$$

We now let

$$T_1 \rightarrow -i\infty, \quad T_0 \rightarrow +i\infty.$$

By inserting a completeness relation constructed with the energy eigenstates, we have

$$\begin{aligned} {}_H\langle q, t | q_0, T_0 \rangle_H &= \langle q | e^{-iH(t-T_0)/\hbar} | q_0 \rangle = \sum_n \phi_n(q) \phi_n^*(q_0) e^{-iE_n(t-T_0)/\hbar} \\ &\xrightarrow{T_0 \rightarrow +i\infty} \phi_0(q) \phi_0^*(q_0) e^{-iE_0(t-T_0)/\hbar}, \end{aligned} \quad (8.11)$$

i.e., in this limit the sum is dominated by a single term. In other words the path integral becomes proportional to the “vacuum to vacuum” amplitude (i.e., ground state to ground state). This important result is known as *Feynman’s theorem*.

In analogy to the ordinary derivative, a “functional derivative” can be defined as

$$\frac{\delta}{\delta J(t)} J(t') = \delta(t - t').$$

Then ($T_1 \rightarrow -i\infty, T_0 \rightarrow +i\infty$)

$$\left. \frac{\delta^n W^{(J)}}{\delta J(t_1) \delta J(t_2) \dots \delta J(t_n)} \right|_{J=0} = \langle 0 | T\{Q_H(t_1) Q_H(t_2) \dots Q_H(t_n)\} | 0 \rangle. \quad (8.12)$$

In other words, $W^{(J)}$ acts as the generating functional for the n -point correlation functions.

The generalization of the path integral to systems with s variables is immediate:

$$\begin{aligned} G(\{q_1\}, \{q_0\}; T_1, T_0) &= \langle \{q_1\} | e^{-iH(T_1-T_0)/\hbar} | \{q_0\} \rangle \\ &= \int \prod_n Dq^{(n)} e^{i \frac{1}{\hbar} \int_{T_0}^{T_1} L(q^{(n)}(t), \dot{q}^{(n)}(t))}. \end{aligned}$$

Systems with infinite degrees of freedom (quantum fields) can be found as a limit of the multiple degrees of freedom. In quantum field theories the analogues of quantity (8.12) are the so-called causal correlation functions (the propagator and n -point functions). (See Section 17.2.)

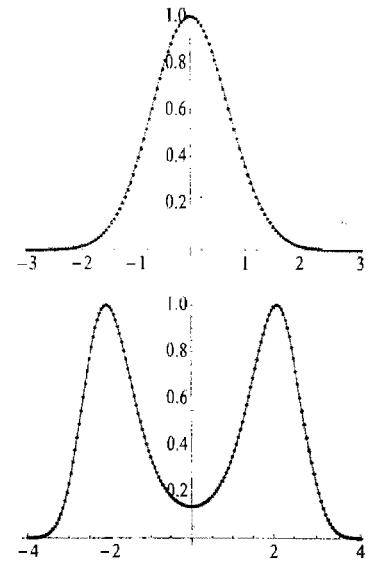


Fig. 8.3 The ground state $|\psi|^2$ computed with the Feynman path integral for the harmonic oscillator and a double well potential; see NB-8.1, NB-8.2.

Important identities can be found by considering the functional change of variables,

$$q(t) \rightarrow q(t) + \delta q(t).$$

To start with, consider a general path integral with an “argument” $G[q]$,

$$\langle G[q] \rangle = \int [\mathcal{D}q] G[q(t)] e^{\frac{i}{\hbar} S},$$

where $G[q]$ is a generic function (or a functional) of $q(t)$. Applying a change of variable, one has

$$\left\langle \frac{\delta G}{\delta q(t)} - \frac{i}{\hbar} G[q(t)] \frac{\delta S}{\delta q(t)} \right\rangle = 0.$$

By using such identities with various choices for $G[q]$ it is possible to reproduce known theorems such as Ehrenfest’s theorem, the virial theorem, and so on. It is quite curious that the relation corresponding to the fundamental commutator in the usual operator formalism of quantum mechanics $[\hat{q}, \hat{p}] = i\hbar$ emerges this way (with $F(q) = q_i$).

8.2.2 Mode expansion

Two particular advantages of the path integral method are the following. First, the ease with which perturbative contributions (Chapter 9) can be organized in a diagrammatic fashion (Feynman graphs), which makes the concrete task of calculations much simpler, especially in complex systems with many degrees of freedom. Second, certain non-perturbative effects (tunnel effects) are elegantly captured by solutions of the classical equation of motion analytically continued to the Euclidean time. These solutions play the role of a sort of functional saddle point.

By going to the Euclidean time,

$$t \rightarrow t = -i\tau,$$

the factor e^{iS} becomes

$$e^{i \int dt \left[\frac{m}{2} \left(\frac{dq}{dt} \right)^2 - V(q) \right]} \rightarrow e^{- \int d\tau \left[\frac{m}{2} \left(\frac{dq}{d\tau} \right)^2 + V(q) \right]} = e^{-S_E},$$

where the Euclidean action is defined as

$$S_E = \int d\tau \left[\frac{m}{2} \left(\frac{dq}{d\tau} \right)^2 + V(q) \right] = \int d\tau L_E(q, \dot{q}) :$$

it describes the motion of the particle in the potential $-V(q)$. The generating functional in the presence of the source term is

$$W_E(J) = \int \mathcal{D}q e^{- \int d\tau [L_E(q, \dot{q}) - J \cdot q]},$$

and

$$\frac{1}{W(J)} \frac{\delta^n W}{\delta J(t_1) \dots \delta J(t_n)} \Big|_{J=0} = i^n \frac{1}{W_E(J)} \frac{\delta^n W_E}{\delta J(\tau_1) \dots \delta J(\tau_n)} \Big|_{J=0, \tau_i = it_i}.$$

This last relation tells us how to retrieve the results for the n -point function in standard real time (Minkowski time), after the calculations have been done in the Euclidean-time formalism.

For the harmonic oscillator, $V(q) = \frac{\omega^2}{2} q^2$, and in the Euclidean time Lagrangian is (by setting $m = 1$)

$$L_E = \frac{\dot{q}^2}{2} + \frac{\omega^2}{2} q^2.$$

Once the path integral

$$\langle q_1 | e^{-H\tau} | q_0 \rangle = \mathcal{N} \int \mathcal{D}q e^{-S_E}, \quad (8.13)$$

$$S_E = \int_{-\tau_0/2}^{\tau_0/2} \left(\frac{\dot{q}^2}{2} + \frac{\omega^2}{2} q^2 \right),$$

is calculated, the ground-state energy can be computed by studying its behavior at $\tau_0 \rightarrow \infty$,

$$\langle q_1 | e^{-H\tau} | q_0 \rangle \simeq e^{-E_0 \tau} \psi_0(q_1) \psi_0(q_0)^*. \quad (8.14)$$

In more general cases, with the potential containing the cubic or higher powers of q , we write

$$S_E = \int d\tau [q(\tau) \hat{A}(\tau) q(\tau) + V_{int}(q(\tau))],$$

where $\hat{A}(\tau) = -\frac{1}{2} \frac{d^2}{d\tau^2} + \frac{1}{2}\omega^2$ is the quadratic part of the (Euclidean) Lagrangian; the remaining part $V_{int} = \lambda q(\tau)^3 + \eta q(\tau)^4 + \dots$ represents the interactions. By introducing a complete set of eigenfunctions of the operator \hat{A} :

$$\hat{A}(\tau) f_k(\tau) = \epsilon_k f_k(\tau), \quad \int d\tau f_k^*(\tau) f_\ell(\tau) = \delta_{k\ell}, \quad (8.15)$$

and by defining

$$[\mathcal{D}q] \equiv \prod_k dc_k, \quad q(t) = \sum_k c_k f_k(\tau), \quad (8.16)$$

the functional integration reduces to the ordinary integrals over the coefficients of the mode expansion, $\prod_k dc_k$. The quadratic part gives

$$\int [\mathcal{D}q] e^{-q \cdot \hat{A} \cdot q} = \prod_k \epsilon_k^{-1/2} = (\det \hat{A})^{-1/2}; \quad (8.17)$$

the interaction part can be treated perturbatively, by introducing the source term, and writing things concisely:⁷

⁷Equation (8.18) is the key formula.

$$\begin{aligned} \int [\mathcal{D}q] e^{-q \cdot \hat{A} \cdot q - J \cdot q - V(q)} &= e^{-V(-\frac{\delta}{8J})} \int [\mathcal{D}q] e^{-q \cdot \hat{A} \cdot q - J \cdot q} \\ &= e^{-V(-\frac{\delta}{8J})} e^{J \cdot \hat{A}^{-1} \cdot J/4} (\det \hat{A})^{-1/2}. \end{aligned} \quad (8.18)$$

where

$$J \cdot \hat{A}^{-1} \cdot J \equiv \int d\tau_1 d\tau_2 \int \int J(\tau_1) D(\tau_1 - \tau_2) J(\tau_2), \quad (8.19)$$

$$D(\tau_1 - \tau_2) \equiv \hat{A}_{\tau_1, \tau_2}^{-1}, \text{ etc.}$$

Equation (8.18) is the key formula both for the standard perturbation theory, i.e., computation of the fluctuations about the trivial minimum (in which case $\omega(t) = \omega = \text{const.}$), as well as for the evaluation of non-perturbative effects, i.e., determination of the effects due to some nontrivial classical minima $q(t) = q^{(cl)}(t)$ and to the fluctuations around it.

8.2.3 Feynman graphs

In order to get an expansion in the interaction potentials, let us first determine the value of the functional integral (8.13) for the harmonic oscillator, with $q_0 = q_1 = 0$ (with $S_{cl} = 0$), and without the interaction and source term ($V_{int} = J = 0$). It is formally equal to

$$(\det \hat{A})^{-1/2}, \quad A = -\frac{d^2}{d\tau^2} + \omega^2,$$

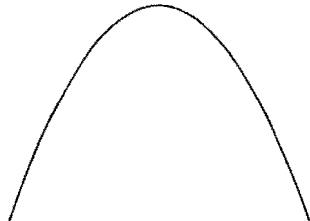


Fig. 8.4

which we shall now compute explicitly. In this case, the “classical solution” in the inverted oscillator potential is just the trivial solution, $q(\tau) = 0, \forall \tau$. (Fig. 8.4). As the fluctuations must vanish at $\tau = \pm \frac{T}{2}$, the problem of finding the eigenvalues of the operator A is identical to the simple quantum mechanical problem of a particle in an infinitely deep well at $x = \pm \frac{T}{2}$:

$$\left(-\frac{d^2}{d\tau^2} + \omega^2 \right) f_n = \epsilon_n f_n, \quad (8.20)$$

$$f_n \left(\frac{T}{2} \right) = f_n \left(-\frac{T}{2} \right) = 0,$$

which has solutions (Section 3.3.1)

$$\epsilon_n - \omega^2 = \frac{\pi^2 n^2}{T^2} \equiv \lambda_n^2; \quad f_n(\tau) = A_n \sin \lambda_n \left(\tau + \frac{T}{2} \right).$$

By expanding

$$\delta q(\tau) = \sum_n c_n f_n(\tau),$$

and using the orthonormality of the eigenfunctions f_k ,

$$S_E = \int d\tau \delta q(\tau) A \delta q(\tau) = \sum_n c_n^2 \epsilon_n,$$

we find that

$$\begin{aligned} \mathcal{N} \int \mathcal{D}q(\tau) e^{-S_E} &= \mathcal{N} e^{-S_{cl}} \int \prod_n dc_n e^{-c_n^2 \epsilon_n} \\ &= \left[\mathcal{N} \int \mathcal{D}q(\tau) e^{-S_E} \right]_{\omega=0} \prod_n \left(1 + \frac{\omega^2 T^2}{\pi^2 n^2} \right)^{-1/2}. \end{aligned}$$

The part we factorized corresponds to the propagation of the free particle, so (with Euclidean time and with $m = \hbar = 1$)

$$\mathcal{N} \int \mathcal{D}q(\tau) e^{-S_E} |_{\omega=0} = \langle 0 | e^{-p^2 T/2} | 0 \rangle = \frac{1}{\sqrt{2\pi T}},$$

(see eqn (8.6)). The “correction” factor is determined by using the formula

$$\prod_{n=1}^{\infty} \left(1 + \frac{z^2}{n^2}\right) = \frac{\sinh \pi z}{\pi z}$$

to be

$$\prod_{n=1}^{\infty} \left(1 + \frac{\omega^2 T^2}{\pi^2 n^2}\right)^{-1/2} = \left(\frac{\sinh \omega T}{\omega T}\right)^{-1/2}.$$

Thus the sum over fluctuations (paths) gives

$$\langle 0 | e^{-H \tau} | 0 \rangle = \mathcal{N} \int \mathcal{D}q e^{-S_E} = \sqrt{\frac{\omega}{2\pi}} \sinh^{-1/2} \omega T. \quad (8.21)$$

This, of course, agrees with eqn (8.8), after setting $q_1 = q_0 = 0$ and going to the Euclidean time. Equation (8.21) yields in the limit $T \rightarrow \infty$,

$$\langle 0 | e^{-H \tau} | 0 \rangle \rightarrow \sqrt{\frac{\omega}{\pi}} e^{-\omega T/2},$$

and gives, in view of eqn (8.14), $E_0 = \frac{\omega}{2}$, $\psi(0) = (\frac{\omega}{\pi})^{1/4}$, in agreement with what was obtained by solving Schrödinger’s equation (Section 3.4).

Next we note that the propagator \hat{A}^{-1} in eqn (8.18) is explicitly given by

$$\hat{A}^{-1} \equiv D(\tau_1 - \tau_2) = \frac{1}{2\omega} e^{-\omega|\tau_1 - \tau_2|}. \quad (8.22)$$

To obtain it, first make a Fourier transform to the energy space

$$q(\tau) = \int_{-\infty}^{\infty} \frac{dE}{2\pi} e^{-iE\tau} \tilde{q}(E),$$

in which the operator \hat{A} is equal to $E^2 + \omega^2$. The inverse is thus $1/(E^2 + \omega^2)$ and \hat{A}^{-1} is given by the inverse Fourier transform,

$$\hat{A}^{-1} \equiv D(\tau_1 - \tau_2) = \int_{-\infty}^{\infty} \frac{dE}{2\pi} \frac{1}{E^2 + \omega^2} e^{-iE(\tau_1 - \tau_2)}. \quad (8.23)$$

We leave it as an exercise to work out the integration by using the residues theorem, to get eqn (8.22). The propagator is just the two-point correlation function in the free theory ($V_{int} = 0$), as it corresponds to the second derivative with respect to the source function.

To get a taste of how things work, let us consider the case of the cubic potential, $V = \lambda q^3(\tau)$, that is, the system

$$H = \frac{p^2}{2} + \frac{\omega^2}{2} q^2 + \lambda q^3$$

(we set $m = \hbar = 1$) and we are going to calculate the corrections to the ground-state energy $\frac{\omega}{2}$ due to the cubic interactions. The strategy is to compute the path integral (8.18) by setting $J = 0$, after an appropriate number of derivatives $\delta/\delta J$ are taken to extract the desired powers of λ , and then to use Feynman's theorem, (8.11). The potential enters eqn (8.18) through

$$e^{-\lambda \int d\tau \frac{\delta^3}{\delta J(\tau)^3}} = 1 - \lambda \int d\tau \frac{\delta^3}{\delta J(\tau)^3} + \frac{\lambda^2}{2!} \int d\tau \frac{\delta^3}{\delta J(\tau)^3} \int d\tau' \frac{\delta^3}{\delta J(\tau')^3} + \dots$$

To the order λ^2 for instance, we have

$$\frac{\lambda^2}{2!} \int_{\tau} \frac{\delta^3}{\delta J^3} \int_{\tau'} \frac{\delta^3}{\delta J^3} \frac{1}{3!} \left(\int_1 \int_2 \frac{JDJ}{2} \right) \left(\int_3 \int_4 \frac{JDJ}{2} \right) \left(\int_5 \int_6 \frac{JDJ}{2} \right).$$

With the use of the functional derivatives, various contributions arise. For instance if three derivatives in $\delta^3/\delta J^3(\tau)$ act on J 's inside three different parentheses, the result would be proportional to

$$\int \int (D_{\tau, \tau'})^3 = \int d\tau \int d\tau' \frac{e^{-3\omega|\tau-\tau'|}}{(2\omega)^3} = \frac{T}{12\omega^4}, \quad (8.24)$$

where T is the total time interval. But the same contribution arises many times as the derivatives $\delta^3/\delta J^3(\tau)$ and $\delta^3/\delta J^3(\tau')$ are distributed in the three groups: taking into account the factorials in the expansion and the combinatoric factor, the above contribution gets multiplied by

$$\frac{\lambda^2}{2!} \frac{1}{3!} 3! 3! = 3 \lambda^2.$$

Another type of contribution occurs when two of the derivatives in $\delta^3/\delta J^3(\tau)$ act on two J 's inside a parenthesis. Necessarily the same occurs for the derivatives in $\delta^3/\delta J^3(\tau')$. In this case the result is

$$\int \int D_{\tau, \tau'} D_{\tau, \tau'} D_{\tau', \tau'} = \int d\tau \int d\tau' \frac{e^{-\omega|\tau-\tau'|}}{(2\omega)^3} = \frac{T}{4\omega^4}. \quad (8.25)$$

The combinatorics for this case is a little more tricky: it is

$$\frac{\lambda^2}{2!} \frac{1}{3!} \frac{3!}{2} \frac{3!}{2} \frac{3!}{2} = \frac{9 \lambda^2}{2},$$

which multiplies the above contribution. The total contribution to this order is equal to

$$\frac{11 T}{8 \omega^4}.$$

This kind of calculation can be pushed to higher orders, but obviously the counting will very quickly become cumbersome. The elegant observation due to Feynman which makes life considerably easier is that these contributions can be reorganized diagrammatically. Indeed, one has a simple set of rules (*Feynman's rules*):

- (i) Each vertex (Fig. 8.5) gives a factor $-\lambda$.

- (ii) Each propagator gives $D(\tau_1 - \tau_2)$ (Fig. 8.6).
- (iii) For a given number of vertices (to a given order in λ), draw all graphs combining vertices and propagators.
- (iv) Integrate over all τ 's (interaction time).
- (v) Insert a factor $1/n!$ if there are n identical vertices.
- (vi) Count how many times a given graph arises.

Thus to the second-order contribution in λ considered above in the system with a cubic potential, there are two graphs A and B of Fig. 8.7 contributing to the “vacuum-to-vacuum” amplitude. Their combinatorial factors (i.e., in how many ways the given graph can be formed) are

$$3 \cdot 3 = 9, \quad 3 \cdot 2 = 6,$$

for the graphs A and B, respectively, while the value of the graphs is easily seen to be equal to eqns (8.24) and (8.25).

To sew things up and to apply Feynman's theorem, there is one more step needed. As we are really looking for the correction proportional to λ^2 in the ground-state energy, which appears in the *exponent* of the functional integral we are computing,

$$\langle q_1 | e^{-H T} | q_0 \rangle \simeq e^{-E_0 T} \psi_0(q_1) \psi_0(q_0)^*,$$

we must exponentiate the contribution we have just computed:

$$1 + (A + B) + \frac{1}{2!}(A + B) \cdot (A + B) + \dots = e^{A+B}.$$

More precisely we are to calculate the vacuum-to-vacuum amplitude to all orders in λ , however keeping only those graphs in which the *connected part* (let us call Σ) consists of the second-order contributions only. Thus the path integral has been computed to be

$$W|_{J=0} = \sqrt{\frac{\omega}{2\pi}} \sinh^{-1/2} \omega T e^{11\lambda^2 T / 8\omega^2} \simeq e^{-(\omega/2 - 11\lambda^2/8\omega^2)T},$$

so that

$$E_0 = \frac{\omega}{2} - \frac{11\lambda^2}{8\omega^2} + \dots$$

where \dots indicates the corrections to higher orders in λ . This result coincides with the one found by using standard perturbation theory, developed in the next chapter (Section 9.1).

In the case of the quartic potential,

$$H = \frac{p^2}{2} + \frac{\omega^2}{2} q^2 + g q^4,$$

the only difference to the previous case is the vertex, see Fig. 8.8. In this case, there is a vacuum-to-vacuum graph already at the first order, Fig. 8.9, given by

$$-g \frac{4 \cdot 3}{2} \frac{1}{2} \int \frac{e^{-2\omega|\tau-\tau'|}}{(2\omega)^2} = -\frac{3}{4} \frac{T}{\omega^2}.$$

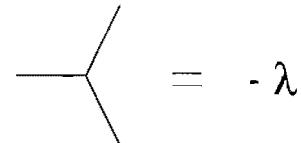


Fig. 8.5

$$\frac{\text{---}}{\tau_1 \quad \tau_2} = \frac{e^{-\omega|\tau_1 - \tau_2|}}{2\omega}$$

Fig. 8.6

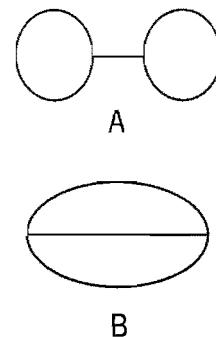


Fig. 8.7

B

To the second order, we find the two graphs shown in Figure 8.10, which sum up to yield

$$\frac{21}{8} \frac{T}{\omega^5}.$$

The correction to the ground-state energy is thus

$$E_0 = \frac{\omega}{2} + \frac{3}{4} \frac{g}{\omega^2} - \frac{21}{8} \frac{g^2}{\omega^5} + \dots,$$

which again, of course, agrees with the result of standard perturbation theory.

Remarks

- Feynman's rules and graphs (diagrams) can be easily generalized to cases with more than one degree of freedom, and in fact to the case of infinite degrees of freedom (quantum field theory).
- A great advantage of the diagrammatic method is that the organization of the various contributions, in particular, the combinatorial factors, are identical in quantum mechanics considered here and in quantum field theory in any dimensions; the only difference is in the propagator (8.23), which is replaced by

$$D(x_1^\mu - x_2^\mu) = \int \frac{d^D p}{(2\pi)^D} \frac{e^{ip \cdot (x_1 - x_2)}}{p^2 + m^2},$$

where the mass of a propagating particle replaces ω of a quantum mechanical oscillator. Also the internal "loop" momenta (Fourier conjugate of the relative positions of the two vertices connected by the propagator) become D -dimensional.

- The power of the path integral formulation is truly appreciated when one faces much more complex problems such as relativistic quantum field theories or statistical mechanics (theories of infinite degrees of freedom). To try to solve a simple quantum mechanical problem with this method is a little like trying to crush a nut with a hydraulic press, not always the smartest thing to do.
- In the problems of elementary particle physics—relativistic quantum field theories—the fact that the formalism is intrinsically relativistic (the Lagrangian density which plays the central role in this formalism is a Lorenz-invariant quantity, while the Hamiltonian density is not), is a great advantage.
- From the formal point of view, the path integral with configurations $\{q\}$ periodic (and summed over) in Euclidean time (call $T = \beta$),

$$\sum_q \langle q | e^{-\beta H} | q \rangle = \text{Tr } e^{-\beta H}$$

can be interpreted as the *partition function* of statistical mechanics, with $\beta \equiv 1/kT$, with T standing now for the temperature. This simple observation is at the basis of an enormously rich

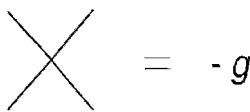


Fig. 8.8

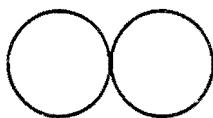


Fig. 8.9



Fig. 8.10

(and successful) fields of research, encompassing condensed matter physics (phase transitions and critical phenomena) on the one hand and quantum field theories and elementary particle physics, on the other [Zinn-Justin (1989)]. Two fields have been enriched by mutual exportation of the techniques and theoretical concepts (even some physicists themselves!), such as the renormalization group, universality, scaling, phase structures of the systems, duality, and so on and so forth.

8.2.4 Back to ordinary (Minkowski) time

The continuation back to the ordinary, real time description must be done with some care. We shall choose to rotate back the time variable as

$$t = -i\tau \rightarrow t \quad \text{real},$$

90 degrees anti-clockwise, while at the same time

$$E = iE \rightarrow E \quad \text{real},$$

by rotating 90 degrees in the clockwise direction. See Fig. 8.11. This choice is dictated by the particular type of correlation functions we are interested in. Indeed, the propagator (8.23) is continued back to

$$D_M(t_1 - t_2) = -i \int_{-\infty}^{\infty} \frac{dE}{2\pi} \frac{1}{E^2 - \omega^2 + i\epsilon} e^{-iE(t_1 - t_2)}, \quad (8.26)$$

where $+i\epsilon$ in the denominator indicates that the singularity at $\pm\omega$ must be avoided by shifting them slightly off the real axis, $\pm(\omega - i\epsilon)$. By picking up the appropriate residues for $t_1 - t_2 > 0$ or $t_1 - t_2 < 0$, one finds the propagator

$$D_M(t_1 - t_2) = \begin{cases} -e^{-i\omega(t_1 - t_2)}/2\omega, & t_1 > t_2; \\ -e^{i\omega(t_1 - t_2)}/2\omega, & t_1 < t_2. \end{cases}$$

As the two-point correlation function in general has the form, e.g., for $t_1 > t_2$ (see eqn (8.10))

$$\begin{aligned} D_M(t_1 - t_2) &= \langle 0 | T(Q(t_1)Q(t_2)) | 0 \rangle \\ &= \sum_n \langle 0 | Q(t_1) | n \rangle \langle n | Q(t_2) | 0 \rangle = \sum_n e^{-iE_n(t_1 - t_2)/\hbar} |\langle 0 | Q | n \rangle|^2, \end{aligned}$$

and analogously

$$D_M(t_1 - t_2) = \sum_n e^{+iE_n(t_1 - t_2)/\hbar} |\langle 0 | Q | n \rangle|^2, \quad t_1 < t_2,$$

we see that $D_M(t)$ represents the *causal* propagator: only the positive (negative) energy states propagate in the future (past) direction.

A similar reasoning explains the form of the causal (Feynman) propagator of a scalar particle in Minkowski spacetime,

$$D_M(x_1^\mu - x_2^\mu) = i \int \frac{d^D p}{(2\pi)^D} \frac{e^{ip \cdot x}}{p^2 - m^2 + i\epsilon},$$

with the so-called $i\epsilon$ prescription.

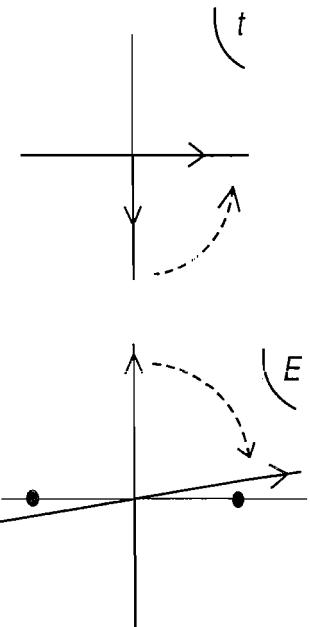


Fig. 8.11

8.2.5 Tunnel effects and instantons

As an example of the application of the path integral to non-perturbative effects in quantum mechanics (e.g., tunnel effects) consider a double-well potential,

$$H = \frac{p^2}{2m} + V(q), \quad V(q) = \lambda (q^2 - \eta^2)^2, \quad (8.27)$$

shown in Fig. 8.12. We know from the standard considerations based on Schrödinger's equation that the ground state of the system is a symmetric combination of the approximate ground state of the two wells, the first excited state antisymmetric combination thereof, and the splitting of the two levels is characterized by the tunneling amplitude between the two wells,

$$\Delta E_{\pm} \sim e^{-\frac{1}{\hbar} \int |p| dq}.$$

(For a more detailed discussion based on the semi-classical approximation see Section 11.1). In this section we are going to analyze the problem by making use of the “sum-over-paths” approach.

We are mainly interested in studying the amplitudes

$$\langle \eta | e^{-HT} | -\eta \rangle = \int_{q(-T/2)=-\eta}^{q(T/2)=\eta} \mathcal{D}q e^{-S_E}; \quad (8.28)$$

$$\langle -\eta | e^{-HT} | -\eta \rangle = \int_{q(-T/2)=-\eta}^{q(T/2)=-\eta} \mathcal{D}q e^{-S_E}; \quad (8.29)$$

and similar ones with $\eta \leftrightarrow -\eta$, where S_E is the Euclidean action

$$S_E = \int d\tau \left(\frac{m}{2} \dot{q}^2 + V(q) \right).$$

Note that near the bottom of each well the potential looks like a harmonic oscillator with

$$V''(q)|_{\eta} = 8\lambda\eta^2 \equiv m\omega^2, \quad \omega = \sqrt{\frac{8\lambda\eta^2}{m}},$$

while the barrier height is

$$V(0) = \lambda\eta^4 = \frac{m^2\omega^4}{64\lambda} \gg \omega, \quad \text{if } \frac{m^2\omega^3}{\lambda} \gg 1.$$

Let us first consider the amplitude (8.29) for the particle traveling from $-\eta$ to η during the time T . The (functional) stationary point of S_E is given by the solution of the Euclidean equation of motion

$$\frac{\delta S_E}{\delta q} = -m\ddot{q} + \frac{dV}{dq} = 0.$$

Note that this describes a particle moving in the potential $-V(q)$ (Fig. 8.13). The desired solution, satisfying the boundary condition $q(-T/2) = -\eta$, $q(T/2) = \eta$, is clearly a solution in which the particle, staying for a long time near $q(-T/2) = -\eta$, moves quickly through the central ditch

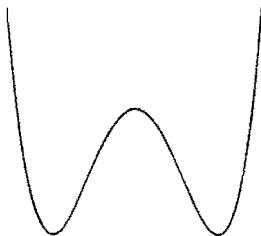


Fig. 8.12

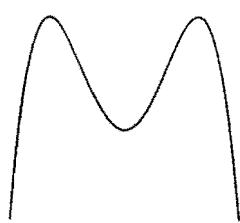


Fig. 8.13

and approaches asymptotically towards $q(T/2) = \eta$. Such a solution in the Euclidean equation of motion is known as an *instanton*. (Fig. 8.14).

In the case of the concrete model (8.27), the instanton solution is given by (for large T)

$$q^{(class)}(\tau) = q^{(inst)}(\tau) = \eta \tanh \frac{\omega}{2}(\tau - \tau_0), \quad (8.30)$$

where τ_0 , the center of the instanton, is arbitrary. It is clear from classical mechanics that an analogous solution always exists for a particle moving in a potential with the same general characteristics as in Fig. 8.13, even though the detailed dependence on τ will depend on the potential. The classical instanton action can be expressed as follows. By integrating the equation of motion, one gets

$$\frac{m}{2} \left(\frac{dq}{d\tau} \right)^2 - V(q) = E = 0,$$

where we used the boundary condition to fix the value of the energy. This gives

$$\frac{dq}{d\tau} = \sqrt{\frac{2V(q)}{m}},$$

and thus (by using the virial theorem)

$$\begin{aligned} S_E^{(inst)} &= \int d\tau \left[\frac{m}{2} \dot{q}^2 + V(q) \right] = \int d\tau m \dot{q}^2 \\ &= \int_{-\eta}^{\eta} dq \sqrt{2mV(q)} = \int_{-\eta}^{\eta} dq |p| \end{aligned} \quad (8.31)$$

which is the well-known reduced action for the tunneling amplitude. In the specific case of the quartic potential (8.27) we find $S_E^{(inst)} = \omega^3 / 12\lambda$.

We now expand $q(\tau)$ around the instanton solution

$$q(\tau) = q^{(class)}(\tau) + \delta q(\tau),$$

$$S_E = S_E^{(inst)} + \frac{1}{2} \int d\tau \delta q(\tau) \left[-m \frac{d^2}{d\tau^2} + V''(q^{(inst)}(\tau)) \right] \delta q(\tau) + \dots;$$

by integrating over the fluctuations δq we formally get

$$\int Dq e^{-S_E} = \mathcal{N} e^{-S_E^{(inst)}} \det \left[-m \frac{d^2}{d\tau^2} + V''(q^{(inst)}) \right]^{-1/2}.$$

But there are problems. First, as the classical solution (8.30) contains a free parameter x_0 and as the action S_E does not depend on it, among the fluctuations around that solution there must be those corresponding to *simple translations* in the time direction, which do not require extra action. There will therefore be a zero eigenvalue among the mode expansion associated with the quadratic operator

$$\left[-m \frac{d^2}{d\tau^2} + V''(q^{(inst)}(\tau)) \right] \xi_n(\tau) = \epsilon_n \xi_n,$$

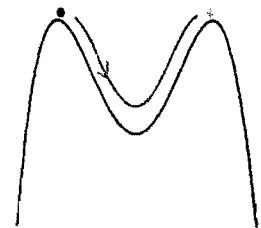


Fig. 8.14

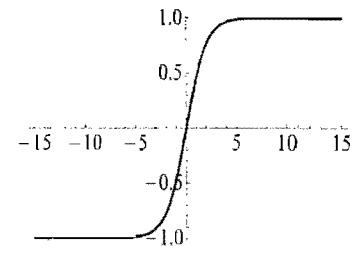


Fig. 8.15

(cf. eqn (8.20)) with $\epsilon_0 = 0$, and this makes the factor $\det[\dots]^{-1/2}$ meaningless. Also, in view of the fact that there are other instanton solutions in which the center is shifted, it is clear that contributions from these solutions (many saddle points) must be somehow summed up to get a sensible answer.

These two points are of course intimately related, and indeed the solution to *both* problems is given by the following (standard) trick. The idea is to explicitly extract the *zero mode*, corresponding to the translation in time,

$$dq^{(class)}(\tau) = \frac{dq^{(class)}(\tau)}{d\tau_0} d\tau_0 \equiv dc_0 \xi_0(\tau),$$

where ξ_0 is the normalized zero mode function⁸

$$\xi_0(\tau) = \left(\frac{S_E^{(inst)}}{m} \right)^{-1/2} \frac{dq^{(class)}(\tau)}{d\tau},$$

and therefore

$$dc_0 = (2\pi\hbar)^{1/2} \left(\frac{S_E^{(inst)}}{m} \right)^{1/2} d\tau_0.$$

Namely we traded the part of the (functional) integration over a particular fluctuation mode with an ordinary integration over the center of the instanton! This type of manipulation is known as the method of collective coordinates (of which τ_0 is an example). The functional integral is defined as⁹

$$\mathcal{D}q \equiv \frac{dc_0}{(2\pi\hbar)^{1/2}} \prod_{n \neq 0} \frac{dc_n}{(2\pi\hbar)^{1/2}} = \left(\frac{S_E^{(inst)}}{m} \right)^{1/2} d\tau_0 \prod_{n \neq 0} \frac{dc_n}{(2\pi\hbar)^{1/2}}.$$

The integration around an instanton solution then gives a contribution

$$\int \mathcal{D}q e^{-S_E} = (2\pi\hbar)^{1/2} \left(\frac{S_E^{(inst)}}{m} \right)^{1/2} T \det' \left[-m \frac{d^2}{d\tau^2} + V''(q^{(inst)}) \right]^{-1/2},$$

where the prime on the determinant indicates that the product is over the nonzero eigenvalues only. By normalizing it to the determinant in the case of the oscillator ($V = 0$), (8.21), we write

$$\mathcal{N} \det' \left[-m \frac{d^2}{d\tau^2} + V''(q^{(inst)}) \right]^{-1/2} = \sqrt{\frac{m\omega}{\pi\hbar}} e^{-\omega T/2} K,$$

where K is the ratio of the quadratic fluctuations around the instanton and those around the trivial solution $q^{(class)} = 0$. We shall not be concerned here with the computation of K , although in the case of the concrete model (8.27) the calculation can be carried through and gives $K = \omega \sqrt{6 S_E^{(inst)} / \pi\hbar}$.

⁸The normalization of the zero mode is known from an integral appearing in eqn (8.31).

⁹This kind of theoretical tool is used in studying *solitons*, *kinks*, *vortices*, etc. which are various finite-energy solutions of non-linear field equations, appearing in diverse fields of physics, from optics, solid state physics, fluid dynamics, superconductivity, and particle physics to cosmology.

We are almost done. At $T \rightarrow \infty$, there must be many solutions which correspond to the particle going between the two peaks of the inverted potential many times. See Fig. 8.16. As the action is concentrated near the center of the instanton (with a finite time spread of the order of $\Delta\tau \sim 1/\omega$)—and this is the reason for its name—the contribution corresponding to n instantons will be roughly proportional to $(Ke^{-S^{(\text{inst})}/\hbar T})^n$. Clearly n must be even for amplitude (8.29) whereas only odd- n solutions contribute to amplitude (8.28). Summing over the centers of the instantons we finally get

$$\langle -\eta | e^{-HT} | -\eta \rangle = \langle \eta | e^{-HT} | \eta \rangle \simeq \left(\frac{m\omega}{\hbar} \right)^{1/2} e^{-\omega T/2} \cosh \left(K e^{-S^{(\text{inst})}/\hbar T} \right);$$

$$\langle \eta | e^{-HT} | -\eta \rangle = \langle -\eta | e^{-HT} | \eta \rangle \simeq \left(\frac{m\omega}{\hbar} \right)^{1/2} e^{-\omega T/2} \sinh \left(K e^{-S^{(\text{inst})}/\hbar T} \right).$$

Clearly the states $|\eta\rangle$ and $|-\eta\rangle$ are not eigenstates of the evolution operator, i.e., of the Hamiltonian. The correct eigenstates are the combinations $|\psi_{\pm}\rangle = (|\eta\rangle \pm |-\eta\rangle)/\sqrt{2}$, in the basis of which e^{-HT} is diagonal. The energy eigenvalues are ($\cosh x \pm \sinh x = e^{\pm x}$)

$$E_{\pm} = \frac{\hbar\omega}{2} \mp K \hbar e^{-S^{(\text{inst})}/\hbar}.$$

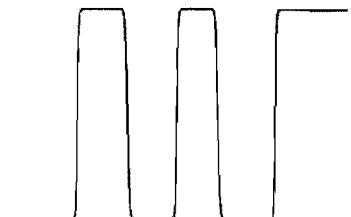


Fig. 8.16

Chapter summary

- The quantum mechanical Green function is given by the sum over paths, each path weighted by $e^{iS/\hbar}$.

Further reading

Special advice for the interested reader: read the original article by Feynman, *Space-time approach to non-relativistic quantum mechanics*, [Feynman (1948)]. For more details on the path integral formulation of quantum mechanics, the reader will find the book *Quantum Mechanics and path integrals* [Feynman and Hibbs (1965)] very stimulating. The first chapters of the book *Quantum Field Theory and Critical Phenomena* [Zinn-Justin (1989)] is a good introduction; this is also an example of a book dedicated both to quantum field theory and to critical phenomena. The review article [Abers and Lee

(1973)] gives a very neat introduction to the path integral, as well as to the modern gauge theories. There are many other good books specialized in path integrals such as [Schulman (1981)] and [Kleinert (2006)].

The path integral method helped as the basis for an enormous advance in the numerical investigations of quantum field theory and statistical mechanics. Many approaches are based on the *Monte Carlo* method. In the numerical problems we give a brief account of these techniques in the case of simple quantum mechanical problems.

Numerical analyses

- (8.1) Write a Monte Carlo simulation for one-dimensional quantum systems. Apply the method to the computation of the propagator for harmonic and anharmonic oscillators.
- (8.2) Compute the path integral, by defining a transfer matrix between the adjacent time slices.

Part II

Approximation methods



Three powerful methods of approximation are developed in Part II of this book: perturbation theory, the variational method, and the semi-classical approximation. They form indispensable tools for solving many physical problems.

9

Perturbation theory

One of the most frequently used approximation methods—perturbation theory—will be discussed in this chapter. Often a physical system is characterized by an “unperturbed” Hamiltonian H_0 whose spectrum is known, and by a small part of the Hamiltonian, the “perturbation” V . Introducing an expansion parameter λ we can write the total Hamiltonian as

$$H(\lambda) = H_0 + \lambda V. \quad (9.1)$$

λ can be set to unity after the calculation. Of course, there are cases in which a physical coupling constant appears in front of the perturbation term; in such a case the expansion is truly a power series expansion in the physical coupling constant.

When the perturbation is constant in time, the main interest is in the shift of spectrum as compared to the unperturbed system. When, instead, the perturbation depends on time, one has a qualitatively different physical problem. The energy of the system no longer is conserved and quantum transitions among the unperturbed levels are induced.

9.1 Time-independent perturbations

Let us first consider the case of static perturbations, i.e., where V is a constant operator. The problem is to find the energy levels and eigenfunctions for H , given the solution of the problem for H_0 . If (one of) the unperturbed energy levels is $E^{(0)}$ —for simplicity we assume it to be a discrete one—and the corresponding eigenvector $|\psi\rangle$, the problem is to find the power-series solution for $E(\lambda)$ and $|\psi(\lambda)\rangle$ such that

$$H(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle, \quad (9.2)$$

with the condition

$$\lim_{\lambda \rightarrow 0} E(\lambda) = E^{(0)} \quad \lim_{\lambda \rightarrow 0} |\psi(\lambda)\rangle = |\psi^{(0)}\rangle. \quad (9.3)$$

We assume for the moment that the unperturbed levels are non-degenerate: a unique $|\psi^{(0)}\rangle$ is associated with the eigenvalue $E^{(0)}$, and we seek the solution of eqn (9.2) in the form¹

$$|\psi\rangle = |\psi^{(0)}\rangle + \lambda |\psi^{(1)}\rangle + \lambda^2 |\psi^{(2)}\rangle + \dots + \lambda^L |\psi^{(L)}\rangle + \dots; \quad (9.4)$$

$$E = E^{(0)} + \lambda \varepsilon_1 + \lambda^2 \varepsilon_2 + \dots. \quad (9.5)$$

9.1 Time-independent perturbations	207
9.2 Quantum transitions	219
9.3 Transitions in the continuum	226
9.4 Decays	228
9.5 Electromagnetic transitions	233
9.6 The Einstein coefficients	240
Guide to the Supplements	242
Problems	242
Numerical analyses	244

¹The index (0) here stands for “unperturbed”; similarly the indices in $\psi^{(1)}$, $\psi^{(2)}$, or $\psi^{(L)}$ indicate the order of approximation in the power of λ . On the other hand, we are considering a particular, say, the n -th, unperturbed level, and the corrections to its eigenvalue and eigenfunction. Thus all unperturbed and perturbed quantities (such as $|\psi\rangle$, E , etc.) below carry the index n , which however will be left implicit so as not to cramp the notation, except when the specification is unavoidable. Also the notations $|n\rangle$, $|k\rangle$ indicate the unperturbed state vectors. Thus, $|\psi^{(0)}\rangle = |n\rangle$.

Equation (9.2) is homogeneous in ψ and the determination of the solution requires fixing the normalization of the vector $|\psi\rangle$, for instance by imposing $\langle\psi|\psi\rangle = 1$. It turns out to be simpler not to impose the normalization condition from the beginning, and use instead the condition

$$\langle\psi^{(0)}|\psi\rangle = 1. \quad (9.6)$$

The standard normalization condition can be imposed later.

Suppose that the unperturbed vector $|\psi^{(0)}\rangle$ is normalized. Equation (9.6) implies that the correction to the vector $|\psi^{(0)}\rangle$ is of the form $|\psi\rangle = |\psi^{(0)}\rangle + |\psi_{\perp}\rangle$, where ψ_{\perp} belongs to the Hilbert subspace orthogonal to the original vector. Equation (9.6) imposes the condition, order by order in λ ,

$$\langle\psi^{(0)}|\psi^{(L)}\rangle = 0, \quad L \geq 1. \quad (9.7)$$

Substituting expansion (9.4) into eqn (9.2) and imposing the condition that the equation be satisfied order by order in λ one finds the system

$$\begin{aligned} (H_0 - E^{(0)})|\psi^{(0)}\rangle &= 0; \\ (H_0 - E^{(0)})|\psi^{(1)}\rangle + (V - \varepsilon_1)|\psi^{(0)}\rangle &= 0; \\ (H_0 - E^{(0)})|\psi^{(2)}\rangle + (V - \varepsilon_1)|\psi^{(1)}\rangle - \varepsilon_2|\psi^{(0)}\rangle &= 0; \\ (H_0 - E^{(0)})|\psi^{(3)}\rangle + (V - \varepsilon_1)|\psi^{(2)}\rangle - \varepsilon_2|\psi^{(1)}\rangle - \varepsilon_3|\psi^{(0)}\rangle &= 0; \\ \dots &\dots; \\ (H_0 - E^{(0)})|\psi^{(L)}\rangle + V|\psi^{(L-1)}\rangle - \sum_{K=1}^L \varepsilon_K|\psi^{(L-K)}\rangle &= 0. \end{aligned} \quad (9.8)$$

Solution to first order

The solution to lowest order in λ can be found by the second of the equations above, projecting it onto the ket $|\psi^{(0)}\rangle$. H_0 is self-adjoint, and as $|\psi^{(0)}\rangle$ is an eigenvector associated with $E^{(0)}$, one has

$$\langle\psi^{(0)}|(H_0 - E^{(0)}) = 0. \quad (9.9)$$

One finds then

$$\varepsilon_1 = \langle\psi^{(0)}|V|\psi^{(0)}\rangle = \langle n|V|n\rangle = V_{nn}, \quad (9.10)$$

where in the last two equations we have assumed that $|\psi^{(0)}\rangle = |n\rangle$. Thus to first order the correction to the n -th energy eigenvalue is simply the diagonal (nn) matrix element of the perturbing potential.

Let $|k\rangle$ be the normalized eigenstates of H_0 , which together form a complete orthonormal basis of the Hilbert space. The correction to the state vector $|\psi^{(1)}\rangle$ can always be written as

$$|\psi^{(1)}\rangle = \sum'_k |k\rangle \langle k|\psi^{(1)}\rangle. \quad (9.11)$$

In this sum the term corresponding to the original vector $|\psi^{(0)}\rangle$ does not appear, by virtue of constraint (9.7); we shall indicate sums of this

type by an index t . For $|k\rangle \neq |\psi^{(0)}\rangle = |n\rangle$ the orthogonality of the eigenvectors of H_0 implies that $\langle k|\psi^{(0)}\rangle = 0$, therefore one finds, acting on the second of eqn (9.8) by $\langle k|$, that

$$(E_k^{(0)} - E_n^{(0)})\langle k|\psi^{(1)}\rangle + \langle k|V|\psi^{(0)}\rangle = 0$$

and thus

$$|\psi^{(1)}\rangle = \sum'_k |k\rangle \frac{1}{E_n^{(0)} - E_k^{(0)}} \langle k|V|\psi^{(0)}\rangle = \sum'_k |k\rangle \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} . \quad (9.12)$$

The sum is extended over all states different from $|n\rangle$. Equation (9.12) is the first-order correction to the wave function.

Iterative solution

Equations (9.8) can be solved by iterating the procedure used above. Suppose that we know the solution up to the $L-1$ -th order. Multiply the last of eqns (9.8) by $\langle \psi^{(0)}|$. Condition (9.9) kills the first term, and one finds as a result

$$\varepsilon_L = \langle \psi^{(0)}|V|\psi^{(L-1)}\rangle , \quad (9.13)$$

which determines the correction to the energy to order λ^L . Multiplying instead the same equation by $\langle k|$ ($k \neq n$), and using $\langle k|\psi^{(0)}\rangle = 0$, one gets:

$$\langle k|\psi^{(L)}\rangle = \frac{1}{E_n^{(0)} - E_k^{(0)}} \langle k|V|\psi^{(L-1)}\rangle - \frac{1}{E_n^{(0)} - E_k^{(0)}} \sum_{K=1}^{L-1} \varepsilon_K \langle k|\psi^{(L-K)}\rangle . \quad (9.14)$$

This equation determines the approximate solution for the eigenstate $\psi^{(L)}$ in terms of an expansion in terms of unperturbed state vectors $|k\rangle$. For example, the second-order correction to the energy eigenvalue is

$$\varepsilon_2 = \langle \psi^{(0)}|V|\psi^{(1)}\rangle = \sum'_k \frac{|\langle k|V|\psi^{(0)}\rangle|^2}{E_n^{(0)} - E_k^{(0)}} = \sum'_k \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}} . \quad (9.15)$$

Use of the projectors

One can formulate the solution in an operatorial form. Introduce the projection operator P onto the unperturbed state $|\psi^{(0)}\rangle$ and the projector Q onto the space orthogonal to $|\psi^{(0)}\rangle$:

$$P = |\psi^{(0)}\rangle\langle\psi^{(0)}| ; \quad Q = \sum'_k |k\rangle\langle k| ; \quad 1 = P + Q .$$

The solution found above can be cast into the form

$$|\psi^{(1)}\rangle = Q \frac{1}{E^{(0)} - H_0} Q V |\psi^{(0)}\rangle . \quad (9.16)$$

The basic idea is the following. Any operator A admits a decomposition

$$A = \begin{pmatrix} PAP & PAQ \\ QAP & QAQ \end{pmatrix}$$

in terms of the two projection operators just introduced. Consider first the case of the operator $A = E^{(0)} - H_0$. This operator has no inverse, because it has a nontrivial kernel, $(E^{(0)} - H_0)|\psi^{(0)}\rangle = 0$. But the operator $Q(E^{(0)} - H_0)Q$ is invertible, because we have assumed that the unperturbed spectrum is non-degenerate. Therefore (9.16) is simply the solution of the equation

$$(E^{(0)} - H_0)|\psi^{(1)}\rangle = V|\psi^{(0)}\rangle, \quad (9.17)$$

in the subspace orthogonal to $|\psi^{(0)}\rangle$. Let us write $V = PV + QV$; the first term does not contribute to the solution by virtue of the orthogonality of the projection operators: we first project eqn (9.17) and then take the inverse to find the solution.

Let

$$G = Q \frac{1}{E^{(0)} - H_0} Q;$$

the above relations then reads

$$\varepsilon_1 = \langle \psi^{(0)} | V | \psi^{(0)} \rangle; \quad |\psi^{(1)}\rangle = GV|\psi^{(0)}\rangle; \quad (9.18a)$$

$$\varepsilon_2 = \langle \psi^{(0)} | V | \psi^{(1)} \rangle = \langle \psi^{(0)} | VGV | \psi^{(0)} \rangle; \quad (9.18b)$$

$$|\psi^{(2)}\rangle = GV|\psi^{(1)}\rangle - \varepsilon_1 G|\psi^{(1)}\rangle. \quad (9.18c)$$

By evaluating the eigenvectors order by order, as well as the corresponding eigenvalues, some interesting relations can be found. For instance,

$$\begin{aligned} \varepsilon_3 &= \langle \psi^{(0)} | V | \psi^{(2)} \rangle = \langle \psi^{(0)} | VGV | \psi^{(1)} \rangle - \varepsilon_1 \langle \psi^{(0)} | VG | \psi^{(1)} \rangle \\ &= \langle \psi^{(1)} | V | \psi^{(1)} \rangle - \varepsilon_1 \langle \psi^{(1)} | \psi^{(1)} \rangle. \end{aligned} \quad (9.19)$$

In practice, once $|\psi^{(1)}\rangle$ has been calculated, it is a simple matter to determine ε_3 .

In general, one finds that

$$|\psi_n\rangle = GV|\psi_{n-1}\rangle - \sum_{k=1}^{n-1} \varepsilon_k G|\psi_{n-k}\rangle = GV|\psi_{n-1}\rangle - \sum_{k=1}^{n-1} \varepsilon_{n-k} G|\psi_k\rangle.$$

For the eigenvalues, we find, by using $|\psi^{(1)}\rangle = GV|\psi^{(0)}\rangle$, that

$$\begin{aligned} \varepsilon_n &= \langle \psi^{(0)} | V | \psi_{n-1} \rangle = \langle \psi^{(0)} | VGV | \psi_{n-2} \rangle - \sum_{k=1}^{n-2} \varepsilon_{n-1-k} \langle \psi^{(0)} | VG | \psi_k \rangle \\ &= \langle \psi^{(1)} | V | \psi_{n-2} \rangle - \sum_{k=1}^{n-2} \varepsilon_{n-1-k} \langle \psi^{(1)} | \psi_k \rangle. \end{aligned}$$

Equation (9.19) is a particular case of this for $n = 3$: the most remarkable feature is that to calculate the correction to the energy to n -th order, $n > 2$, we need to know the eigenvector only up to the order $n - 2$.

Remarks

- The result for the eigenvector to order λ is automatically normalized: in fact one has, by using $\langle \psi^{(0)} | \psi^{(1)} \rangle = 0$,

$$(\langle \psi^{(0)} | + \lambda \langle \psi^{(1)} |) (\langle \psi^{(0)} \rangle + \lambda | \psi^{(1)} \rangle) = 1 + \mathcal{O}(\lambda^2).$$

- The second-order correction ϵ_2 to the ground-state energy is always negative, as $E_n > E_0$. This result is particularly relevant if the first-order correction vanishes, since in this case the perturbation always lowers the energy of the ground state.
- The eigenfunction found above can be normalized, multiplying it by a constant:

$$|\psi\rangle_N = Z_\psi^{1/2} |\psi\rangle; \quad N \langle \psi | \psi \rangle_N = 1 \Rightarrow Z_\psi^{-1} = \langle \psi | \psi \rangle. \quad (9.20)$$

Z_ψ represents the probability of finding the unperturbed state $\psi^{(0)}$ in the correct eigenfunction ψ :

$$|\langle \psi^{(0)} | \psi \rangle_N|^2 = Z_\psi |\langle \psi^{(0)} | \psi \rangle|^2 = Z_\psi; \quad (9.21)$$

thus in general $Z_\psi \leq 1$. To the lowest nontrivial order,

$$Z_\psi^{-1} = 1 + \lambda^2 \langle \psi^{(1)} | \psi^{(1)} \rangle.$$

Thus from eqn (9.12) and the orthogonality of the states $\langle n | k \rangle = \delta_{nk}$ it follows that

$$\begin{aligned} Z_\psi &= 1 - \lambda^2 \langle \psi^{(1)} | \psi^{(1)} \rangle = 1 - \lambda^2 \sum_n \langle \psi^{(0)} | V | n \rangle \frac{1}{(E_0 - E_n)^2} \langle n | V | \psi^{(0)} \rangle \\ &= 1 - \lambda^2 \sum_n \frac{|\langle \psi^{(0)} | V | n \rangle|^2}{(E_0 - E_n)^2} = 1 + \lambda^2 \frac{\partial \epsilon_2}{\partial E_0}. \end{aligned} \quad (9.22)$$

In this formula the derivative with respect to the unperturbed energy is taken keeping all the matrix elements of V fixed. Equation (9.22) actually holds to all orders. In fact, consider a perturbation of the form of $\delta V = \delta E_0 |\psi^{(0)}\rangle \langle \psi^{(0)}|$, i.e., proportional to the projection operator onto the unperturbed state. Using first-order perturbation theory, the variation of E is

$$\delta E = \delta E_0 \cdot N \langle \psi | \psi^{(0)} \rangle \langle \psi^{(0)} | \psi \rangle_N = \delta E_0 |\langle \psi^{(0)} | \psi \rangle_N|^2 = Z_\psi \delta E_0;$$

so that

$$Z_\psi = \frac{\partial E}{\partial E_0}.$$

- Let us come back to condition (9.6). In considering the power series solution in λ one is assuming analyticity in λ . The limits

$$\lim_{\lambda \rightarrow 0} |\psi(\lambda)\rangle, \quad \lim_{\lambda \rightarrow 0} E(\lambda),$$

are well defined as the spectrum of H_0 is assumed to be non-degenerate. As Schrödinger's equation is homogeneous, if $|\psi(\lambda)\rangle$

is a solution, so is $c(\lambda)|\psi(\lambda)\rangle$. Consider therefore the function of λ , $a(\lambda) = \langle\psi^{(0)}|\psi(\lambda)\rangle$. Clearly $a(0) = 1$ and for continuity, $a(\lambda) \neq 0$, in some neighborhood of $\lambda = 0$. The ket $[1/a(\lambda)]|\psi(\lambda)\rangle$ then satisfies eqn (9.6).

This simple discussion can be generalized, bringing to the fore some of the subtleties of the procedure. Consider a variation of λ as a new perturbation, $\delta\lambda \cdot V$. Suppose also that the state has been normalized at each λ , by dividing it by $\|\psi\|$. The preceding discussion, by regarding $\psi(\lambda)$ as $\psi^{(0)}$ and $\psi(\lambda + \delta\lambda)$ as the perturbed wave function, implies that it is always possible to take the normalization such that

$$\langle\psi(\lambda)|\psi(\lambda + \delta\lambda)\rangle = \langle\psi(\lambda)|\psi(\lambda)\rangle,$$

at least for sufficiently small $\delta\lambda$. In other words, it must be always possible to satisfy

$$\left\langle\psi(\lambda)\left|\frac{\partial}{\partial\lambda}\psi(\lambda)\right.\right\rangle = 0 \quad (9.23)$$

locally. Dividing then by $\|\psi\|$ we can assume the state to be normalized so that

$$0 = \frac{\partial}{\partial\lambda}\langle\psi(\lambda)|\psi(\lambda)\rangle = \left\langle\psi(\lambda)\left|\frac{\partial}{\partial\lambda}\psi(\lambda)\right.\right\rangle + \left\langle\frac{\partial}{\partial\lambda}\psi(\lambda)\left|\psi(\lambda)\right.\right\rangle,$$

and thus

$$\left\langle\psi(\lambda)\left|\frac{\partial}{\partial\lambda}\psi(\lambda)\right.\right\rangle = i\beta, \quad \text{pure imaginary.} \quad (9.24)$$

By taking advantage of the freedom of choosing the phase of the state, $|\psi'\rangle = e^{-i\alpha(\lambda)}|\psi\rangle$, it follows that

$$\left\langle\psi'(\lambda)\left|\frac{\partial}{\partial\lambda}\psi'(\lambda)\right.\right\rangle = -i\frac{\partial\alpha}{\partial\lambda} + i\beta(\lambda).$$

Imposing α so that

$$\frac{\partial\alpha}{\partial\lambda} = \beta(\lambda), \quad (9.25)$$

one has

$$\left\langle\psi'(\lambda)\left|\frac{\partial}{\partial\lambda}\psi'(\lambda)\right.\right\rangle = 0,$$

which is eqn (9.23). Equation (9.25) always admits a solution locally. We shall see later that for large values of λ there can be problems.

9.1.1 Degenerate levels

The perturbation theory introduced above applies to cases where the matrix elements $|\langle n|V|k\rangle|$ are much smaller than the unperturbed level

splittings $|E_k^{(0)} - E_n^{(0)}|$. When there is degeneracy among the unperturbed levels, there will be states $k \neq n$, for which $E_k^{(0)} = E_n^{(0)}$ but $\langle n|V|k\rangle \neq 0$; such formulas as (9.12) are obviously inapplicable in such a case. Physically, this means that if unperturbed states (which do not “know” about V) are chosen arbitrarily, the effects of even an infinitesimal perturbation can be very large. Generally speaking, the degenerate system gets aligned with the perturbation, upon taking into account the latter; the corrections will be small if the unperturbed states are “prepared” appropriately so that the perturbation is smooth.

Let G_0 be the vector space spun by the eigenvectors corresponding to the level under consideration, and let g_0 be the degree of degeneracy, i.e., the dimension of G_0 , the number of linearly independent eigenvectors belonging to this sub-level.

Let us, again, introduce the projection operator $P = \sum_{i=1}^{g_0} |i\rangle\langle i|$ corresponding to this level: it is now a $g_0 \times g_0$ matrix; Q denotes the projection orthogonal to this level.

The unperturbed equation $(H_0 - E^{(0)})|\psi^{(0)}\rangle = 0$ is valid for any $|\psi^{(0)}\rangle$.

Let us consider the first-order equation

$$(H_0 - E^{(0)})|\psi^{(1)}\rangle + (V - \varepsilon_1)|\psi^{(0)}\rangle = 0. \quad (9.26)$$

As before we project this onto G_0 ,

$$P(V - \varepsilon_1)|\psi^{(0)}\rangle = 0, \quad (9.27)$$

as the first term vanishes due to the unperturbed equation. This is now a matrix equation, actually a system of homogeneous linear equations. By choosing any given base in G_0 we take

$$|\psi^{(0)}\rangle = \sum_{i=1}^{g_0} c_i |\varphi_i\rangle$$

as the unperturbed state. Substituting this into eqn (9.27) and multiplying it by $\langle \varphi_i |$ from the left, we find finally that

$$\langle \varphi_i | V | \varphi_j \rangle c_j = \varepsilon_1 c_i \quad \Rightarrow \quad V_{ij} c_j = \varepsilon_1 c_i. \quad (9.28)$$

This is an eigenvalue equation for ε_1 : it has a nontrivial solution only if

$$\det(V - \varepsilon_1) = 0, \quad (9.29)$$

which is just the secular equation for V . This equation, which generalizes eqn (9.10) of the non-degenerate case, has g_0 roots: the eigenvalues of the matrix V . The corresponding eigenvectors

$$|\tilde{\varphi}_1\rangle, |\tilde{\varphi}_2\rangle \dots |\tilde{\varphi}_{g_0}\rangle$$

form the basis of *unperturbed* states in which the effect of perturbation is smooth.

When the g_0 roots are all distinct, the degeneracy is completely *lifted* (eliminated) at this order, and the original level splits into g_0 sub-levels.

When some of the eigenvalues are equal, the degeneracy is lifted only partially.

In the first case, choose one of the eigenvectors of V , say $|A\rangle$, corresponding to the eigenvalue ε_A . This state will play the role of the state $|\psi^{(0)}\rangle$ in the non-degenerate case. We project eqn (9.26) with Q : we then have the mixing of this state with the states $|k\rangle$ due to the perturbation

$$\begin{aligned} Q(H_0 - E^{(0)})|\psi^{(1)}\rangle + Q(V - \varepsilon_A)|A\rangle &= 0 \quad \Rightarrow \\ Q(H_0 - E^{(0)})|\psi^{(1)}\rangle + QV|A\rangle &= 0. \end{aligned}$$

The matrix $Q(H_0 - E^{(0)})Q$ continues to be invertible as in the non-degenerate case, and one has

$$|\psi^{(1)}\rangle = Q \frac{1}{E^{(0)} - H_0} QV|A\rangle.$$

Now we proceed as before and

$$\varepsilon_2 = \langle A | VQ \frac{1}{E^{(0)} - H_0} QV | A \rangle, \quad (9.30)$$

and iteratively find the higher-order corrections. An important point is that Q is not the projection operator onto the states orthogonal to $|A\rangle$ but the operator projecting onto the states orthogonal to G_0 . Writing eqn (9.30) more explicitly for instance,

$$\varepsilon_2 = \sum'_m \langle A | V | m \rangle \frac{1}{E^{(0)} - E_m^{(0)}} \langle m | V | A \rangle;$$

we see that the states $|m\rangle$ are those corresponding to eigenvalues $E_m^{(0)} \neq E^{(0)}$ of H_0 , and *not*, the states $|B\rangle, |C\rangle \dots$ in G_0 .

Suppose instead that some of the eigenvalues of the secular equation (9.29) are equal. In this case, it is necessary to repeat the procedure. $|\psi^{(1)}\rangle$ corresponding to the degenerate sub-level is not uniquely determined. Substituting an arbitrary linear combination of these into the equation for ε_2 gives another secular equation, and so on. We shall not dwell on this further. There are cases in which things simplify: because of some symmetry, two or more states remain degenerate to all orders of perturbation. In such a case, we choose, $|A\rangle, |B\rangle$, etc., so that V is diagonal; these states will not mix and for each of these the preceding formulas apply.

9.1.2 The Stark effect on the $n = 2$ level of the hydrogen atom

A typical and well-known example of the degenerate perturbation theory is the Stark effect on the hydrogen atom: (partial) splitting of the levels due to an external electric field. For simplicity and concreteness, let us

consider the case of the $n = 2$ level, which is four times degenerate, with the states

$$|2s\rangle, \quad |2p, 0\rangle, \quad |2p, \pm 1\rangle.$$

Let us take the electric field in the z direction (the axis of quantization of the angular momentum can always be chosen in the direction of the external electric field); the perturbation has the form

$$V = -e z \mathcal{E},$$

where \mathcal{E} is the external electric field.

A selection rule

We first observe the following selection rule:

1. V is odd under parity, so that it connects only states of opposite parity: only the matrix elements of V between an s - and a p -state are non-vanishing.
2. V commutes with L_z so that only the matrix elements between the states with the same L_z can be nonzero.

It follows that the only non-vanishing matrix elements are

$$\langle 2s | V | 2p, 0 \rangle$$

and their Hermitian conjugate. The relevant wave functions in atomic units ($r_B = 1$) are

$$\psi_{2s} = \frac{1}{\sqrt{8\pi}} e^{-r/2} \left(1 - \frac{r}{2}\right), \quad \psi_{2p,0} = \frac{r e^{-r/2}}{2\sqrt{6}} \sqrt{\frac{3}{4\pi}} \cos \theta \equiv \frac{ze^{-r/2}}{2\sqrt{8\pi}}.$$

Remembering that the angular average of $\cos^2 \theta$ gives $\frac{1}{3}$, we see that

$$\begin{aligned} \langle 2s | V | 2p, 0 \rangle &= -e \mathcal{E} \frac{1}{16\pi} \int d\Omega r^2 dr e^{-r} z^2 \left(1 - \frac{r}{2}\right) = \\ &= -e \mathcal{E} \frac{1}{16\pi} \frac{4\pi}{3} \int_0^\infty dr r^4 \left(1 - \frac{r}{2}\right) e^{-r} = -e \mathcal{E} \frac{1}{12} \left(4! - \frac{1}{2} 5!\right) = 3e \mathcal{E}. \end{aligned}$$

In standard units the result is $\langle 2s | V | 2p, 0 \rangle = 3e \mathcal{E} r_B$. The matrix H in the subspace $(2s, 2p)$ is then given, in the basis of the states $|2s\rangle, |2p, 0\rangle, |2p, 1\rangle, |2p, -1\rangle$, by

$$\begin{pmatrix} E_2 & 3\mathcal{E}r_B & 0 & 0 \\ 3\mathcal{E}r_B & E_2 & 0 & 0 \\ 0 & 0 & E_2 & 0 \\ 0 & 0 & 0 & E_2 \end{pmatrix}. \quad (9.31)$$

We see that the external electric field does not completely remove the degeneracy. Only the states $|2s\rangle, |2p, 0\rangle$ are mixed and their energy shifted by the perturbation. The corrected energy can be found from

$$\det \begin{pmatrix} -\varepsilon_2 & 3er_B\mathcal{E} \\ 3er_B\mathcal{E} & -\varepsilon_2 \end{pmatrix} = 0 :$$

that is,

$$\varepsilon_2 = \pm 3 e r_B \mathcal{E}.$$

The corresponding eigenstates are

$$\begin{aligned} |2p, \pm 1\rangle, & \quad E = E_2, \\ |A\rangle \equiv \frac{1}{\sqrt{2}}(|2s\rangle + |2p, 0\rangle), & \quad E = E_2 - 3 e r_B \mathcal{E}, \\ |B\rangle \equiv \frac{1}{\sqrt{2}}(|2s\rangle - |2p, 0\rangle), & \quad E = E_2 + 3 e r_B \mathcal{E}. \end{aligned}$$

These are together known as the *linear* Stark effect. Note that the states $|A\rangle, |B\rangle$ have non-vanishing dipole moment,

$$\begin{aligned} \langle A|z|A\rangle &\simeq \frac{1}{2}(\langle 2s|z|2p, 0\rangle + \langle 2p, 0|z|2s\rangle) = -3r_B, \\ \langle B|z|B\rangle &\simeq -\frac{1}{2}(\langle 2s|z|2p, 0\rangle + \langle 2p, 0|z|2s\rangle) = +3r_B, \end{aligned}$$

which is possible because these states are not parity eigenstates. This in turn can be understood: parity is violated by the perturbation Hamiltonian hence by the total Hamiltonian.

Remarks

The $n = 2$ level of the hydrogen atom thus splits into three levels with the level spacing $3 r_B \mathcal{E}$. As $r_B \simeq 0.5 \times 10^{-8}$ cm, the spacing is

$$3 \mathcal{E} e r_B \simeq 1.5 \times 10^{-8} \mathcal{E} \text{ eV}.$$

The correction is small for electric fields $\mathcal{E} \ll 10^9$ V/cm and perturbation theory gives the correct answer. To be more precise:

- (1) Relativistic interactions between the orbital angular momentum and spin partially removes the degeneracy of the $2p$ level. ℓ is no longer a good quantum number and the levels are labeled by the total angular momentum, j^2 , where $j = l + s$. The $2p$ level, including spin, is split into a $j = \frac{3}{2}$ sub-level and another, $j = \frac{1}{2}$ sub-level. In this approximation the state $2s_{1/2}$ remains degenerate with the state $2p_{1/2}$. We have neglected these effects (known as *fine structure*, see Section 15.3.1, they are of the order of 4.5×10^{-5} eV) in the calculation above.
- (2) For very weak fields there are other effects to take into account: the interactions between the magnetic moments of the nucleus and the electron, as well as the splitting induced by the virtual emission and re-absorption of the photons, which gives rise to the splitting between the $2s_{1/2}$ and $2p_{1/2}$ levels. The latter, known as the *Lamb shift*, is about 10^{-6} eV. For the $n = 2$ level the Stark effect becomes comparable with the Lamb shift for a field of about 475 V cm^{-1} . In such a situation and for weaker fields the Stark effect becomes quadratic, as in some two-level systems.

9.1.3 Dipole interactions and polarizability

The effect of an external electric field \mathcal{E} on a system without a net charge, such as atoms and molecules, is described by a Hamiltonian of the type

$$H = H_0 + V; \quad V = -\mathbf{d} \cdot \mathcal{E}; \quad \mathbf{d} = \sum_a e_a \mathbf{x}_a$$

where H_0 is the Hamiltonian in the absence of the external field and \mathbf{d} is the *dipole* moment of the system. For an atom,

$$\sum a e_a \mathbf{x}_a = \sum_{\text{el}} -|e| \mathbf{x}_{\text{el}} + Z|e| \mathbf{x}_N = -|e| \sum_{\text{el}} (\mathbf{x}_{\text{el}} - \mathbf{x}_N).$$

In the usual approximation of an infinitely massive nucleus the center of mass of the system coincides with the position of the nucleus and we can set $\mathbf{x}_N = 0$.

Suppose that the Hamiltonian H_0 is invariant under parity. The parity operator P commuting with the Hamiltonian exists such that

$$P \mathbf{x}_a P^\dagger = -\mathbf{x}_a; \quad P^\dagger = P^{-1}; \quad \text{with} \quad [P, H_0] = 0.$$

It follows that the eigenstates of H_0 can be taken to be eigenstates of parity. For non-degenerate levels this is necessarily so, and each energy eigenstate has a definite parity, ± 1 . It follows that the expectation value of the dipole operator in *any* stationary state vanishes. Indeed,

$$\begin{aligned} \langle \psi | \mathbf{d} | \psi \rangle &\equiv \langle \psi | P^{-1} P \mathbf{d} P^{-1} P | \psi \rangle = \langle \psi | P^\dagger P \mathbf{d} P^\dagger P | \psi \rangle \\ &= |\eta_P|^2 \langle \psi | P \mathbf{d} P^\dagger | \psi \rangle = -\langle \psi | \mathbf{d} | \psi \rangle, \end{aligned}$$

and therefore

$$\langle \psi | \mathbf{d} | \psi \rangle = 0. \quad (9.32)$$

The only exception to the above rule, as already noted in the discussion of the Stark effect on the $n = 2$ levels of the hydrogen atom is the case with a degenerate level, such as the s and p states in a Coulomb potential having the same energy but the opposite parity. This kind of degeneracy is usually a result of some approximation (such as a non-relativistic treatment of the system) and removed when a more complete Hamiltonian is considered. Some systems, however, do possess such degeneracy to a good approximation, and in certain conditions it is perfectly legitimate to talk about a *permanent dipole* of the system.

From an observational point of view a dipole moment is defined by the response of the system to an infinitesimal variation of the external electric field:

$$\mathbf{D} = -\frac{\partial E}{\partial \mathcal{E}},$$

where E is the energy of the system in the presence of the field. If

$$\lim_{\mathcal{E} \rightarrow 0} \mathbf{D} = \mathbf{D}_0 \neq 0,$$

we say that the system possesses an intrinsic (or permanent) dipole moment, \mathbf{D}_0 . In the absence of degeneracy, eqn (9.32) imposes the

condition $\mathbf{D}_0 = 0$. The quadratic term in the field \mathcal{E} produces a dipole proportional to \mathcal{E} : this is called induced dipole. The variation of the energy levels and spectral lines in the presence of an external electric field is called the *Lo Surdo-Stark* effect.

Let $|\psi^{(0)}\rangle$ be an unperturbed state with definite parity. Equation (9.32) implies that to first order there is no shift of energy due to the external field. To second order, one has

$$\delta E^{(2)} = \sum'_n \langle \psi^{(0)} | \mathbf{d} \cdot \mathcal{E} | n \rangle \frac{1}{E_0 - E_n} \langle n | \mathbf{d} \cdot \mathcal{E} | \psi^{(0)} \rangle \equiv -\frac{1}{2} \alpha_{ij} \mathcal{E}_i \mathcal{E}_j ,$$

where we have introduced the *polarization tensor*:

$$\alpha_{ij} = \sum'_n \langle \psi^{(0)} | d_i | n \rangle \frac{1}{E_n - E_0} \langle n | d_j | \psi^{(0)} \rangle + (j \leftrightarrow i) .$$

Thus such a system has no permanent dipole but only an induced dipole:

$$\mathbf{D} = -\frac{\partial E}{\partial \mathcal{E}} \Rightarrow D_i = \alpha_{ij} \mathcal{E}_j .$$

The terminology is indeed appropriate: classically it corresponds to a deformation of the electron distribution in the presence of the field, which in turn yields a dipole moment. This can be explicitly checked in two ways:

- By using the Feynman–Hellman theorem (3.3). From $H = H_0 - \mathbf{d} \cdot \mathcal{E}$:

$$\alpha_{ij} \mathcal{E}_j = -\frac{\partial E}{\partial \mathcal{E}_i} = -\langle \psi | \frac{\partial H}{\partial \mathcal{E}_i} | \psi \rangle = \langle \psi | d_i | \psi \rangle .$$

- By using the first-order perturbation theory. The wave function in first-order approximation is $|\psi^{(0)}\rangle + |\psi^{(1)}\rangle$ (eqn (9.12)):

$$|\psi^{(1)}\rangle = \sum'_k |k\rangle \frac{1}{E_0 - E_k} \langle k | - d_i \mathcal{E}_i | \psi^{(0)} \rangle = \sum'_k |k\rangle \frac{\langle k | d_i | \psi^{(0)} \rangle}{E_k - E_0} \mathcal{E}_i .$$

Thus for the expectation value of the dipole one finds that

$$\begin{aligned} D_i &= \langle \psi^{(1)} | d_i | \psi^{(0)} \rangle + \langle \psi^{(0)} | d_i | \psi^{(1)} \rangle \\ &= \sum'_k \frac{\mathcal{E}_j}{E_k - E_0} \left[\langle \psi^{(0)} | d_j | k \rangle \langle k | d_i | \psi^{(0)} \rangle + \langle \psi^{(0)} | d_i | k \rangle \langle k | d_j | \psi^{(0)} \rangle \right] \\ &= \alpha_{ij} \mathcal{E}_j . \end{aligned}$$

As is seen from these formulas the order of magnitude of the effect being considered is

$$\alpha \sim \frac{e^2 a^2}{\Delta E} ; \quad [\alpha] = \text{cm}^3 .$$

If the binding energy is of electrostatic nature we expect that $\Delta E \sim e^2/r_B$ and hence $\alpha \sim r_B^3$, that is, the polarizability is proportional to the volume of the system.

Remarks The polarizability tensor α_{ij} is symmetric. It can be decomposed into a part proportional to the identity and another, traceless, as

$$\alpha_{ij} = \alpha_{kk} \frac{1}{3} \delta_{ij} + \left(\alpha_{ij} - \alpha_{kk} \frac{1}{3} \delta_{ij} \right) \equiv \alpha \delta_{ij} + \beta_{ij}; \quad (9.33a)$$

$$\alpha = \frac{2}{3} \sum'_n \langle \psi^{(0)} | d_i | n \rangle \frac{1}{E_n - E_0} \langle n | d_i | \psi^{(0)} \rangle. \quad (9.33b)$$

The operator in eqn (9.33b),

$$\sum'_n d_i | n \rangle \frac{1}{E_n - E_0} \langle n | d_i | ,$$

is obviously invariant under rotations, as the sum is taken over all possible states. By the Wigner-Eckart theorem the expectation value of α in the state $|\psi^{(0)}\rangle = |n, J, j_z\rangle$ is independent of J_z .

The tensor β_{ij} , on the other hand, transforms as an operator of spin $J = 2$. The Wigner-Eckart theorem tells us that the expectation value of β_{ij} in various states $|\psi^{(0)}\rangle = |n, J, j_z\rangle$ is proportional to $J_i J_j + J_j J_i - \frac{2}{3} \mathbf{J}^2 \delta_{ij}$, with proportionality constant B . Thus if the electric field in the z direction, the shift of the levels induced by it has the form

$$\delta E(J, J_z) = \frac{1}{2} \mathcal{E}^2 \left[\alpha + B \left(J_z^2 - \frac{1}{3} J(J+1) \right) \right]. \quad (9.34)$$

α represents the center of mass of the level shifts; by taking the trace over all states one sees that the term proportional to B vanishes, as can also be checked by noting that

$$\frac{1}{2J+1} \sum_{J_z=-J}^{J_z=+J} J_z^2 = \frac{1}{3} J(J+1).$$

Note also that the states with the same $|J_z|$ but with opposite signs of J_z remain degenerate. This can be seen as the result of the fact that the Hamiltonian, including the perturbation, is invariant under reflection with respect to a plane including the z axis, such as xz .

9.2 Quantum transitions

When the perturbation depends on time, the situation is *qualitatively* different from what has been studied in the previous section. The energy of the system is no longer conserved, and quantum transitions among the different levels are now possible. We shall be mainly concerned with the problem of calculating the rate of transition between given levels per unit interval of time, when a small perturbation is added to the system. We assume that the Hamiltonian has the form

$$H = H_0 + V(t)$$

and that the energy levels and eigenvectors $E_k, |k\rangle$ of the unperturbed Hamiltonian

$$H_0 |k\rangle = E_k |k\rangle$$

are known. The time evolution of the system is described by

$$|\Psi(t)\rangle = U(t, t_0)|\Psi(t_0)\rangle \Rightarrow i\hbar \frac{\partial \Psi}{\partial t} = H\Psi. \quad (9.35)$$

Let us suppose that initially (at time $t = 0$) the system is in one of the eigenstates of H_0 , $|\Psi(0)\rangle = |i\rangle$. What is the probability that the system at time t is in the state k ? According to the standard rule of quantum mechanics, it is given by

$$P_{ki}(t) = |\langle k|\Psi(t)\rangle|^2.$$

As the unperturbed eigenvectors $\{|k\rangle\}$ form a complete set, one can always expand the wave function in terms of these,

$$|\Psi(t)\rangle = \sum_k b_k(t)|k\rangle; \quad P_{ki} = |b_k(t)|^2, \quad (9.36)$$

with time-dependent coefficients. To find $b_k(t)$ we substitute this into Schrödinger's equation (9.35). It is convenient to factorize the standard time dependence of the unperturbed states

$$b_k(t) = e^{-iE_k t/\hbar} a_k(t); \quad P_{ki} = |a_k(t)|^2$$

so that the equation for $a_k(t)$ becomes, with $a_k(0) = \delta_{ki}$:

$$i\hbar \dot{a}_k = \sum_s e^{iE_k t/\hbar} \langle k|V|s\rangle e^{-iE_s t/\hbar} a_s \equiv V_{ks}^I(t) a_s, \quad (9.37)$$

where we have indicated by V_{ks}^I the matrix elements of the perturbing potential between the unperturbed states, including the factor $e^{i\omega_{ks} t}$:

$$V_{ks}^I(t) \equiv e^{i\omega_{ks} t} \langle k|V|s\rangle = e^{i\omega_{ks} t} V_{ks}, \quad \omega_{ks} = \frac{E_k - E_s}{\hbar}.$$

In the last of eqns (9.37) we have also introduced Einstein's convention where summation over the repeated indices is understood, a convention which will be frequently used below.

The equation for $a_k(t)$, with initial condition (9.37), can be converted into an integral equation,

$$a_k(t) = a_k(0) - \frac{i}{\hbar} \int_0^t V_{ks}^I(\tau) a_s(\tau) d\tau,$$

as can be easily verified. This form allows us to solve for $a_k(t)$ recursively,

$$a_k^{(n+1)}(t) = a_k(0) - \frac{i}{\hbar} \int_0^t V_{ks}^I(\tau) a_s^{(n)}(\tau) d\tau; \quad a(t) = \lim_{n \rightarrow \infty} a^{(n)}(t),$$

where $a_k^{(n)}$ is the solution for a_k with effects up to the order of n in powers of V included. Indeed, to lowest orders the approximate solution

is

$$a_k^{(1)}(t) = \begin{cases} -\frac{i}{\hbar} \int_0^t V_{ki}^I(\tau) d\tau ; & (k \neq i) \\ 1 & k = i \end{cases}; \quad (9.38a)$$

$$a_k^{(2)}(t) = \begin{cases} -\frac{i}{\hbar} \int_0^t V_{ki}^I(\tau) d\tau - \frac{1}{\hbar^2} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 V_{ks}^I(\tau_1) V_{si}^I(\tau_2); & k \neq i \\ 1 - \frac{1}{\hbar^2} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 V_{is}^I(\tau_1) V_{si}^I(\tau_2) & k = i \end{cases}. \quad (9.38b)$$

We leave it to the reader to verify that the formula to the second order respects the unitarity constraint (i.e., conservation of the total probability).

9.2.1 Perturbation lasting for a finite interval

If the perturbation persists only for a finite interval of time, the probability of finding the system, which was in the i -th state initially, in the k -th level at time $t = \infty$ is given by ($k \neq i$)

$$P_{i \rightarrow k} = \left| a_{ki}^{(1)}(\infty) \right|^2 = \frac{1}{\hbar^2} \left| \int_{-\infty}^{\infty} dt V_{ki} e^{i\omega_{ki} t} \right|^2,$$

to lowest order.

It is interesting to consider the cases in which the perturbation, absent at $t = -\infty$, approaches a (small) constant operator towards $t = +\infty$. In these cases, the final system is slightly different from the original one, and the variation of the energy levels and of the energy eigenfunctions (which have been studied in the previous section) must be taken into account appropriately, in calculating the *transition rate*. In fact, by integrating eqn (9.38a) by parts one finds that

$$\begin{aligned} a_{ki}^{(1)} &= -\frac{V_{ki}(\infty) e^{i\omega_{ki} t}}{\hbar\omega_{ki}} + \int_{-\infty}^t dt' \frac{\partial V_{ki}}{\partial t'} \frac{e^{i\omega_{ki} t'}}{\hbar\omega_{ki}}; \\ a_{ii}^{(1)} &= -\frac{i}{\hbar} \int_{-\infty}^t dt' V_{ii} \simeq -\frac{i}{\hbar} V_{ii}(\infty) t. \end{aligned}$$

The wave function is then

$$\begin{aligned} \psi(t) &\simeq \left(1 - \frac{i}{\hbar} V_{ii}(\infty) t \right) \psi_i^{(0)}(t) \\ &- \sum'_k \frac{V_{ki}(\infty) e^{i\omega_{ki} t}}{\hbar\omega_{ki}} \psi_k^{(0)}(t) + \sum'_k \left(\int_{-\infty}^t dt' \frac{\partial V_{ki}}{\partial t'} \frac{e^{i\omega_{ki} t'}}{\hbar\omega_{ki}} \right) \psi_k^{(0)}(t). \end{aligned}$$

The first term represents the shift of the energy level, as it is equivalent, to this order, to

$$\simeq e^{-iV_{nn}(\infty)t/\hbar} \psi_n^{(0)}(t) = e^{-i(E_n^{(0)} + V_{nn}(\infty))t/\hbar} \psi_n^{(0)}(0);$$

the second term is the first-order correction to (mixing of) the eigenfunctions, (9.12). To this order, then, the wave function at time t in

terms of the eigenfunction of the asymptotic Hamiltonian, $H_0 + V(\infty)$, is

$$\psi(t) \simeq \tilde{\psi}_n(t) + \sum'_k \left(\int_{-\infty}^t dt' \frac{\partial V_{ki}}{\partial t'} \frac{e^{i\omega_{ki}t'}}{\hbar\omega_{ki}} \right) \tilde{\psi}_k(t). \quad (9.39)$$

The required *transition probability* to the (final) k -th level starting from the (initial) i -th level is thus

$$P_{n \rightarrow k} = \left| \lim_{t \rightarrow \infty} \langle \tilde{\psi}_k(t) | \psi(t) \rangle \right|^2 = \left| \int_{-\infty}^t dt' \frac{\partial V_{ki}}{\partial t'} \frac{e^{i\omega_{ki}t'}}{\hbar\omega_{ki}} \right|^2. \quad (9.40)$$

Remarks

- These cases thus bridge the two situations considered in static perturbation theory (the previous section) and in time-dependent perturbation theory and quantum transitions.
- In the limit of a slow variation of V (the *adiabatic limit*) it follows from eqns (9.40) that

$$P_{n \rightarrow k} \simeq 0, \quad k \neq n, \quad (9.41)$$

if

$$\left| \frac{\partial V_{ki}}{\partial t} \right| \frac{1}{|V_{ki}|} \ll \omega_{ki}. \quad (9.42)$$

In fact, under these conditions V_{fi} does not contain the Fourier components comparable to ω_{kn} appreciably and the second term of eqn (9.39) vanishes. This is an example of a more general result (not necessarily related to perturbation theory), the so-called adiabatic theorem: a stationary state remains an instantaneous eigenstate, in the limit of slow variations of the Hamiltonian (see Section 12.3).

- In the opposite situation of the impulse approximation, i.e., in an almost instantaneous variation of the Hamiltonian, the exponential factor in the second term of eqn (9.39) can be brought outside the integral, as the variation $\frac{\partial V_{ki}}{\partial t}$ is non-vanishing only in a very short interval of time around $t = t_0$. Thus one finds that

$$a_{ki} \simeq \frac{e^{i\omega_{ki}t_0}}{\hbar\omega_{ki}} \int_{-\infty}^t \frac{\partial V_{ki}}{\partial t} dt = \frac{e^{i\omega_{ki}t_0}}{\hbar\omega_{ki}} V_{ki},$$

and for the transition rate

$$P_{i \rightarrow k} = |a_{ki}|^2 = \frac{|V_{ki}|^2}{\hbar^2\omega_{ki}^2}. \quad (9.43)$$

It is easy to show that this result is consistent with a more general statement of the impulse approximation, i.e., that if there is an insufficient amount of time for evolution the wave function remains invariant, during a short time interval.

9.2.2 Periodic perturbation

A very important class of perturbations correspond to the case of a small perturbative potential which varies periodically with time. We shall assume that the perturbation is turned on at $t = 0$: the general form of a self-adjoint operator with a given periodicity is

$$V(t) = \theta(t) [F e^{-i\omega t} + F^\dagger e^{i\omega t}]. \quad (9.44)$$

By inserting this into eqn (9.38a) we get

$$a_k^{(1)}(t) = -\frac{1}{\hbar} \left[F_{ki} \frac{e^{i(\omega_{ki}-\omega)t} - 1}{\omega_{ki} - \omega} + F_{ki}^\dagger \frac{e^{i(\omega_{ki}+\omega)t} - 1}{\omega_{ki} + \omega} \right]. \quad (9.45)$$

Equation (9.45) contains two terms. Each of them becomes much larger than the other when $\omega = \pm\omega_{ki}$: we deal with the *resonant frequencies* in these cases. Given $\omega > 0$, the frequencies with $\omega = \omega_{ki} = \frac{1}{\hbar}(E_k - E_i)$ correspond to a transition in which the energy increases, that is, the system absorbs the energy from the perturbation, while those with $\omega = -\omega_{ki}$ correspond to transitions in which the energy is taken away from the system. The meaning and consequences of the preceding formula vary somewhat according to whether one is dealing with a discrete or continuous spectrum, either in the initial or in the final state.

9.2.3 Transitions in a discrete spectrum

Let us suppose that the states i and k in eqn (9.45) both belong to a discrete spectrum, with $E_i < E_k$. Let us rewrite eqn (9.45) as

$$a_k^{(1)}(t) = -\frac{1}{\hbar} \left[e^{i(\omega_{ki}-\omega)t/2} F_{ki} \frac{\sin(\frac{\omega_{ki}-\omega}{2}t)}{\frac{\omega_{ki}-\omega}{2}} + e^{i(\omega_{ki}+\omega)t/2} F_{ik}^* \frac{\sin(\frac{\omega_{ki}+\omega}{2}t)}{\frac{\omega_{ki}+\omega}{2}} \right].$$

The transition probability can be written as

$$\begin{aligned} P_k(t) &= \frac{1}{\hbar^2} \left[|F_{ki}|^2 D(t, \omega_{ki} - \omega) + |F_{ki}|^2 D(t, \omega_{ki} + \omega) + \right. \\ &\quad \left. + 2 \operatorname{Re}[F_{ik} F_{ki} e^{-i\omega t}] \sqrt{D(t, \omega_{ki} - \omega) D(t, \omega_{ki} + \omega)} \right]; \\ D(t, \alpha) &= \left(\frac{\sin \alpha t / 2}{\alpha / 2} \right)^2. \end{aligned} \quad (9.46)$$

The function $D(t, \alpha)$ has a typical diffraction pattern: it has a marked maximum at $\alpha = 0$, where it takes the value t^2 . See Fig. 9.1. Its first zero is at $\alpha = 2\pi/t$; hence one can take $4\pi/t$ as the width of the curve:

$$\max(D(t, \alpha)) = t^2; \quad \Delta\alpha = \Delta\omega \sim \frac{4\pi}{t}.$$

The function $P_k(t)$ therefore has two peaks as a function of ω , at the two resonant frequencies, $\omega = \pm\omega_{ki}$.

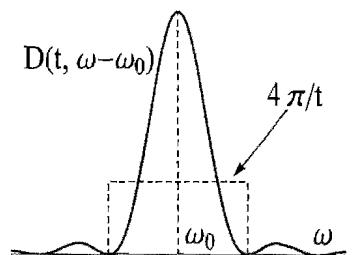


Fig. 9.1 The graph of $D(t, \omega - \omega_0)$.

Non-resonant frequencies

For ω outside the resonance region both terms in eqn (9.46) contribute. In particular, for high frequencies and for times $t \gg 1/\omega$ we may take an average, $\sin^2 x = \frac{1}{2}$, $\cos x = 0$, and find that

$$P_{ki} \simeq \frac{4|F_{ki}|^2}{\hbar^2 \omega^2}, \quad \text{for } \omega \gg \omega_{ki}.$$

In the other limit, $\omega = 0$, i.e., a constant perturbation turned on at $t = 0$, the result is

$$P_k(t) = \frac{|\mathcal{F}_{ki}|^2}{\hbar^2} \left(\frac{\sin \omega_{ki} t / 2}{\omega_{ki} / 2} \right)^2,$$

where $\mathcal{F} = F + F^\dagger$.

Resonance frequencies

For $t \rightarrow 0$

$$a_k \rightarrow -\frac{1}{\hbar} \mathcal{F}_{ki} t; \quad P_k \rightarrow \frac{|\mathcal{F}_{ki}|^2}{\hbar^2} t^2; \quad (9.47)$$

at small t the transition probabilities increase quadratically with t ; such a result cannot obviously hold at larger times, as the probabilities must satisfy $P_k \leq 1$ (unitarity) for each k . A condition for the validity of the first-order formula is therefore

$$t < T_L = \frac{\hbar}{|F_{ki}|}. \quad (9.48)$$

We must actually be more precise about what is meant by small t . If the frequency ω is well distant from the resonance region $|\omega_{ki}|$ the argument of the sine is small for $t \ll 1/\max(|\omega_{ki}|, \omega)$. In both cases, large and small frequencies, limitation (9.48) is not really significant: in fact,

- (a) For $\omega \ll |\omega_{ki}|$ the power series expansion makes sense only for $t \ll 1/|\omega_{ki}|$, but this is much smaller than (9.48) if in any case the condition for the validity of perturbation theory, i.e., $|F_{ki}| \ll \omega_{ki}\hbar$, must be satisfied.
- (b) For $\omega \gg |\omega_{ki}|$ the expansion is meaningful for $t \ll 1/|\omega|$, which is *a fortiori* much less than (9.48).

In other words, well outside the resonance region (9.48) does not present a problem, but near the resonance frequency the validity of the perturbative formula is not at all self-evident. In the following the problem will be studied by using a different approximation valid at resonance, in which the effects of non-resonant levels are neglected but otherwise the system is treated exactly, i.e., without appealing to perturbation theory.

9.2.4 Resonant oscillation between two levels

Consider a harmonic perturbation, with frequency ω in resonance with the transition frequency, $|\omega_{fi}|$. Let us call the upper state f . The time evolution of these states is principally determined by the term proportional to $e^{-i\omega t}$ in eqn (9.45) in the transition $i \rightarrow f$, and by the term $e^{+i\omega t}$ for the opposite transition $f \rightarrow i$. We can, to a good approximation, restrict ourselves to a consideration of a 2×2 subspace. The most general form of the Hamiltonian is then

$$H = \begin{pmatrix} \frac{1}{2}E_0 & Fe^{-i\omega t} \\ F^*e^{i\omega t} & -\frac{1}{2}E_0 \end{pmatrix}.$$

For convenience, we introduce

$$E_0 = \hbar\omega_0 : \quad F = \frac{\hbar\omega_1}{2} :$$

this way ω_0 is the resonance frequency, and the Hamiltonian becomes

$$\begin{aligned} H &= \frac{\hbar}{2} \begin{pmatrix} \omega_0 & \omega_1 \cos \omega t - i\omega_1 \sin \omega t \\ \omega_1 \cos \omega t + i\omega_1 \sin \omega t & -\omega_0 \end{pmatrix} \\ &\equiv \frac{\hbar}{2} (\omega_0 \sigma_z + \omega_1 (\sigma_x \cos \omega t + \sigma_y \sin \omega t)) . \end{aligned}$$

Formulated this way the problem is reduced to spin- $\frac{1}{2}$ system, with a magnetic moment $-g\mu$, placed in a static magnetic field in the z direction and in a rotating magnetic field in the (xy) plane,²

$$\mathbf{B} = B_0 \hat{\mathbf{z}} + \mathbf{B}_\perp(t), \quad \mathbf{B}_\perp(t) \equiv B_1 (\hat{\mathbf{x}} \cos \omega t + \hat{\mathbf{y}} \sin \omega t),$$

$$\hbar\omega_0 = \mu g B_0, \quad \hbar\omega_1 = \mu g B_1.$$

This problem can be solved exactly. A particularly convenient method is to use a time-dependent unitary transformation

$$|\Psi^R(t)\rangle = R(t)|\Psi(t)\rangle ;$$

$$R(t) = \exp(i \frac{\omega t}{2} \sigma_z); \quad R(0) = 1.$$

The Hamiltonian becomes

$$H^R = R(t) H R^\dagger(t) - \hbar \frac{\omega}{2} \sigma_z = \frac{\hbar}{2} ((\omega_0 - \omega) \sigma_z + \omega_1 \sigma_x),$$

it is independent of time. The problem is solved first by computing the evolution operator

$$U^R(t, 0) = e^{-iH^R t / \hbar} = e^{-it((\omega_0 - \omega) \sigma_z + \omega_1 \sigma_x) / 2},$$

which can be easily done by going to the base in which H^R is diagonal, and then transforming back by $R(t)^{-1}$. The result is (see Section 12.2 for more details):

$$U_R = \cos(\Omega t) + i \frac{\omega - \omega_0}{2\Omega} \sin(\Omega t) \sigma_z - i \frac{\omega_1}{2\Omega} \sin(\Omega t) \sigma_x,$$

²This kind of system appears in the phenomenon of *nuclear magnetic resonance*, or simply, NMR. Related phenomena of resonant absorption (and emission) of light by atoms play a central role in laser optics and atomic physics, for optical pumping, laser cooling, etc.

where

$$\Omega = \sqrt{\frac{(\omega_0 - \omega)^2}{4} + \frac{\omega_1^2}{4}} = \sqrt{\frac{(\omega_0 - \omega)^2}{4} + \frac{|F|^2}{\hbar^2}}$$

is the Rabi frequency. One finds for the transition probability

$$P_{fi}(t) = |\langle + | U_S(t) | - \rangle|^2 = |\langle + | U_R(t) | - \rangle|^2 = \frac{|F|^2}{\hbar^2 \Omega^2} \sin^2(\Omega t); \quad (9.49a)$$

$$P_{ii}(t) = 1 - P_{fi}(t). \quad (9.49b)$$

Result (9.49) has a remarkable feature. It is a non-perturbative, exact result, apart from the fact that we have neglected other, non-resonant levels, and approximated the system with a two-level system. In particular, for the resonance frequency, $\omega = \omega_0$, $|F| = \Omega \hbar$ and the amplitude of the oscillation reaches a maximum, and the spin-up state transforms to the spin-down state (and vice versa) with unit probability at half-periods, $T_{1/2} = \pi/\Omega$, even for an infinitesimal perturbation, $|F| \ll E_0$ ($\omega_1 \ll \omega_0$). Note that the problem mentioned in the previous subsection (unitarity) is absent in this treatment, even though at early times, $t \ll 1/\Omega$, it is consistent with quadratic growth, eqn (9.47).

9.3 Transitions in the continuum

For transitions in the continuum the preceding formulas requires an appropriate re-interpretation: the basic problem is that $|a_k|^2$ no longer represents the probability but the *probability density*.

Let us first of all fix the notation concerning the normalization of the states. Let α be a complete set of quantum numbers and $|\alpha\rangle$ be the corresponding states. Often we use normalization such that

$$\langle \alpha' | \alpha \rangle = N(\alpha) \delta(\alpha - \alpha'). \quad (9.50)$$

The projection operator on the states around a given value of α is then

$$|\alpha\rangle \frac{d\alpha}{N(\alpha)} \langle \alpha| \equiv |\alpha\rangle d\Phi \langle \alpha|. \quad (9.51)$$

$d\Phi$ is known as the *phase space* of the states around $|\alpha\rangle$. The probability of transition to states near $|\alpha\rangle$ is then given by

$$dP_\alpha = |\langle \alpha | \Psi(t) \rangle|^2 d\Phi. \quad (9.52)$$

In the case of harmonic (periodic) perturbation, (9.44), the transition probability from a state $|i\rangle$ to states around $|\alpha\rangle$, by restricting ourselves to the resonant contribution (and to $E_\alpha > E_i$), is given by:

$$dP_\alpha = \frac{1}{\hbar^2} |\langle \alpha | F | i \rangle|^2 \left(\frac{\sin(\frac{\omega_{\alpha i} - \omega}{2} t)}{\frac{\omega_{\alpha i} - \omega}{2}} \right)^2 d\Phi.$$

As this expression is formally infinitesimal we can take the limit of large t , by using a representation of the Dirac delta function,

$$\lim_{t \rightarrow \infty} \frac{\sin^2(xt)}{\pi t x^2} = \delta(x); \quad (9.51)$$

that is,³

$$\left(\frac{\sin(\frac{\omega_{\alpha i} - \omega}{2} t)}{\frac{\omega_{\alpha i} - \omega}{2}} \right)^2 \rightarrow \pi t \delta\left(\frac{\omega_{\alpha i} - \omega}{2}\right) = 2\pi \hbar t \delta(E_\alpha - E_i - \hbar\omega),$$

³Remember that $\delta(cx) = \delta(x)/c$.

so finally

$$dP_\alpha = t \frac{2\pi}{\hbar} |F_{\alpha i}|^2 \delta(E_\alpha - E_i - \hbar\omega) d\Phi.$$

This allows us to conclude that the transition probability *per unit time interval* is given by

$$dW_{fi} = \frac{2\pi}{\hbar} |F_{fi}|^2 \delta(E_f - E_i - \hbar\omega) d\Phi. \quad (9.52)$$

This result is known as *Fermi's golden rule*.

Remarks

- (1) The delta function in eqn (9.52) has the obvious meaning of energy conservation: the energy quantum (the photon, in the case of electromagnetic perturbation) $\hbar\omega$ of the external field is absorbed by the system which jumps to the higher level, with $E_f = E_i + \hbar\omega$.
- (2) In the case of resonance with the second term in eqn (9.44), where $E_f < E_i$, and we are dealing with the emission of an energy quantum, the argument of the delta function is $E_f - E_i + \hbar\omega$ in this case.
- (3) Formula (9.52) does not, as expected, depend on the normalization of the states chosen, eqn (9.50): the normalization factor cancels between $|f\rangle$ (which appears squared) and $d\Phi$. The initial state is normalized to unity; otherwise, the formula must be divided by $\langle i| i\rangle$.

The delta function in eqn (9.52) can be eliminated by integrating over the final states. By writing $\alpha = \{E, \beta\}$, where β stands for quantum numbers other than the energy, specifying the state $|\alpha\rangle$, we write

$$d\Phi = \rho(E, \beta) dE d\beta;$$

integration over E then gives

$$dW_{fi} = \frac{2\pi}{\hbar} |F_{fi}|^2 \rho(E_f = E_i + \hbar\omega, \beta) d\beta, \quad (9.53)$$

where the sum is over all states (β) having the same energy. Integrating over β gives the total transition rate. We note that the first argument of the state density ρ is fixed by the energy conservation.

9.3.1 State density

In the case of a free particle in the final state,

$$\psi_{\mathbf{p}}(\mathbf{r}) = e^{i\mathbf{p}\mathbf{r}/\hbar}; \quad \langle \mathbf{p}' | \mathbf{p} \rangle = (2\pi\hbar)^3 \delta^3(\mathbf{p} - \mathbf{p}'),$$

the density of states can be easily determined. The phase space is given by

$$d\Phi = \frac{d^3\mathbf{p}}{(2\pi\hbar)^3}.$$

The final state energy has the form

$$E_f = \frac{\mathbf{p}^2}{2m} + E_R,$$

where E_R is the energy of the rest of the system. From the relation $m dE = p dp$ one gets

$$\delta(E_f - E_i) d\Phi = \frac{p^2 dp d\Omega}{(2\pi\hbar)^3} \delta\left(\frac{\mathbf{p}^2}{2m} + E_R - E_i\right) \rightarrow \frac{d\Omega}{(2\pi\hbar)^3} m p_f, \quad (9.54)$$

to be used in Fermi's formula. In eqn (9.54) $p_f \equiv \sqrt{2m(E_i + R_R)}$ and $d\Omega$ is the element of the solid angle $d\Omega = d\theta \sin\theta d\phi$ of the emitted particle.

9.4 Decays

Let us now consider an initial state $|i\rangle$ which is a normalizable eigenstate of H_0 (a "bound state"). The Hamiltonian H_0 is assumed to have both continuous and discrete spectra, then perturbation V can couple the state in the discrete spectrum to the continuum. Fermi's golden rule states in this case the probability per unit interval of time for the transition, the decay rate,⁴

$$dW = \frac{2\pi}{\hbar} |V_{fi}|^2 \delta(E_f - E_i) d\Phi.$$

Summing over the final states one finds the total decay rate

$$W = \sum_f W_{i \rightarrow f} \equiv \frac{\Gamma}{\hbar} \equiv \frac{1}{\tau}. \quad (9.55)$$

Γ introduced above has the dimension of an energy; it is called the *decay width* for reasons which will be clear shortly.

Consider a system which at $t = 0$ is in the state i . If eqn (9.55) represents the decay probability of that state, the probability that the system remains in that state at the instant t must vary as

$$\frac{dP}{dt} = -\frac{\Gamma}{\hbar} P(t) \quad \Rightarrow \quad P(t) = e^{-\Gamma t/\hbar} P(0) = e^{-t/\tau} P(0). \quad (9.56)$$

Formally this result can be interpreted as follows: due to the interaction V the eigenvalue E_i of the unperturbed Hamiltonian has acquired an

⁴ It is a good exercise to check the dimensions of the various factors: we have seen that the normalization factor in the final states is taken into account by a compensating factor in $d\Phi$. The state $|i\rangle$ is normalized so that

$$[W] = [\hbar^{-1}] [V]^2 [\delta(E)] = \frac{1}{E \cdot t} E^2 \frac{1}{E} = \frac{1}{t},$$

which is the correct dimension for the decay rate.

imaginary part, $-i\Gamma/2$. The probability of finding the system in the same state is then given by the standard rule of quantum mechanics:

$$P_i(t) = |\psi(t)|^2 = \left| \psi(0) e^{-it(E_i - i\frac{\Gamma}{2})/\hbar} \right|^2 = P(0) e^{-\Gamma t/\hbar}. \quad (9.57)$$

If the system has various decay channels, i.e., various final states $\{f_k\}$, one can define various “partial decay widths” $\Gamma_k = W_{i \rightarrow f_k} \hbar$; their sum, the *total decay width*, appears in eqn (9.57).

No matter how reasonable it may look from the probabilistic point of view, eqn (9.55) is not a proof. The definition of probability used there is a macroscopic one, as in statistical mechanics. The definition of the quantum-mechanical probability $P(t)$ is

$$P(t) = |\langle i | \psi(t) \rangle|^2; \quad |\psi(0)\rangle = |i\rangle.$$

Equation (9.56), in any case, cannot be exact, as we know that at small times the transition probability grows as t^2 , and not as t , which follows from eqn (9.56). In fact, Fermi’s formula is valid only for $t \gg \hbar/\Delta$, if Δ is the typical time scale of the problem.

Let us reconsider the problem, always from a perturbative point of view, going back to eqn (9.37):

$$i\hbar \dot{a}_i = \sum_{\alpha} \langle i | V | \alpha \rangle e^{it(E_i - E)/\hbar} a_{\alpha}; \quad (9.58a)$$

$$i\hbar \dot{a}_{\alpha} = \langle \alpha | V | i \rangle e^{-it(E_i - E)/\hbar} a_i. \quad (9.58b)$$

The perturbative solution found in Section 9.2 was based on the substitution of the right-hand side by the initial condition $a_i(0) = 1$, $a_{\alpha}(0) = 0$. Let us try to solve the equation now without appealing to such an iterative procedure. Taking a hint from what has been said above, let us try to find a solution of the form

$$a_i = \exp \left[-\frac{it}{\hbar} \left(\delta E - i\frac{\Gamma}{2} \right) \right]. \quad (9.59)$$

In the exponent we have simply written an arbitrary complex number, with the real part δE and the imaginary part $-\Gamma/2$. By substituting this expression in eqn (9.58b) and integrating, one obtains $a_{\alpha}(t)$:

$$a_{\alpha}(t) = \frac{\langle \alpha | V | i \rangle}{E_i - E + \delta E - i\frac{\Gamma}{2}} \left[e^{-\frac{it}{\hbar} (E_i - E + \delta E - i\frac{\Gamma}{2})} - 1 \right],$$

and substituting it into eqn (9.58a)

$$\delta E - i\frac{\Gamma}{2} = \sum_{\alpha} \frac{|\langle \alpha | V | i \rangle|^2}{E_i - E + \delta E - i\frac{\Gamma}{2}} \left[1 - e^{\frac{it}{\hbar} (E_i - E + \delta E - i\frac{\Gamma}{2})} \right]. \quad (9.60)$$

If Ansatz (9.59) is a correct one the right-hand side of eqn (9.60) must be independent of time, at least for $t \gg \hbar/\Delta$. For large t the exponential function oscillates rapidly so the integral over α vanishes.

⁵More formally one could argue that the right-hand side is already second order in V , so that in the rest of the expression it is legitimate to set $\Gamma = \delta E = 0$.

The oscillation is mainly due to the factor $E - E_i$ in the exponent, so that in a first approximation one can set $\Gamma = \delta E = 0$ and get⁵

$$\delta E - i\frac{\Gamma}{2} \simeq \sum_{\alpha} \frac{|\langle \alpha | V | i \rangle|^2}{E_i - E} \left[1 - e^{\frac{i\pi}{\hbar}(E_i - E)} \right]. \quad (9.61)$$

As in eqn (9.51) one can approximate

$$\frac{1 - e^{\frac{i\pi}{\hbar}(E_i - E)}}{E_i - E} \xrightarrow{t \rightarrow \infty} \mathcal{P} \frac{1}{E_i - E} - i\pi \delta(E_i - E), \quad (9.62)$$

where \mathcal{P} stands for Cauchy's principal value. Such a limit is valid for $t \gg \hbar/\Delta$ in the sense that it is sufficient to assume that the integrand is smooth for such energy scales. We find that, after the initial transient, eqns (9.58) are satisfied by a function of form (9.59). The expressions for δE and Γ can be found by substituting (9.62) into eqn (9.61):

$$\delta E = \mathcal{P} \sum_{\alpha} \frac{|\langle \alpha | V | i \rangle|^2}{E_i - E} \equiv \mathcal{P} \int \frac{dE}{E_i - E} \int d\beta \rho(\beta, E) |\langle \beta, E | V | i \rangle|^2; \quad (9.63a)$$

$$\Gamma = 2\pi \sum_{\alpha} |\langle \alpha | V | i \rangle|^2 \delta(E_i - E) = 2\pi \int d\beta \rho(\beta, E_i) |\langle \beta, E_i | V | i \rangle|^2. \quad (9.63b)$$

Equation (9.63b) is exactly what has been found by using Fermi's golden rule; eqn (9.63a) tells us that the interactions cause the shift of energy, but this is of course expected from static perturbation theory. The approximation described here was proposed by Weisskopf and Wigner in 1930. The net result is that the result from perturbation theory is actually valid even for times $\Gamma t / \hbar \gg 1$ where the variation of the probabilities is no longer small.

This result allows us to obtain information about the final state of the system, after the initial state has decayed away. The final states are distributed according to the probabilities

$$\lim_{t \rightarrow \infty} |a_{\alpha}(t)|^2 = \frac{|\langle \alpha | V | i \rangle|^2}{(E_i - E + \delta E)^2 + \frac{\Gamma^2}{4}},$$

or by integrating over quantum numbers other than the energy,

$$\begin{aligned} P_E dE &= dE \int d\beta \rho(\beta, E) |\langle \alpha | V | i \rangle|^2 \frac{1}{(E_i - E + \delta E)^2 + \frac{\Gamma^2}{4}} \\ &= \frac{1}{\pi} \frac{\Gamma/2}{(E_i - E + \delta E)^2 + \frac{\Gamma^2}{4}} dE. \end{aligned} \quad (9.64)$$

Note that the distribution is correctly normalized. The meaning of eqn (9.64) is that due to the interactions the initial state acquired an

uncertainty of the energy of the order of Γ . It is quite reasonable as the initial state is no longer an energy eigenstate (stationary state): it is a metastable state. The mean lifetime τ and the energy uncertainty $\Delta E \Gamma$ satisfy the relation

$$\Delta E \cdot \tau \sim \hbar,$$

sometimes referred to as the energy-time uncertainty relation. For the excited states of the atom, eqn (9.64) implies the natural width of the spectral lines.

Beta decay

As an illustration let us consider the beta decay of a nucleus of atomic number Z and mass number A ,

$$N(A, Z) \rightarrow N(A, Z+1) + e^- + \bar{\nu}_e . \quad (9.65)$$

In the process the energy

$$Q = M_{A,Z} c^2 - M_{A,Z+1} c^2$$

is released. As the wavelengths of the electron and the neutrino involved in the process,⁶ $\hbar/p_e, \hbar/p_\nu$, are much larger than the size of the nuclei, the interaction can be considered to be point-like for all purposes, and the relevant matrix element can be parametrized in the form

$$\langle f | V | i \rangle = G_F . \quad (9.66)$$

G_F is a constant with dimension $E L^3$, known as *Fermi's constant*. The matrix element of an operator which converts the neutron into a proton can be regarded as already included in the definition of G_F . As the final state involves two free particles, the decay probability is given by

$$dW = \frac{2\pi}{\hbar} |V|^2 \delta(Q - E_e - E_\nu) \frac{d^3 p_e}{(2\pi\hbar)^3} \frac{d^3 p_\nu}{(2\pi\hbar)^3} .$$

Integration over the emission angles gives 4π for each particle. By using the relation $p^2 c^2 = E^2 - m^2 c^4$, and setting the neutrino mass to zero,

$$\begin{aligned} \frac{d^3 p_e}{(2\pi\hbar)^3} \frac{d^3 p_\nu}{(2\pi\hbar)^3} &\rightarrow \frac{(4\pi)^2}{(2\pi\hbar)^6} p_e^2 dp_e p_\nu^2 dp_\nu \\ &= \frac{1}{4\pi^4 (\hbar c)^6} \sqrt{E_e^2 - m_e^2 c^4} E_e dE_e E_\nu^2 dE_\nu . \end{aligned} \quad (9.67)$$

The integration over dE_ν eliminates the delta function and yields

$$dW = \frac{1}{\hbar} \left[\frac{G_F}{(\hbar c)^3} \right]^2 \frac{1}{2\pi^3} \sqrt{E_e^2 - m_e^2 c^4} E_e (Q - E_e)^2 dE_e . \quad (9.68)$$

Expression (9.68) is the celebrated *electron spectrum of Fermi* (see Fig. 9.2) in beta decay. Note the concavity at the high-energy end of the spectrum: it is due to the assumption of $m_\nu = 0$.

⁶ Actually, by convention, the particle which appears in the final state of the beta decay process is called the *antineutrino*, as indicated by the bar over ν_e .

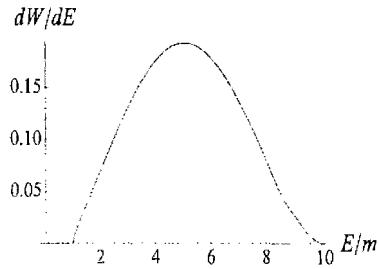


Fig. 9.2 The electron energy spectrum in a β decay.

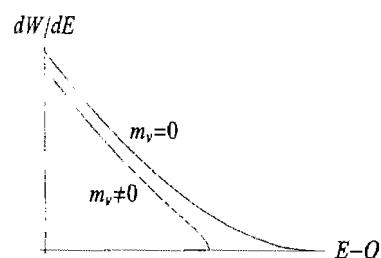


Fig. 9.3 The higher end of the electron spectrum in β decay

In the case of a non-vanishing neutrino mass, the highest end of the electron spectrum, instead of being quadratic $(Q - E_e)^2$, becomes of the form $(E_{\max} - E_e)^{1/2}$, as the factor E_ν^2 in eqn (9.67) gets replaced by $\sqrt{E_\nu^2 - m_\nu^2 c^4} E_\nu$. See Fig. 9.3.

Experiments using this idea to determine the neutrino mass from the upper end of Fermi's spectrum, however, turned out to present formidable difficulties and have not been experimentally successful to this day.

Quite recently, the fact that neutrinos have non-zero mass has been experimentally established through the observation of so-called neutrino oscillations.

Neutrino oscillations

Today three kinds of neutrinos are known to exist: the electron neutrino ν_e (which enters beta decay, eqn (9.65)), the muon neutrino ν_μ , which is produced as a main decay product of a charged pion,

$$\pi^- \rightarrow \mu^- + \bar{\nu}_\mu,$$

and the neutrino tau, ν_τ , the weak-interaction partner of the tau lepton.⁷ Let us, for simplicity and for the moment, assume that there are only two kinds of neutrinos, ν_e and ν_μ . It is quite possible that these particles, which are produced in various weak-interaction processes, are not eigenstates of the total Hamiltonian, call them ν_1 and ν_2 , but are related to the latter by a unitary transformation,

$$\nu_1 = \nu_e \cos \theta + \nu_\mu \sin \theta; \quad \nu_2 = -\nu_e \sin \theta + \nu_\mu \cos \theta;$$

$\nu_{1,2}$ have definite masses $m_{1,2}$ and evolve, in their rest frame, as

$$\nu_1 \rightarrow e^{-im_1 c^2/\hbar} \nu_1; \quad \nu_2 \rightarrow e^{-im_2 c^2/\hbar} \nu_2,$$

the evolution in a generic reference system given by Lorentz transformation. The ν_e produced in beta decay, for instance, as it travels, will oscillates between the ν_e and ν_μ states, just as a non-stationary state does in any simple two-level system (e.g., Exercise 2.7). In the case of three neutrinos, they will oscillate among the three possible states ν_e , ν_μ , and ν_τ , their oscillation rates depending on the mass differences, $m_i^2 - m_j^2$, the distance they travel, their mixing angles as well as on the neutrino energy.

The first uncontroversial evidence for neutrino oscillation was given in the so-called atmospheric neutrino experiment, in the super-Kamiokande experiment in 1998.⁸ In this experiment the muon neutrinos produced as in eqn (9.3) in the earth's atmosphere by cosmic ray collisions with atmospheric particles are seen to show a marked directional dependence, their upward flux (of the neutrinos coming through the earth's interior) being significantly less than the downward flux. The analogous phenomenon of the attenuation of the *solar neutrino* flux in the journey from the sun to the Earth (which used to be known as the "solar-neutrino problem") was confirmed as being due to the neutrino oscillations in an independent, reactor-based experiment recently (KamLAND in 2003).

⁷The names and main properties of presently known elementary particles are listed in a table in Supplement 24.

⁸This experiment, using 50000 tons of pure water and about 10000 photomultiplier tubes, is set deep in an old mine near Kamioka, Japan. The original Kamiokande experiment was designed to detect proton decays and subsequently improved so as to be a neutrino observatory.

9.5 Electromagnetic transitions

One of the most important applications of eqn (9.52) is in the study of electromagnetic transitions. We shall approach the problem here in a semi-classical approximation, by treating the electromagnetic radiation as an external, classical field.⁹ In such an approximation the Hamiltonian of a system of charged particles is given by

$$H = \sum_i \frac{1}{2m_i} \left(\mathbf{p}_i - \frac{e_i}{c} \mathbf{A} \right)^2 + V_{\text{coul}} - \mu \cdot \mathbf{B}, \quad (9.69)$$

where \mathbf{A} is the vector potential representing the radiation field, $\mathbf{B} = \nabla \times \mathbf{A}$. For simplicity in the rest of the text we shall treat atomic systems by attributing an infinite mass to the nuclei: the only variables are then those associated with the electrons.

For the electromagnetic field, we shall use the following form of plane wave, in the Coulomb gauge,

$$A_0 = 0, \quad \nabla \mathbf{A} = 0; \quad (9.70)$$

$$\mathbf{A}(\mathbf{r}) = \mathbf{A}_0 e^{i(\mathbf{k}\mathbf{r}-\omega t)} + \mathbf{A}_0^* e^{-i(\mathbf{k}\mathbf{r}-\omega t)}; \quad \mathbf{A}_0 = |\mathbf{A}_0| \boldsymbol{\varepsilon}. \quad (9.71)$$

\mathbf{k} is the wave vector, related to the angular frequency ω as $|\mathbf{k}| = \omega/c$. $\boldsymbol{\varepsilon}$ is the *polarization* vector. If the light propagates in the \mathbf{z} direction, $\mathbf{k} \parallel \hat{\mathbf{z}}$, the polarization is given by

$$\begin{aligned} \boldsymbol{\varepsilon}_x &= \hat{\mathbf{x}}; & \boldsymbol{\varepsilon}_y &= \hat{\mathbf{y}}; \\ \boldsymbol{\varepsilon}_+ &= -\frac{i}{\sqrt{2}}(\hat{\mathbf{x}} + i\hat{\mathbf{y}}); & \boldsymbol{\varepsilon}_- &= \frac{i}{\sqrt{2}}(\hat{\mathbf{x}} - i\hat{\mathbf{y}}), \end{aligned}$$

for the two cases (linear or circular polarization). $\boldsymbol{\varepsilon}_+$ (or $\boldsymbol{\varepsilon}_-$) represents light with left (or right) circular polarization; $\boldsymbol{\varepsilon}_x$ (or $\boldsymbol{\varepsilon}_y$) stands for a linearly polarized light in the x (or y) direction. The electromagnetic fields are given by

$$\mathbf{E}(\mathbf{r}) = -\frac{1}{c} \dot{\mathbf{A}} = -i \frac{\omega}{c} \mathbf{A}_0 e^{i(\mathbf{k}\mathbf{r}-\omega t)} + \text{c.c.} \quad (9.72a)$$

$$\mathbf{H}(\mathbf{r}) = \nabla \times \mathbf{A} = i \mathbf{k} \times \mathbf{A}_0 e^{i(\mathbf{k}\mathbf{r}-\omega t)} + \text{c.c.} \quad (9.72b)$$

If we consider a fixed point of space, $\mathbf{r} = 0$, the left-circular light is described classically by the electric field

$$\mathbf{E}(0) = -\sqrt{2} |\mathbf{A}_0| \frac{\omega}{c} (\sin \omega t \hat{\mathbf{x}} - \cos \omega t \hat{\mathbf{y}}).$$

(and an orthogonal, magnetic field) whose direction rotates anti-clockwise in the xy plane. The macroscopic electromagnetic energy flux is given, by an average over the time period $t \gg 1/\omega$ of the Poynting vector. Using the fact that for large time intervals $e^{-i\omega t} = 0$, it follows from eqn (9.72) that

$$\mathbf{S} = \frac{c}{4\pi} \overline{\mathbf{E} \times \mathbf{H}} = \hat{\mathbf{k}} \frac{c}{4\pi} 2 |\mathbf{A}_0|^2 \left(\frac{\omega}{c} \right)^2 = \frac{1}{2\pi} \frac{\omega^2}{c} |\mathbf{A}_0|^2 \hat{\mathbf{k}}.$$

⁹ In principle, the matter-radiation system must be treated as a coupled quantum system $H_{\text{matter}} + H_{\text{radiation}}$, with an interaction term H_I . The approximation here consists of treating the radiation as an external, time-dependent (but classical) electromagnetic field, and neglecting the quantum effects associated with the radiation fields. See Supplement 22.6 for a simplified treatment of quantization of the electromagnetic field.

The absolute value of the Poynting vector is, for a plane wave, equal to the intensity of radiation, that is the energy flux through a unit surface, perpendicular to the direction of propagation, $\hat{\mathbf{k}}$:

$$I = \frac{1}{2\pi} \frac{\omega^2}{c} |\mathbf{A}_0|^2 = n_\gamma \hbar \omega . \quad (9.73)$$

¹⁰This is a purely pragmatic way to relate the energy carried by the photons to the amplitude and frequency of the semi-classical electromagnetic wave. In the case of a single harmonic oscillator, we have discussed (Section 3.4) how the quantized motion of the oscillator compares with that of the classical solution. As in that simple example, we expect that the present approach is a reasonably good approximation for higher excitations (many photons).

We have introduced here the “number of photons” n_γ , each with energy $\hbar \omega$, which constitute the wave.¹⁰

Incoherent radiation

General electromagnetic radiation can be decomposed into a sum of plane waves. For simplicity we shall write the superposition as a discrete sum,

$$\mathbf{A} = \sum_i \mathbf{A}_0 e^{i\varphi_i} e^{i(\mathbf{k}_i \cdot \mathbf{r} - \omega_i t)} + \text{c.c.} \quad (9.74)$$

The relative phases among the various components, φ_i , are related to the degree of coherence. We shall assume below a *totally incoherent* monochromatic radiation in which the phases φ_i are randomly distributed. This implies that, in the calculation of the Poynting vector and in general quadratic forms,

$$\overline{e^{i(\varphi_i - \varphi_j)}} = \delta_{ij} . \quad (9.75)$$

The average is intended over a statistical ensemble of the phases. For the Poynting vector one finds that

$$\mathbf{S} = \sum_i \hat{\mathbf{k}}_i \frac{1}{2\pi} \frac{\omega_i^2}{c} |\mathbf{A}_0^{(i)}|^2 . \quad (9.76)$$

For a well-collimated beam, we can assume that the direction of the propagation is the same for all the components, and eqn (9.76) gives for the intensity of the radiation

$$I = \sum_i \frac{1}{2\pi} \frac{\omega_i^2}{c} |\mathbf{A}_0^{(i)}|^2 = \sum_i I_i ,$$

that is, the intensity of the light is the sum of those of the components. Passing to the integral from the sum, the spectral intensity can be defined as

$$I(\omega) \Delta\omega = \sum_{\omega_i \in \omega \pm \Delta\omega/2} I_i ;$$

$$I = \int d\omega I(\omega) .$$

9.5.1 The dipole approximation

¹¹We have used the transversality of \mathbf{A} to write $\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p} = 2 \mathbf{A} \cdot \mathbf{p}$.

To first order in the electromagnetic interaction, and neglecting all the effects of magnetic dipoles, interaction (9.69) has the form¹¹

$$V = -\frac{e}{mc} \sum_e \mathbf{A}(\mathbf{r}_e) \cdot \mathbf{p}_e,$$

and the relevant matrix elements have the form

$$V_{fi} = -\frac{e}{mc} |\mathbf{A}_0| \sum_e \langle f | e^{i\mathbf{k}\mathbf{r}_e} \boldsymbol{\epsilon} \cdot \mathbf{p}_e | i \rangle + c.c., \quad (9.77)$$

where eqn (9.74) has been used. In most transitions the wavelength of the electromagnetic radiation is much larger than the characteristic size of the system, for instance, $\lambda \sim 10^4 \text{ \AA}$ for optical transitions while $r_B \sim 1 \text{ \AA}$. This means that for wave functions of limited space extension, such as those of the bound electrons in atoms, one can make a substitution $k\tau = 2\pi r/\lambda \ll 1$ in the exponent of (9.77) to a good approximation. The expression further simplifies if we note that

$$\begin{aligned} \langle f | \mathbf{p} | i \rangle &= m \langle f | \dot{\mathbf{r}} | i \rangle \\ &= m \frac{i}{\hbar} \langle f | [H, \mathbf{r}] | i \rangle = m \frac{i(E_f - E_i)}{\hbar} \langle f | \mathbf{r} | i \rangle = i m \omega_{fi} \langle f | \mathbf{r} | i \rangle. \end{aligned}$$

The resulting matrix element is that of an electric dipole, and the approximation just described is known as the *dipole approximation*. The matrix element (9.77) can be rewritten as

$$V_{fi} = -i \frac{e}{c} \omega_{fi} |\mathbf{A}_0| \boldsymbol{\epsilon} \cdot \mathbf{r}_{fi}; \quad \mathbf{r}_{fi} \equiv \sum_e \langle f | \mathbf{r}_e | i \rangle. \quad (9.78)$$

\mathbf{r}_{fi} is the matrix element of the unit dipole moment.

Selection rules

Equation (9.78) imposes stringent selection rules for possible transitions (called *allowed transitions*) in the dipole approximation:

- (r1) \mathbf{r} is a polar vector; therefore assuming that parity is a good quantum number the parity of the states $|i\rangle$ and $|f\rangle$ must be opposite: $P_f = -P_i$.
- (r2) \mathbf{r} is a vector under space rotations. Thus the Wigner–Eckart theorem implies the conditions

$$(J_f - J_i) = \pm 1, 0; \quad 0 \not\rightarrow 0,$$

as the total angular momentum is conserved.

- (r3) If the spin–orbit interactions $\propto \mathbf{L} \cdot \mathbf{S}$ are neglected, the total orbital angular momentum L and the total spin S are good quantum numbers according to which the states are classified. The operator \mathbf{r} acts only on the orbital variables, so consideration of the point (r2) above can be again applied to give the selection rule

$$S_f = S_i; \quad (L_f - L_i) = \pm 1, 0; \quad 0 \not\rightarrow 0$$

Let us recall, to avoid any misunderstanding, that the parity of an electronic system in an atom is the product of the orbital parity of individual electrons $P = (-1)^{\sum_i \ell_i}$ and that the sum $\sum_i \ell_i$ does not in general coincide with L .

There are also selection rules related to the polarization states.

- (p1) In general $\epsilon \cdot r$ can be decomposed into the sum of three spherical components r_z, r_+, r_- , corresponding to the three spherical harmonics $Y_{10}, Y_{1\pm 1}$. This implies that for a dipole transition the eigenvalue M of J_z should satisfy

$$M_f - M_i = \pm 1, 0.$$

In case L, S are good quantum numbers, one also has

$$S_{z,f} = s_{z,i}; M_f^{(L)} - M_i^{(L)} = \pm 1, 0.$$

- (p2) If the direction of light propagation and its polarization are also specified, we can make a more detailed prediction.

Let us discuss the last point (p2), taking as a concrete example the absorption of light with left-circular polarization. The quantization axis can be chosen to coincide with the direction of the propagation of light, z . In the absorption process only the first term of eqn (9.71) is in resonance, and the matrix element is therefore proportional to ϵ . The selection rule in this case is

$$\epsilon_+ \cdot r \propto x + iy \Rightarrow M_f = M_i + 1.$$

(Vice versa, for the incoming, right-circular polarized light, we would have $M_f = M_i - 1$.)

Let us in particular note that as $\epsilon_z = 0$ for light propagating in the z direction the transition with $M_f = M_i$ is forbidden. In terms of the quantized picture of the electromagnetic field (photons), this fact has a simple interpretation. A photon moving in the direction z has only the projection of the spin, and not of its orbital angular momentum L_z , as $k/\parallel \hat{z}$. The projection of spin along the direction of motion is known as *helicity*. The left- or right-circularly polarized light corresponds to photons of helicity plus or minus 1.¹²

In an *emission* process, it is the second term of eqn (9.71), proportional to ϵ^* , that matters. For the emission of the left-polarized photons the matrix element is then proportional to

$$\epsilon_+^* \cdot r \propto x - iy \Rightarrow M_f = M_i - 1.$$

This expresses the fact that the emission of a photon now takes away a unit of angular momentum.

We shall leave to the reader the exercise of analyzing various different cases. These considerations will be important, for instance, in the analysis of spectral lines in the presence of a magnetic field, the Zeeman effect, which will be studied in Chapter 15 dedicated to atoms.

To make progress, it is necessary to make a distinction between the two cases of monochromatic radiation and “wide-band” radiation. As we shall see, the atomic energy levels are in general not exactly determined, having non-vanishing widths, Γ , except for the ground state. What is meant by the two types of radiation is really whether or not the spectral distribution in the radiation is narrower or wider, with respect to the level widths involved in the transition: $\hbar\Delta\omega \ll \Gamma$ or $\hbar\Delta\omega \gg \Gamma$.

¹²The fact that the photon, a particle with vanishing rest mass, has only two helicity states ± 1 follows from the representation theory of the Lorenz group: it is a consequence of special relativity; it is a special case of the result valid for any particle without rest mass, but with any spin. In the case of the electromagnetic field, the fact that its quantum, the photon, has only two helicity states also follows from the gauge invariance of the theory. Due to the possibility of imposing a gauge choice such as in eqn (9.70), the number of independent degrees of freedom described by (\mathbf{A}, ϕ) is reduced to two from four.

Monochromatic radiation

This case corresponds to the case treated in Subsection 9.2.4. In the resonant background radiation there is an oscillation between the two levels, a and b . The relevant matrix element is

$$V_{ba} = -i \frac{e}{c} \omega_{ba} \mathbf{A}_0 \mathbf{r}_{ba} = -i \frac{1}{c} \omega_{ba} A_0 d_{ba}; \quad d_{ba} = e \boldsymbol{\varepsilon} \cdot \mathbf{r}_{ba}. \quad (9.79)$$

By using eqn (9.73) one finds that

$$A_0^2 = \frac{2\pi c}{\omega^2} I; \quad |V_{ba}|^2 = \frac{2\pi}{c} \left(\frac{\omega_{ba}}{\omega} \right)^2 I d_{ba}^2 \simeq \frac{2\pi}{c} I d_{ba}^2;$$

and, from eqn (9.49), the probability of oscillation for a system which was originally in the state $|a\rangle$ is given by

$$P_{ba}(t) = \frac{|V_{ba}|^2}{\hbar^2 \Omega^2} \sin^2(\Omega t); \quad \Omega^2 = \frac{(\omega_{ba} - \omega)^2}{4} + \frac{2\pi}{\hbar^2 c} I d_{ba}^2.$$

Note that the oscillation frequency depends on the intensity of the radiation, and in perfect resonance, $\Omega \propto \sqrt{I}$.

We warn the reader that the formulas derived here are valid only for the absorption or emission *induced* by the external field. See Subsection 9.5.4 for a discussion of spontaneous emission from an excited atom.

9.5.2 Absorption of radiation

A more common case is that of the absorption of non-monochromatic light by a system, say an atom, which transits from a state a to another state b , with the energies $E_b > E_a$. In this case only the first term of eqn (9.71) is in resonance, and by using eqns (9.79) and (9.74) we see that the amplitudes reads

$$a_{ba} = -\frac{\omega_{ba}}{\hbar c} \sum_{\omega} e^{i\varphi_{\omega}} A_0(\omega) d_{ba} \frac{\sin(\frac{\omega_{ba}-\omega}{2}t)}{\frac{\omega_{ba}-\omega}{2}}. \quad (9.80)$$

This is the sum of the amplitudes from the various frequencies which compose the radiation. In eqn (9.80) the time-dependent phases are included in φ_{ω} . We now make the assumption of incoherent light; in this case eqn (9.75) tells us that

$$\begin{aligned} |a_{ba}|^2 &= \frac{\omega_{ba}^2}{\hbar^2 c^2} |d_{ba}|^2 \sum_{\omega, \omega'} A_0(\omega) A_0(\omega') \frac{\sin(\frac{\omega_{ba}-\omega}{2}t)}{\frac{\omega_{ba}-\omega}{2}} \frac{\sin(\frac{\omega_{ba}-\omega'}{2}t)}{\frac{\omega_{ba}-\omega'}{2}} e^{i(\varphi_{\omega} - \varphi_{\omega'})} \\ &= \frac{\omega_{ba}^2}{\hbar^2 c^2} |d_{ba}|^2 \sum_{\omega} A_0^2(\omega) \left(\frac{\sin(\frac{\omega_{ba}-\omega}{2}t)}{\frac{\omega_{ba}-\omega}{2}} \right)^2. \end{aligned}$$

Equations (9.51) and (9.73) then give

$$\begin{aligned} P_{ba} &= \frac{\omega_{ba}^2}{\hbar^2 c^2} |d_{ba}|^2 \sum_{\omega} A_0^2(\omega) \pi t \delta\left(\frac{\omega_{ba}-\omega}{2}\right) \\ &= \int d\omega I(\omega) \frac{2\pi c}{\omega^2} \frac{\omega_{ba}^2}{\hbar^2 c} |d_{ba}|^2 2\pi t \delta(\omega_{ba} - \omega), \end{aligned}$$

and for the transition probability per unit interval of time (transition rate)

$$W_{ba} = \frac{4\pi^2}{\hbar^2 c} |d_{ba}|^2 I(\omega_{ba}) . \quad (9.81)$$

In concrete applications one needs to specify the atomic states and the polarization of the light. Often the atoms will not be in pure states, and the part dependent on the dipole moment in eqn (9.81) must be substituted as

$$|d_{ba}|^2 = \langle b | \boldsymbol{\varepsilon} \cdot \mathbf{d} | a \rangle \langle a | \boldsymbol{\varepsilon}^* \cdot \mathbf{d} | b \rangle \rightarrow \text{Tr} (\Pi_b \boldsymbol{\varepsilon} \cdot \mathbf{d} \rho_a \boldsymbol{\varepsilon}^* \cdot \mathbf{d}) ,$$

where ρ_a is the density matrix for the initial atoms and Π_b is the projection operator onto the state we are going to observe. Let us consider the case in which the angular momentum of the final state is not measured, and the initial state is unpolarized. Such an initial state is described by a density matrix,

$$\rho_a^0 = \frac{1}{2J_a + 1} \sum_{J_z} |J_z\rangle \langle J_z| ;$$

that is, one takes an average over J_z . Summing over all possible states in the final state is equivalent to using the density matrix for the unpolarized mixed state and multiplying by the multiplicity of the state, $g_b = 2J_b + 1$. Thus the matrix element can be simplified as

$$|d_{ba}|^2 = g_b \text{Tr} (\rho_b^0 \boldsymbol{\varepsilon} \cdot \mathbf{d} \rho_a^0 \boldsymbol{\varepsilon}^* \cdot \mathbf{d}) . \quad (9.82)$$

In eqn (9.82) the matrices ρ_a^0 and ρ_b^0 are invariant under rotations so that

$$\begin{aligned} \text{Tr} (\rho_b^0 d_x \rho_a^0 d_x) &= \text{Tr} (\rho_b^0 d_y \rho_a^0 d_y) = \text{Tr} (\rho_b^0 d_z \rho_a^0 d_z) = \frac{1}{3} \text{Tr} (\rho_b^0 \mathbf{d} \rho_a^0 \mathbf{d}) ; \\ \text{Tr} (\rho_b^0 d_x \rho_a^0 d_y) &= \text{Tr} (\rho_b^0 d_x \rho_a^0 d_z) = \text{Tr} (\rho_b^0 d_y \rho_a^0 d_z) = 0 ; \end{aligned}$$

that is,

$$\text{Tr} (\rho_b^0 d_i \rho_a^0 d_j) = \frac{1}{3} \text{Tr} (\rho_b^0 \mathbf{d} \rho_a^0 \mathbf{d}) \delta_{ij} \equiv \frac{1}{3} \overline{\mathbf{d}_{ba}^2} \delta_{ij} . \quad (9.83)$$

In this case the transition probability between the two levels per unit interval of time is given by

$$W_{ba} = B_{ba} I(\omega_{ba}) , \quad B_{ba} = g_b \frac{4\pi^2}{3\hbar^2 c} \overline{\mathbf{d}_{ba}^2} . \quad (9.84)$$

9.5.3 Induced (or stimulated) emission

Let us consider again the transition between two states $|a\rangle, |b\rangle$, with $E_b > E_a$, but suppose now that the initial state is the excited state b . The probability amplitude $b \rightarrow a$ is given, if we limit ourselves to the resonant contribution, by

$$V_{ab} = -i \frac{e}{c} \omega_{ab} \mathbf{A}_0^* \mathbf{r}_{ab} = -i \frac{1}{c} \omega_{ab} A_0 d_{ab} ; \quad d_{ab} = e \boldsymbol{\varepsilon}^* \cdot \mathbf{r}_{ba} .$$

Formally the only difference from the case of absorption is the substitution $\epsilon \rightarrow \epsilon^*$ and the exchange of the indices a, b . From a physical point of view, it is important that the polarization and frequency of the outgoing light and those of the incoming light are exactly the same. As $\epsilon \perp \mathbf{k}$ and because the formula is valid for any initial polarization, this means that the direction of the propagation of the final radiation is also the same as the initial radiation. In this way the system emits coherent light with identical characteristics as the incoming light, “amplifying” the latter.¹³

The determination of the transition probability is identical to the previous case (absorption), except for the exchange of the indices a and b , so one gets

$$W_{ab} = \frac{4\pi^2}{\hbar^2 c} |d_{ab}|^2 I(\omega_{ba}). \quad (9.85)$$

For unpolarized initial states and for transitions in which the final polarization is not observed, the considerations of the preceding paragraph are still valid, and one finds that the transition probability per unit time between the two levels is given by

$$W_{ab} = B_{ab} I(\omega_{ba}), \quad B_{ab} = g_a \frac{4\pi^2}{3\hbar^2 c} \overline{d_{ab}^2}. \quad (9.86)$$

9.5.4 Spontaneous emission

An excited state $|b\rangle$ can actually decay into a lower state $|a\rangle$ by emitting a photon, with energy $\hbar\omega = E_\gamma = E_b - E_a$, *without* there being initially any external radiation field of the right frequency. One deals in this case with *spontaneous emission*. This important process cannot be calculated by a semi-classical treatment of radiation as has been done up to now, simply because there is no external radiation to start with, and also because the final state “radiation” consists of just one photon, which is not interpretable classically.

A proper approach to such a process is to treat the whole system quantum mechanically, including the Hamiltonian of the electromagnetic field and the radiation-matter electromagnetic interactions, in the so-called “second quantization” formalism. Such a formalism will be sketched briefly in Supplement 22.6 of this chapter. Initially, the atom is in an excited state while the radiation system $H_{\text{radiation}}$ is in its ground state (vacuum), i.e. in a state with no photons. In the final state the atom is in the lower state, while the radiation system is in an excited state, with one photon. This is a simple application of Fermi’s golden rule to compute the transition rate.

Here in the main text we shall bypass these problems, by appealing to the so-called correspondence principle, advocated by Bohr. This states in this case that for large quantum numbers n (very excited states), if a classical motion (i.e., atomic oscillation) is decomposed into various Fourier components, then the quantum-mechanical matrix elements $\langle n+k|q|n\rangle$, $k = 1, 2, \dots$, correspond to classical k -th harmonics of the

¹³This important quantum mechanical property of the stimulated emission, first noted by Einstein during his re-derivation of Planck’s formula, is at the basis of important applications such as the *maser* (microwave amplification of stimulated emission of radiation), or *laser* (light amplification by stimulated emission of radiation).

classical frequencies. The solution for the Liénard–Wiechert potential in the presence of an oscillating charge (with a given frequency) will indeed have all the harmonics, $\omega, 2\omega, \dots$. Justification for such a “principle” will be given in Chapter 11 dedicated to the semi-classical (WKB) approximation; here we shall use it as a practical (heuristic?) way to deduce the transition probability due to a spontaneous emission.

Classically the total energy irradiated from a system, in a dipole approximation, has the well-known form

$$-\frac{dE}{dt} = I = \frac{2}{3c^3} \dot{\mathbf{d}}^2.$$

If the motion is multi-periodic, it can be decomposed into many harmonics with frequencies ω_n ; the intensity of the emitted radiation is

$$I_n = \frac{4\omega_n^4}{3c^3} |\mathbf{d}_n|^2. \quad (9.87)$$

Equation (9.87) refers to the total emitted energy, summed over the final polarization of the light and over the final state of the matter.

By using the correspondence principle we now translate formula (9.87) into a quantum-mechanical one: the energy irradiated per unit time interval is equal to the probability of decay per second times the energy of the single photon, $\hbar\omega$:

$$\hbar\omega_{ba} W_{ab}^{(S)} = \frac{4\omega_{ba}^4}{3c^3} \sum_{pol.a} |\langle a|\mathbf{d}|b\rangle|^2.$$

The sum over the final polarization can be substituted again by the average times the number of the states, g_a , of the level. Having summed over all the directions of emission and of polarization the formula no longer depends on the initial orientation of the angular momentum, so that one gets, by using the notation of eqn (9.83),

$$W_{ab}^{(S)} = g_a \frac{4\omega_{ba}^3}{3\hbar c^3} \overline{\mathbf{d}_{ab}^2}. \quad (9.88)$$

Note that $W_{ab}^{(S)}$ and the quantity B_{ab} appearing in the formula for the induced emission, eqn (9.86), are related by

$$W_{ab}^{(S)} = \frac{\hbar\omega_{ba}^3}{\pi^2 c^2} B_{ab}. \quad (9.89)$$

9.6 The Einstein coefficients

It is interesting to note that previous relations between probabilities of absorption, induced emission, and spontaneous emission were derived by Einstein prior to the formulation of modern quantum mechanics. A by-product of this analysis is a new derivation of the Planck distribution law. The coefficients A, B of the previous sections are known as Einstein’s coefficients.

Let us consider a two-level system immersed in black body radiation, with intensity, $I(\omega)$, or with energy density

$$u(\omega) = \frac{I(\omega)}{c},$$

which we suppose to be unknown. Let N_a and N_b be the populations of the two levels, with constant $N_a + N_b$. The population of each level will change with time due to the electromagnetic transitions studied above: for the upper level one has

$$\frac{dN_b}{dt} = -W^{(S)} N_b - B_{ab} N_b I(\omega) + N_a B_{ba} I(\omega), \quad (9.90)$$

where we have defined

$$\omega = \frac{E_b - E_a}{\hbar}.$$

The first term stands for the decrease of the population of the upper level due to spontaneous emission; the other two terms correspond to induced emission and absorption, respectively.

In thermal equilibrium, the number of atoms in the two levels must be stationary and furthermore their ratio must be given by Boltzmann's formula,

$$\frac{dN_b}{dt} = 0; \quad \frac{N_a}{N_b} = \frac{g_a e^{-E_a/kT}}{g_b e^{-E_b/kT}} = \frac{g_a}{g_b} e^{\frac{(E_b - E_a)}{kT}}. \quad (9.91)$$

We first note that there is a simple relation

$$B_{ab} g_b = B_{ba} g_a \quad (9.92)$$

between the B 's appearing in formulas (9.84) and (9.86) for the induced absorption and emission processes. Such an equality is necessary for having a stationary result for N_b , as the intensity $I(\omega) = c u(\omega)$ is known to diverge as $\propto kT$ as $T \rightarrow \infty$, from the Rayleigh-Jeans formula, (1.7), which is known to be valid at low frequencies (which means high temperatures at fixed ω). One gets from eqn (9.90), by using eqns (9.92) and (9.91),

$$I(\omega) = \frac{W^{(S)} N_b}{N_a B_{ba} - N_b B_{ab}} = \frac{W^{(S)} / B_{ba}}{\frac{N_a}{N_b} - \frac{B_{ab}}{B_{ba}}} = \frac{W^{(S)} g_b}{\frac{B_{ba}}{e^{(E_b - E_a)/kT} - 1}}. \quad (9.93)$$

We now use

- (a) Wien's law, eqn (1.9), which is known to be valid at low temperatures (or equivalently, at high frequencies at fixed T) to identify $\frac{E_b - E_a}{kT} = \beta \omega/T$, with $\beta = \hbar/k$.
- (b) The Rayleigh-Jeans law (valid at high temperatures) to get the consistency condition

$$\frac{W^{(S)} g_b}{B_{ba}} \frac{kT}{g_a \hbar \omega} = c \frac{\omega^2}{\pi^2 c^3} kT \Rightarrow W^{(S)} = \frac{g_a \hbar \omega^3}{g_b \pi^2 c^2} B_{ba}.$$

But this relation is indeed satisfied ((9.89)) by the formulas we explicitly obtained for $W^{(S)}$ and B_{ab} in the dipole approximation! Substituting this into eqn (9.93), we find the Planck distribution,

$$c u(\omega) = I(\omega) = \frac{\hbar \omega^3}{\pi^2 c^2} \frac{1}{e^{\hbar \omega/kT} - 1},$$

showing that there is indeed a remarkable consistency between thermodynamics and quantization (of matter *and* radiation), and that Planck's formula represents just such a consistency condition.

Guide to the Supplements

Perturbation theory has a wide variety of physical applications which could not be satisfactorily covered in the discussion here. Supplement 21.1 will discuss various problems which involve the application of perturbation theory, as well as the more theoretical issue of divergence of perturbative series and possible methods of resummation.

Some of these issues are considered in the numerical notebooks. Using Mathematica it is possible to derive several analytical results not easily obtainable otherwise; we quote as an example the analytical form for the Stark effect on an arbitrary level of hydrogen atom (in principle to arbitrary order) contained in NB-9.3.

Problems

- (9.1) Consider the Hamiltonian $H = H_0 + H_1$, where

$$H_0 = \frac{p^2}{2m} + \frac{m}{2} \omega^2 x^2; H_1 = g \frac{\omega}{2} (xp + px), g \in \mathbb{R}.$$

(a) Compute the exact spectrum of H .

(b) Apply perturbation theory, with H_1 as a perturbation, up to second order in g and compare the results with that of (a).

- (9.2) A harmonic oscillator with mass m and frequency ω is subject to an external perturbation. Compute the corrections to the energy eigenvalues due the following perturbations

$$g_1 q; \quad \frac{1}{2} g_2 q^2, \quad \frac{1}{2} g_3 q^3, \quad \frac{1}{2} g_4 q^4.$$

to first and second orders of perturbation theory.

- (9.3) Consider the proton as a small uniformly charged sphere of radius R . Compute how the hydrogen levels are affected by this hypothesis.

- (9.4) Suppose that the Coulomb potential has the behavior $1/r^{(1+\epsilon)}$, with $\epsilon \ll 1$. Compute the effect on the hydrogen levels and derive a bound on ϵ by comparing the $2p-2s$ induced energy gap with the observed Lamb shift correction. The theory agrees with experiment at least up to $\Delta E/h = 10^4$ kHz.

- (9.5) Compute the effect of an electric field on the levels of a charged harmonic oscillator. Compute the induced electric dipole and verify the Feynman-Hellmann theorem.

- (9.6) Solve the two-level system

$$H = E_0 + \begin{pmatrix} -E_1 & -\delta \\ -\delta^* & E_1 \end{pmatrix} \equiv E_0 - \sigma \cdot \mathbf{B},$$

exactly, and compare the result with that of perturbation theory as $B \rightarrow 0$. Discuss how the phases of the eigenstates depend on B .

- (9.7) A two-level system as in the previous problem can be considered as a simplified model of an amino-

nia molecule, NH_3 . The nitrogen atom's position with respect to the plane of three hydrogen atoms corresponds, classically, to two equivalent configurations. Define a parity operator for this model and discuss its properties. Study the effect of an electric field on the system.

- (9.8) Study the effect of an electric field (the Lo Surdo-Stark effect) on the $n = 2$ states of the hydrogen atom, neglecting the spin.

- (9.9) A particle moves in a one-dimensional potential U . Suppose that we know all the eigenfunctions for this system and that a perturbation $V[a]$ acts on the system. The computation of first-order corrections to the eigenvalues is, in normal cases, reduced to an integral. The computation of the first-order correction $\Psi^{(1)}$ to the wave functions generically involves a sum over infinite terms. Show that the problem of finding $\Psi^{(1)}$ can be recast into the form of solving an inhomogenous partial differential equation. Set $\Psi^{(1)}(x) = f(x)\Psi^{(0)}(x)$ for first-order eigenfunctions and write an equation for f . In particular consider the case of a spherically symmetric potential and a perturbation in the form of a constant electric field. This method of solution is known as the Dalgarno-Lewis' method.

- (9.10) Use the results of problem (9.9) to compute the approximate polarizability for a particle moving in a one-dimensional potential well of width a , with the condition $a\chi \ll 1$, where $\chi = \sqrt{2m|E|/\hbar^2}$ and E is the binding energy.

- (9.11) Use the results of problem (9.9) to compute the polarizability for the ground-state hydrogen atom. Give an estimate of the contribution of the continuum states.

- (9.12) Spin interactions split $n = 2$ degenerate levels of the hydrogen atom into two levels ($2s_{1/2}, 2p_{1/2}$) and $2p_{3/2}$. Study the effect of an electric field (the Lo Surdo-Stark effect) taking into account this separation. The level ($2s_{1/2}, 2p_{1/2}$) is split due to radiative corrections (the Lamb shift), the separation being about 10^{-6} eV. What are the effects of this separation on the Lo Surdo-Stark effect?

- (9.13) The parabolic coordinates (ξ, η, φ) are defined by

$$x = \sqrt{\eta\xi} \cos(\varphi), \quad y = \sqrt{\eta\xi} \sin(\varphi), \quad z = \frac{\xi - \eta}{2}.$$

In a notebook (NB-6.4-ParabolicCoordinates.nb) it has been shown that Schrödinger's equation for a hydrogen atom is separable in these coordinates. Study the Lo Surdo-Stark effect in parabolic coordinates. Compute first- and second-order effects for an arbitrary state.

- (9.14) In a helium atom consider the electron-electron interaction as a small perturbation. Compute to lowest order the ground-state energy of the helium atom. Compute the three-dimensional Fourier transform for the functions

$$\frac{1}{r}, \quad \frac{e^{-r\mu}}{r}, \quad e^{-r\mu},$$

and show how these results can be used to solve the problem.

- (9.15) In a helium atom consider the electron-electron interaction as a small perturbation. Compute to lowest order the energy of the first excited S state of the helium atom. Discuss how Pauli's principle selects possible states.

- (9.16) Consider the helium atom in a generic $(1s, nL)$ state. Interactions between the electrons are taken into account by perturbation theory. As the unperturbed Hamiltonian for excited states, take an asymmetric form with potential Z/r for one electron and $(Z - 1)/r$ for the other. Compute the ground-state energy.

- (9.17) An excited level of an alkali atom can be described by the wave function of the outermost electron in a screened Coulomb potential due to the nucleus and the other electrons (with the net charge $|e|$) corrected by a small central perturbation $V(r)$. Show that in this approximation the spectrum of the optical electron can be described by a corrected Rydberg type formula.

- (9.18) A free particle moves inside a box of dimensions (a, b, c) . Discuss how the energy levels change upon varying a, b, c . Show that for isotropic modification of the size, i.e. changes of length unit, the expression for the mean energy of a stationary state reduces to the equation of state for a non-relativistic perfect gas.

- (9.19) A free particle moves inside a spherical well of radius R . Discuss how the energy levels change if the sphere is deformed to an ellipsoid of axes (b, b, a) , with $b < a$. Generalize the result to an arbitrary deformation.

- (9.20) Compute the cross section for the photoelectric effect on a hydrogen atom in the ground state, assuming $ka_B \ll 1$, where k is the wave number of the photon. Approximate the wave function of the outgoing electron with a plane wave and discuss the validity of the approximations used.

- (9.21) Write explicitly the form of the Hamiltonian for the matter-radiation interactions taking into account the dipole, quadrupole and magnetic dipole interactions. Discuss the selection rules for each case.

- (9.22) An atomic system is subject to an external oscillating electric field. Compute the induced dipole. (The dispersion law).
- (9.23) Consider the electron-electron interactions as a small perturbation in a helium atom. The unperturbed Hamiltonian H_0 describes two independent electrons in a Coulomb potential. Write the ionization energy of the system to zeroth order in the perturbation. Let us suppose that the helium is in a state $2s^2$ (both electrons in the $2s$ level). Show that the electron-electron interactions can induce a decay of the system and write the probability per unit time of this process (autoionization).

Numerical analyses

- (9.1) Use a finite matrix formulation based on harmonic oscillator states to implement perturbation theory. This approach can give exact results for polynomial interaction potentials to arbitrary order of perturbation theory. Formulate the same approach using operators instead of numerical matrices and write a program which can in principle compute in analytic form the perturbation theory up to an arbitrary order for a quartic oscillator.
- (9.2) Use the Dalgarno–Lewis method to compute the polarization of the ground-state hydrogen atom up to order \mathcal{E}^4 .
- (9.3) Use parabolic coordinates to compute to arbitrary order in perturbation theory the energy shift due to an electric field on an arbitrary bound level of the hydrogen atom. Do the computation in numerical and analytical forms.
- (9.4) Find a numerical recursive relation for the Hamiltonian eigenvalues of a quartic oscillator. Compute the first 50 or 60 orders in perturbation theory and apply the Padé resummation technique to approximate the series.

10

Variational methods

An old but generally very powerful method of approximation is the variational approach. The main ideas involved and a few applications are considered in this chapter.

10.1 The variational principle

One of the main problems in quantum mechanics is the determination of the eigenvalues and eigenstates of a given Hamiltonian,

$$H\psi = E\psi. \quad (10.1)$$

When the system involves many particles (as in molecules), or when there is no dominant part of the Hamiltonian which is exactly solvable, perturbation theory is not of much help. Often a variational approach turns out to be a powerful way to solve the problem.

The basic idea is the following. We introduce a set of “trial” wave functions, $\psi(q; \{\beta\})$, where $\{\beta\}$ stands for one or more variational parameters. Now for *any* normalized wave function ψ (therefore for $\psi(q; \{\beta\})$) an inequality

$$\langle \psi | H | \psi \rangle \geq E_0 \quad (10.2)$$

holds, where E_0 is the ground-state energy. The proof is elementary: any function can be expanded in terms of the true eigenstates $\psi_n(q)$ of H (10.1),

$$\psi(q; \{\beta\}) = \sum_n c_n \psi_n(q); \quad \sum_n |c_n|^2 = 1. \quad (10.3)$$

Substituting this into the left-hand side of eqn (10.2) one finds that

$$\langle \psi(\beta) | H | \psi(\beta) \rangle = \sum_n |c_n|^2 E_n \geq E_0 \sum_n |c_n|^2 = E_0.$$

The minimization of $\langle \psi(\beta) | H | \psi(\beta) \rangle$ with respect to β will give an approximation for E_0 , $E_0^{(var)}$, such that

$$E_0^{(var)} \geq E_0. \quad (10.4)$$

More generally let us consider any (not necessarily normalized) function $|\psi\rangle$ in Hilbert space and consider the expectation value of the Hamiltonian in this state,

$$Q(\psi) = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}.$$

10.1 The variational principle	245
10.2 Simple applications	250
10.3 The ground state of the helium	255
Guide to the Supplements	261
Problems	261
Numerical analyses	262

Let $|\bar{\psi}\rangle$ be the eigenvector corresponding to the minimum of Q with respect to any variation of ψ , and let us call \bar{E} the value of Q at the minimum:

$$\bar{E} = Q(\bar{\psi}) = \frac{\langle \bar{\psi} | H | \bar{\psi} \rangle}{\langle \bar{\psi} | \bar{\psi} \rangle}.$$

The minimum of Q is a stationary point, so to first order in the variation $|\psi\rangle \rightarrow |\psi\rangle + |\delta\psi\rangle$

$$\delta Q = \frac{\langle \delta\psi | H | \bar{\psi} \rangle}{\langle \bar{\psi} | \bar{\psi} \rangle} - \frac{\langle \bar{\psi} | H | \bar{\psi} \rangle}{\langle \bar{\psi} | \bar{\psi} \rangle} \frac{\langle \delta\psi | \bar{\psi} \rangle}{\langle \bar{\psi} | \bar{\psi} \rangle} = \frac{1}{\langle \bar{\psi} | \bar{\psi} \rangle} [\langle \delta\psi | H | \bar{\psi} \rangle - \bar{E} \langle \delta\psi | \bar{\psi} \rangle] = 0.$$

As this must hold for any variation one finds that

$$H|\bar{\psi}\rangle = \bar{E}|\bar{\psi}\rangle, \quad (10.5)$$

which is just Schrödinger's equation, \bar{E} being its eigenvalue. When the variations are considered only within a subset of functions in \mathcal{H} we shall get an approximate eigenvalue.

An equivalent formulation is to introduce a Lagrange multiplier and consider the variational problem for

$$Q'(\psi) = [\langle \psi | H | \psi \rangle - \lambda (\langle \psi | \psi \rangle - 1)].$$

Imposing the stationary condition for Q' with respect to the variations both of ψ and λ yields

$$\delta_\psi Q' = \langle \delta\psi | (H - \lambda) | \psi \rangle = 0; \quad \delta_\lambda Q' = \delta\lambda (\langle \psi | \psi \rangle - 1) = 0.$$

The second of these gives the normalization constraint, while the first gives Schrödinger's equation.

In order to get the energy of a generic state an orthogonality condition with all other lower (either exact or variational) states must be imposed as a further constraint, either by use of the Lagrange multipliers or by using an appropriately chosen set of functions.

In spite of the simplicity of the basic idea and in spite of the archaic flavor which accompanies it, the method is usually very efficient, and allows one to solve problems which are difficult to analyze with other methods. Note that the quality of a variational solution critically depends on the choice of the trial wave functions: if the class of the trial functions $\psi(q; \{\beta\})$ includes by luck the correct wave function within it, the method is bound to produce the exact answer. Usually this does not happen, but if a wide enough class of trial functions (e.g., with a sufficient number of free parameters) is used, the result is often rather good.

The reason for such good results from the variational method can be traced to the fact that if the error in the wave function is of the order $O(\epsilon)$, then the error for the energy is of the order of $O(\epsilon^2)$. To see this, suppose that the minimum of $\langle \psi_\beta | H | \psi_\beta \rangle$ is realized by the wave function ψ_{\min} ,

$$\psi_{\min} = (\psi_0 + \epsilon \psi_1) / \sqrt{1 + \epsilon^2},$$

where ψ_0 is the correct wave function of the ground state; ψ_\perp is a (normalized) linear combination of ψ_n , $n \neq 0$, orthogonal to it. Substitution of this function into $\langle\psi_\beta|H|\psi_\beta\rangle$ gives

$$E|_{\min} \simeq E_0 + O(\epsilon^2).$$

Remarks

- One of the advantages of the variational method lies in the fact that the original problem (usually a complicated differential equation of the second order) is replaced by a minimization problem with respect to a finite number of parameters, which are *algebraic* equations, and in general easier.
- The fundamental limitation of the method lies in the fact that there are no universally valid ways for deciding the set of trial functions to be used. One should find a reasonably wide class of the trial functions, perhaps taking into account the symmetry of the system, if any, but often a sound physical intuition with regard to what the exact wave function should look like is a key ingredient for getting a good estimate with a reasonable amount of numerical computation.

10.1.1 Lower limits

The variational method yields an upper limit of the eigenvalues E_i of the Hamiltonian, (10.4), but it is also possible to get a lower limit for them which, together, will allow us to estimate the precision of the result. A method has been developed in [Weinstein (1928), MacDonald (1934)]. Let us consider the dispersion of the Hamiltonian in a state

$$\sigma = \langle H\psi|H\psi\rangle - \langle\psi|H|\psi\rangle^2 \equiv D_\psi - \mathcal{E}_\psi^2.$$

It follows immediately that $\sigma \geq 0$. Indeed, if E_k are the exact eigenvalues of H and if the generic vector is expanded in terms of the eigenvectors of H

$$\psi = \sum_k a_k |e_k\rangle; \quad H |e_k\rangle = E_k |e_k\rangle, \quad k = 0, 1, \dots,$$

then

$$\begin{aligned} \mathcal{E}_\psi &= \sum_k E_k |a_k|^2; \quad D_\psi = \sum_k |a_k|^2 E_k^2; \quad \sum_k |a_k|^2 = 1; \quad (10.6) \\ \sigma &= \sum_k |a_k|^2 E_k^2 - 2\mathcal{E}_\psi \sum_k E_k |a_k|^2 + \mathcal{E}_\psi^2 \sum_k |a_k|^2 \\ &= \sum_k |a_k|^2 (E_k - \mathcal{E}_\psi)^2 \geq 0. \end{aligned}$$

Among the eigenvalues E_k let E_j be the one closest to \mathcal{E}_ψ , so that

$$(E_j - \mathcal{E}_\psi)^2 \leq (E_k - \mathcal{E}_\psi)^2 \quad \forall k.$$

It follows that

$$\sigma \geq (E_j - \mathcal{E}_\psi)^2 \sum_k |a_k|^2 = (E_j - \mathcal{E}_\psi)^2.$$

We find immediately that

$$\mathcal{E}_\psi - \sqrt{\sigma} \leq E_j \leq \mathcal{E}_\psi + \sqrt{\sigma}. \quad (10.7)$$

Thus once \mathcal{E}_ψ is found one can conclude that there is at least one eigenvalue in interval (10.7). By considering the coefficients $|a_k|^2$ as unknown variational parameters, if the approximation is good enough, we find \mathcal{E}_ψ as an estimate for E_j , with σ a measure of its error.

One often very efficient method is due to Temple [Temple (1934)]. Consider for definiteness the limits for the ground-state energy. Let $E_0, E_1 \dots$ be the exact eigenvalues of H . One has

$$\langle (H - E_0)\psi | (H - E_1)\psi \rangle \geq 0, \quad \forall \psi. \quad (10.8)$$

Expanding ψ as usual as

$$|\psi\rangle = \sum_k a_k |e_k\rangle, \quad H |e_k\rangle = E_k |e_k\rangle,$$

we have

$$\begin{aligned} \langle (H - E_0)\psi | (H - E_1)\psi \rangle &= \left[\sum_{k \neq 0} a_k^* (E_k - E_0) \langle e_k | \right] \left[\sum_{j \neq 1} a_j (E_j - E_1) |e_j\rangle \right] \\ &= \sum_{k \geq 2} |a_k|^2 (E_k - E_0)(E_k - E_1) \geq 0. \end{aligned}$$

By using the notation of eqn (10.6), it follows from eqn (10.8) that

$$E_0 \geq \mathcal{E}_\psi - \frac{\sigma}{E_1 - \mathcal{E}_\psi}. \quad (10.9)$$

Note that in order to use eqn (10.6) one needs an estimate for E_1 , which can be obtained in the standard variational method. The second term of eqn (10.9) can be regarded as an estimate of error. The estimate would not be very accurate if $E_1 \sim E_0$.

The method can be applied to any state, see [Delves (1972)]:

$$E_j \geq \mathcal{E}_\psi - \frac{\sigma}{E_{j+1} - \mathcal{E}_\psi}. \quad (10.10)$$

The practical problem in using estimates (10.7) and (10.10) is the evaluation of D . In any case, these provide for the estimate of the error committed in a variational procedure.

10.1.2 Truncated Hilbert space

The first step of the variational procedure is the choice of a set of functions dependent on one or more variational parameters; minimization with respect to those parameters determines the wave function as well as the approximate energy.

One of the simplest such choices consists in keeping a finite number out of the base vectors, which can for instance be the eigenvectors of some reference Hamiltonian, with some variational parameters. From the algebraic point of view, keeping n functions $\{\phi_i\}$, $i = 1, 2, \dots, n$, out of the infinite number of base vectors means truncating the Hilbert space to a subset spanned by the former. By expressing the Hamiltonian of the problem under consideration as a finite-dimensional matrix,

$$\mathbf{H}_{ij} = \langle \phi_i | H | \phi_j \rangle,$$

we see that the problem is reduced to an algebraic one of diagonalizing the matrix \mathbf{H} .

Concretely, let us consider Schrödinger's equation,

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi + U(x) \psi(x) = E \psi(x), \quad (10.11)$$

and choose a set of linear independent functions $\varphi_i(x)$, $i = 1 \dots n$, not necessarily orthogonal to each other, as the basis. Let us choose as our set of trial functions a linear combinations of these:

$$\Phi = \sum_{i=1}^n c_i \varphi_i(x).$$

The variational parameters are just the expansion parameters, c_i . The energy expectation value in Φ is

$$Q(c) = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle},$$

and the stationary condition yields, as we have already seen, Schrödinger's equation,

$$0 = \delta Q = \frac{\langle \delta \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} - \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} \frac{\langle \delta \Phi | \Phi \rangle}{\langle \Phi | \Phi \rangle} \Rightarrow H | \Phi \rangle = E | \Phi \rangle; E \equiv Q(\Phi). \quad (10.12)$$

Setting

$$H_{ij} = \langle \varphi_i | H | \varphi_j \rangle; \quad N_{ij} = \langle \varphi_i | \varphi_j \rangle,$$

and multiplying eqn (10.12) by $\langle \varphi_i |$, we find that

$$H_{ij} c_j = E N_{ij} c_j. \quad (10.13)$$

If the basis vectors are orthogonal, $N_{ij} = \delta_{ij}$, but no additional difficulties arise when considering the more general cases. Equation (10.13) is Schrödinger's equation projected onto the subspace. The solution of

eqn (10.13) gives the lowest eigenvalue, \tilde{E}_1 , which represents an approximation of the exact eigenvalue, E_1 . Equation (10.13) in general has n eigenvalues \tilde{E}_i with associated eigenvectors $|\tilde{\psi}_i\rangle$:

$$|\tilde{\psi}_i\rangle = \sum_i c_i \varphi_i; \quad H|\tilde{\psi}_i\rangle = \tilde{E}_i |\tilde{\psi}_i\rangle. \quad (10.14)$$

The vectors $|\tilde{\psi}_i\rangle$, being eigenvectors belonging to different eigenvalues, are automatically orthogonal. Although not *a priori* self-evident, the second eigenvalue provides for an estimate (in excess) of the second true eigenvalue, E_2^{th} , and so on. In fact, consider any state $\tilde{\Phi}$ orthogonal to the true ground state, $|\psi_1\rangle$. $\tilde{\Phi}$ can be expanded in terms of ψ_i , $i \geq 2$. Therefore one has

$$\langle \tilde{\Phi} | H | \tilde{\Phi} \rangle = \sum_{i=2} E_i |\langle \tilde{\Phi} | \psi_i \rangle|^2 \geq E_2 \sum_{i=2} |\langle \tilde{\Phi} | \psi_i \rangle|^2 = E_2. \quad (10.15)$$

Consider now a linear combination of the first two, approximate states $|\tilde{\psi}_1\rangle, |\tilde{\psi}_2\rangle$:

$$|\tilde{\Phi}\rangle = x|\tilde{\psi}_1\rangle + y|\tilde{\psi}_2\rangle.$$

The two parameters x, y can always be chosen so that this state is orthogonal to $|\psi_1\rangle$. If we impose the normalization condition also, we have two equations for the two unknowns x, y :

$$\langle \psi_1 | \tilde{\Phi} \rangle = x \langle \psi_1 | \tilde{\psi}_1 \rangle + y \langle \psi_1 | \tilde{\psi}_2 \rangle = 0; \quad x^2 + y^2 = 1.$$

So one can use eqns (10.14) and (10.15) to write

$$\langle \tilde{\Phi} | H | \tilde{\Phi} \rangle = \tilde{E}_1 x^2 + \tilde{E}_2 y^2 = \tilde{E}_2 - x^2 (\tilde{E}_2 - \tilde{E}_1) \geq E_2 \Rightarrow \tilde{E}_2 \geq E_2.$$

The last inequality follows from the fact that $\tilde{E}_2 - \tilde{E}_1 \geq 0$. Analogously one can proceed to other (discrete) levels.

10.2 Simple applications

These ideas will now be illustrated in the context of a few elementary examples.

10.2.1 The harmonic oscillator

Consider a harmonic oscillator (setting $\hbar = 1, m = 1$):

$$H = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} \omega^2 x^2.$$

In this case we know the exact answer for the ground state:

$$E_0 = \frac{1}{2} \omega; \quad \psi_0 = \left(\frac{\omega}{\pi} \right)^{1/4} e^{-\frac{1}{2} \omega x^2},$$

but let us try to solve the problem by a variational method.

The first approximation

Suppose that we (with some luck) adopt (normalized) trial functions of the form

$$\varphi = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2}, \quad (10.16)$$

where α is the variational parameter. The expectation value of H in state (10.16) is given by

$$E(\alpha) = \frac{\alpha}{4} + \frac{\omega^2}{4\alpha}.$$

The minimum of $E(\alpha)$ with respect to α is given by

$$\frac{dE(\alpha)}{d\alpha} = 0 \Rightarrow 1 - \frac{\omega^2}{\alpha^2} = 0 \Rightarrow \alpha = \omega,$$

and by substituting back it into $E(\alpha)$ we get

$$E(\alpha)|_{\alpha=\omega} = \frac{\omega}{4} + \frac{1}{4} \frac{\omega^2}{\omega} = \frac{\omega}{2},$$

which is the exact result.

The second approximation

Suppose now that we are not so lucky and have chosen trial functions of the form

$$\varphi = \sqrt{\alpha} e^{-\alpha|x|}.$$

By using parity we can write

$$\begin{aligned} E(\alpha) &= 2 \int_0^\infty \varphi^* H \varphi = \alpha \int_0^\infty dx \left\{ \left(\frac{d}{dx} e^{-\alpha x} \right)^2 + \omega^2 x^2 e^{-2\alpha x} \right\} \\ &= \frac{1}{2} \left(\alpha^2 + 2\omega^2 \frac{1}{4\alpha^2} \right). \end{aligned}$$

$E(\alpha)$ has a minimum at $\alpha^2 = \omega/\sqrt{2}$; for such a value of α we get

$$E_{\min} = \frac{\omega}{\sqrt{2}} \simeq 0.707 \omega > \frac{\omega}{2},$$

a rather poor result (40%).

The third approximation

Let us try to improve the approximation by

$$\varphi = (1 + \beta x^2) e^{-\alpha|x|}.$$

We set $\omega = 1$ to simplify the expressions. One has

$$\frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} = \frac{2(\alpha^4 + 2\alpha^8) - 4\alpha^2(-3 + \alpha^4)\beta + (45 + 2\alpha^4)\beta^2}{8\alpha^6 + 8\alpha^4\beta + 12\alpha^2\beta^2}.$$

In this case the minimum can be found numerically: it turns out that

$$\alpha = -0.0523; \quad \beta = 0.73; \quad E_{\min} = 0.64,$$

which is an improvement with respect to the preceding case.

10.2.2 Helium: an elementary variational calculation

We have already treated the ground state of the helium atom in perturbation theory, but here the same system will be re-considered in a simple variational approach. In atomic units for the length and energy, $r_B = \frac{\hbar^2}{me^2} = 1$ and $\epsilon_0 = \frac{me^4}{\hbar^2} = 2 \text{ Ry} \simeq 27.2 \text{ eV}$, the Hamiltonian is

$$H = H_1 + H_2 + H_{12} = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|r_1 - r_2|}. \quad (10.17)$$

The unperturbed Hamiltonian was taken to be $H_1 + H_2$, with the corresponding unperturbed wave function for the ground state, $\Psi^{(0)} = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)$,

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} Z^{3/2} e^{-Zr},$$

For the helium atom, $Z = 2$, but all formulas are valid for helium-like atoms so the computations will be done for generic Z . The result to first order in the perturbation H_{12} was

$$E_{\text{pert}} = Z^2 - \frac{5}{8}Z,$$

in atomic units.

The first step of the variational procedure is the choice of the trial wave function. In our case, a hint comes from a physical idea, that each of the electrons “sees” the charge of the nucleus partially screened by the cloud of the negative charge of the other electron. Let us therefore take as the variational wave function

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \varphi(r_1)\varphi(r_2); \quad \varphi(r) = \frac{1}{\sqrt{\pi}} Z_1^{3/2} e^{-Z_1 r}.$$

where Z_1 ($Z_1 |e|$) is the effective charge each electron feels. The computation is simple as it has the form of the product of the hydrogenoid wave function but with a charge Z_1 instead of Z . Let us remember that for a hydrogenoid atom there is a simple relation¹ between the kinetic energy K and the potential energy U :

$$\langle K \rangle = -\frac{1}{2}\langle U \rangle = -E.$$

Therefore

$$\begin{aligned} \left\langle \frac{p_1^2}{2} \right\rangle &= \frac{Z_1^2}{2}; \quad \left\langle -\frac{Z_1}{r} \right\rangle = -2\frac{Z_1^2}{2} \Rightarrow \left\langle -\frac{Z}{r} \right\rangle = -ZZ_1; \\ \langle H_1 \rangle &= \frac{Z_1^2}{2} - ZZ_1 \Rightarrow \langle H_1 + H_2 \rangle = Z_1^2 - 2ZZ_1. \end{aligned}$$

The evaluation of the term describing the Coulomb repulsion between the two electrons is identical to what was done in perturbation theory, apart from the substitution of Z by Z_1 :

$$\langle H_{12} \rangle = \frac{5}{8}Z_1.$$

¹ It is a special case of the virial theorem which will be discussed shortly.

So one has

$$\langle H \rangle = E(Z_1) = Z_1^2 - 2ZZ_1 + \frac{5}{8}Z_1 = Z_1^2 - 2Z_1 \left(Z - \frac{5}{16} \right). \quad (10.18)$$

The minimization of (10.18) gives

$$\frac{dE}{dZ_1} = 0 \Rightarrow Z_1 = Z - \frac{5}{16}; \quad \langle H \rangle_{\min} = - \left(Z - \frac{5}{16} \right)^2.$$

Experimentally the directly accessible data are those of the ionization energy, that is, the energy required to remove one of the electrons. After the removal of an electron the energy for the remaining bound electron is $E_0 = -Z^2/2$, and therefore the ionization energy is given by $J(Z) = E_0 - E$. For the perturbative and variational estimates, we have, respectively,

$$\begin{aligned} J_{\text{pert}}(Z) &= \left(\frac{Z^2}{2} - \frac{5}{8}Z \right) \text{ a.u.} = \left(Z^2 - \frac{5}{4}Z \right) \text{ Ry;} \\ J_{\text{var}}(Z) &= \left(Z - \frac{5}{16} \right)^2 - \frac{Z^2}{2} = \left(\frac{Z^2}{2} - \frac{5}{8}Z + \frac{25}{256} \right) \text{ a.u.} \\ &= \left(Z^2 - \frac{5}{4}Z + \frac{25}{128} \right) \text{ Ry.} \end{aligned}$$

where the results are given in Rydbergs (Ry), recalling that 1 a.u. = 2 Ry. Shown in Table 10.1 are the perturbative, variational, and experimental results for the first few helium-like systems. It should be noted

	H ⁻	He	Li ⁺	Be ⁺⁺
J_{pert}	-0.25	1.5	5.25	11.0
J_{var}	-0.055	1.695	5.445	11.195
J_{exp}	+0.055	1.807	5.560	11.312

Table 10.1 Approximate and experimental values of the ionization potential for some atoms.

that the difference $J_{\text{exp}} - J_{\text{var}}$ is a constant in Z . Both perturbation theory and the simple variational approach considered here fail to account for the existence of the bound-state ion H⁻, but for other elements, there is an appreciable improvement with respect to perturbation theory.

Remark

The result found above has an interesting re-interpretation. Let us consider the exact Hamiltonian (10.17) and decompose it into the “unperturbed” Hamiltonian and “perturbation” as follows

$$H = \left[\frac{1}{2} p_1^2 - \frac{Z_1}{r_1} + \frac{1}{2} p_2^2 - \frac{Z_1}{r_2} \right] + \left[\frac{1}{r_{12}} + \frac{Z_1 - Z}{r_1} + \frac{Z_1 - Z}{r_2} \right] \equiv H_{Z_1} + V_{Z_1} .$$

In other words we have introduced a fictitious “unperturbed” system H_{Z_1} and all the rest is now treated as perturbation. To first order, one gets the result

$$E(Z_1) = \langle \psi | H_{Z_1} | \psi \rangle + \langle \psi | V_{Z_1} | \psi \rangle .$$

But the eigenstate of H_{Z_1} —the unperturbed wave function—is precisely the trial wave function adopted above. Minimization of $\langle \psi | H_{Z_1} | \psi \rangle$ in the variational procedure corresponds to adjusting the artificial division of H into $H_{Z_1} + V_{Z_1}$ so that the effect of “perturbation” is as small as possible. Indeed, the latter,

$$\langle \psi | V_{Z_1} | \psi \rangle = \frac{5}{8} Z_1 + 2 \cdot (Z_1 - Z) Z_1 = 2Z_1 \left(Z_1 - Z + \frac{5}{16} \right) ,$$

vanishes precisely at the variational value for the effective charge $Z_1 = Z - (5/16)$. In other words, the variational wave function used is the one which best simulates the true ground-state wave function.

10.2.3 The virial theorem

The virial theorem, discussed in Section 3.2 establishes a relation between the expectation value of the kinetic term and that of the potential energy taken in a stationary state, when the potential energy is homogeneous in the position operator. There is also a classical analogue which involves the time average over many periods. It is interesting that the theorem can be proven also by using a variational consideration.

Let us consider a homogeneous potential of order ν , i.e., $V(kx) = k^\nu V(x)$, where x stands for all the position operators of the problem.

Consider any state $\varphi(x)$ and

$$\begin{aligned} N &= \int d^D x \varphi^*(x) \varphi(x); \\ \langle \varphi | T | \varphi \rangle &= \frac{1}{N} \int d^D x \varphi^*(x) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right] \varphi(x); \\ \langle \varphi | V | \varphi \rangle &= \frac{1}{N} \int d^D x \varphi^*(x) V(x) \varphi(x). \end{aligned}$$

Consider now another state, $\varphi_k(x)$, obtained by a rescaling of the position operators x :

$$\varphi_k(x) = \varphi(kx).$$

The expectation values are scaled as

$$\langle T \rangle_k = k^2 \langle \varphi | T | \varphi \rangle; \quad \langle V \rangle_k = k^{-\nu} \langle \varphi | V | \varphi \rangle.$$

This implies for the expectation value of the energy in the state $\varphi(kx)$

$$E(k) = k^2 \langle \varphi | T | \varphi \rangle + k^{-\nu} \langle \varphi | V | \varphi \rangle.$$

Suppose now that $\varphi(x)$ is the true wave function for a stationary state. As H should be stationary in this state, $\langle H \rangle$ must have a vanishing variation with respect to any modification of the wave function around it, in particular for $x \rightarrow kx$, so

$$\frac{d}{dk} E(k) \Big|_{k=1} = 0;$$

that is,

$$2\langle \varphi | T | \varphi \rangle = \nu \langle \varphi | V | \varphi \rangle. \quad (10.19)$$

By considering variations in the subspace orthogonal to the ground state, we see the theorem holds in any stationary state.

Formula (10.19) is the *virial theorem*. By using $\langle H \rangle = \langle T \rangle + \langle V \rangle$ one also has

$$\langle \varphi | T | \varphi \rangle = \frac{\nu}{\nu+2} E; \quad \langle \varphi | V | \varphi \rangle = \frac{2}{\nu+2} E.$$

For instance, $\nu = -1$ for the Coulomb potential; $\nu = 2$ for the harmonic oscillator. In case the potential is the sum of homogeneous terms, the theorem is generalized to

$$2\langle \varphi | T | \varphi \rangle = \sum_k \nu_k \langle \varphi | V_k | \varphi \rangle.$$

10.3 The ground state of the helium

The computation of the ground-state energy of the helium atom played an important historic role. The system is non-integrable, in the sense that there are no known canonical variables of action-angle type, and this makes Bohr–Sommerfeld quantization unavailable. Perturbation theory does not give a satisfactory result [Born (1927)], and the success of the variational estimate turned out to be one of the first milestones in the birth of quantum mechanics.

The experimental data on the ionization potential (the energy required to extract one of the electrons from the atom in the ground state) is listed in Table 10.2, in units of cm^{-1} , as is often done in presenting the spectroscopic data. The conversion factor is

$$E(\text{cm}^{-1}) = \frac{1}{hc} E.$$

In particular,

$$1 \text{ cm}^{-1} = 1.239\,842\,44(15) \times 10^{-4} \text{ eV}.$$

$$1 \text{ Ry} = 109\,737.315\,6 \text{ cm}^{-1}; \quad 1 \text{ a.u.} = 2 \text{ Ry} = 219\,474.631\,3 \text{ cm}^{-1}.$$

H^-	He	Li^+	Be^{++}
$6\ 100 \pm 100$	$198\ 310.82 \pm 0.15$	$610\ 079 \pm 25$	$124\ 122.5 \pm 100$

Table 10.2 Ionization potentials for helium and some other ions. The numbers are given in cm^{-1} .

The Hamiltonian of the system is (in atomic units)

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}.$$

r_1, r_2 stand for the radial distances of the two electrons from the nucleus, r_{12} their relative distance. The eigenstates of this system are an orbital wave function, to which a spin wave function must be appropriately associated. By the Pauli principle, the orbital wave function must be symmetric or anti-symmetric, according to whether the total spin of the two electrons is 0 or 1, respectively. We shall limit ourselves here to the study of the symmetric orbital wave functions, so-called *para-helium*, in particular the ground state with $S = 0$. The other type, corresponding to $S = 1$, is known as *ortho-helium*. For our purpose this amounts to searching for the solution of Schrödinger's equation that is symmetric with respect to the exchange of the two electrons,

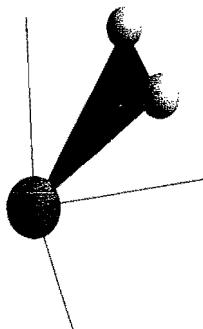


Fig. 10.1 Invariant triangle defined by the variables s, t, u .

$$s = r_1 + r_2; \quad t = r_1 - r_2; \quad u = r_{12},$$

with the range

$$0 \leq t \leq u \leq s < \infty,$$

instead of r_1, r_2, r_{12} ; the Jacobian of the transformation is

$$d^3x_1 d^3x_2 = 2\pi^2 u (s^2 - t^2) ds dt du,$$

where we have integrated over the angular variables on which the trial wave function does not depend. In determining the range of the parameters we have taken into account that we are looking for a function which is even in $t \rightarrow -t$. In terms of these variables, the integrals to be

considered are

$$\begin{aligned}\langle \psi | H | \psi \rangle &= \int_0^\infty ds \int_0^s du \int_0^u dt \left\{ u(s^2 - t^2) \left[\left(\frac{\partial \psi}{\partial s} \right)^2 + \left(\frac{\partial \psi}{\partial t} \right)^2 + \left(\frac{\partial \psi}{\partial u} \right)^2 \right] \right. \\ &\quad \left. + 2 \frac{\partial \psi}{\partial u} \left[s(u^2 - t^2) \frac{\partial \psi}{\partial s} + t(s^2 - u^2) \frac{\partial \psi}{\partial t} \right] - [4Zsu - s^2 + t^2] \psi^2 \right\}; \\ \langle \psi | \psi \rangle &= \int_0^\infty ds \int_0^s du \int_0^u dt u(s^2 - t^2) \psi^2,\end{aligned}$$

where a real function $\psi(s, t, u)$ has been assumed.

The variational procedure is set up by introducing parameters describing the scale change (λ) and the change of the shape of the wave function, c_i . In order to do a realistic calculation we follow the original work [Hylleraas (1929)] and take trial functions of the form

$$\psi = \sum_i c_i \tilde{\varphi}_i(\lambda s, \lambda t, \lambda u),$$

where the scale parameter enters as

$$\tilde{\varphi}_i = \lambda^6 \varphi_i(\lambda s, \lambda t, \lambda u),$$

while the functions φ_i are chosen as

$$\varphi_{\ell m n}(s, t, u) = s^\ell t^{2m} u^n e^{-\frac{s}{2}}, \quad (10.21)$$

$$\ell = 0, 1, \dots, d_s, \quad m = 0, 1, \dots, d_t, \quad n = 0, 1, \dots, d_u.$$

Symmetry under $t \rightarrow -t$ (exchange of the two electrons) imposes the condition that only even powers of t can appear. We make a natural choice to keep all powers in s, t^2, u : there will be in all $N = (d_s + 1)(d_t + 1)(d_u + 1)$ independent monomials. The triple index (ℓ, m, n) appearing in the formula is equivalent to the single index i , $i = 1, \dots, N$, through

$$i = \ell + (d_s + 1) \cdot m + (d_t + 1) \cdot n + 1.$$

The simplest choice $N = 1$ ($\ell = m = n = 0$) corresponds to the elementary treatment discussed in Subsection 10.2.2.

The effect of the scale parameter λ can be seen to be simply (as can be checked by doing a change of variables, $s' = \lambda s, t' = \lambda t, u' = \lambda u$)

$$\langle \psi | H | \psi \rangle = \lambda^2 \mathcal{M} - \lambda \mathcal{L} \quad \langle \psi | \psi \rangle = \mathcal{N};$$

where the following simplified notation has been introduced:

$$\begin{aligned}\int_0^\infty ds \int_0^s du \int_0^u dt &\equiv \int; \\ \mathcal{M} &= \int u(s^2 - t^2) \left[\left(\frac{\partial \varphi}{\partial s} \right)^2 + \left(\frac{\partial \varphi}{\partial t} \right)^2 + \left(\frac{\partial \varphi}{\partial u} \right)^2 \right] \\ &\quad + 2 \frac{\partial \varphi}{\partial u} \left[s(u^2 - t^2) \frac{\partial \varphi}{\partial s} + t(s^2 - u^2) \frac{\partial \varphi}{\partial t} \right]; \\ \mathcal{L} &= \int [4Zsu - s^2 + t^2] \varphi^2; \quad \mathcal{N} = \int u(s^2 - t^2) \varphi^2.\end{aligned}$$

Upon substitution of trial functions (10.21), $\mathcal{M}, \mathcal{L}, \mathcal{N}$ become quadratic forms in c_i :

$$\mathcal{M} = M_{ij} c_i c_j ; \quad \mathcal{L} = L_{ij} c_i c_j ; \quad \mathcal{N} = N_{ij} c_i c_j ,$$

where obvious notation is used for the matrices M, N, L ; for instance

$$L_{ij} = \int [4Zsu - s^2 + t^2] \frac{1}{2} (\varphi_i \varphi_j + \varphi_j \varphi_i) .$$

The requirement of stationarity with respect to c_i and λ imply, respectively,

$$\lambda^2 M_{ij} c_j - \lambda L_{ij} c_j = E N_{ij} c_j ; \quad E = \frac{\lambda^2 \mathcal{M} - \lambda \mathcal{L}}{\mathcal{N}} ; \quad (10.22)$$

$$2\lambda \mathcal{M} - \mathcal{L} = 0 : \quad \lambda = \frac{\mathcal{L}}{2\mathcal{M}} . \quad (10.23)$$

The last ingredients of the calculation are the matrix elements M_{ij} , L_{ij} , N_{ij} . The integrals needed are of the form

$$A(\alpha, \beta, \gamma) = \int_0^\infty ds \int_0^s du \int_0^u dt s^\alpha t^\beta u^\gamma e^{-s} ,$$

with some integers α, β, γ . The integral is elementary:

$$A(\alpha, \beta, \gamma) = \frac{(2 + \alpha + \beta + \gamma)!}{(1 + \beta)(2 + \beta + \gamma)} .$$

The eigenvalues E of eqn (10.22) and the value of λ in eqn (10.23) do not depend on the normalization of the state φ , as expected. We note that E depends on λ , which, in turn, is fixed, once the coefficients c_i are known from eqn (10.23). The simplest way to solve system (10.22) and (10.23) is to proceed iteratively:

- (1) Choose an initial value for λ , for instance, to be equal to the value suggested by the elementary calculation of the Subsection 10.2.2.
- (2) Solve the eigenvalue problem in eqn (10.22).
- (3) Repeat the calculation by varying λ , $\lambda \rightarrow \lambda + d\lambda$. If the eigenvalue E decreases for the new value of λ , then accept the new value of λ and repeat procedures (1) and (2); otherwise, one should try to halve the interval of λ to $d\lambda/2$: at each step it should be possible to check the convergence of the result. The choice of introducing the scale parameter λ has been purely one of convenience: the aim is to obtain a convergence with a relatively small number of functions ϕ_i .

²The program proposed is far from maximally optimized, and becomes unstable after $N = 150$; it is given to illustrate the power of the variational method only.

Result

A detailed numerical evaluation is proposed as one of the problems to be solved numerically at the end of this chapter.² The results for the energy (in atomic units) and for the ionization potential J (in cm^{-1})

are given in the following table (first column), by using the base of the functions with $N = 120$:

	variational	δ -mass	δ -polar.	our result
E	-2.903 724 13	0.000 397 92	0.000 021 8	-2.903 304 41 a.u.
J	198 344.520 8	-27.180 546 24	-4.784 846 35	198 312.555 4 cm^{-1} (10.24)

Experimentally we have for helium,

$$J_{\text{exp}} = 198 310.67[1] \text{ cm}^{-1}. \quad (10.25)$$

The variational result is a good agreement with this but is not excellent. In particular, the variational result should produce an upper limit for the energy, and so a lower limit for the ionization potential, and our result is in contradiction with the data. However, the discrepancy between theory and experiment at this stage is of the order of $\Delta J/J \sim 10^{-1}$, and there are other corrections we neglected which become significant at this precision. The most important one turns out to be of kinematic origin: it is due to the finite mass of the nucleus.

Corrections due to the finite mass of the nucleus

The result found above is the approximate value for the ground state of helium, in which the nucleus is assumed to be infinitely heavy: the center of the Coulomb potential is fixed at the origin. Let us briefly recall how the corrections due to the finite mass of the nucleus can be taken into account. In the center of mass of the atom,

$$\mathbf{P}_N + \sum_{i=1}^Z \mathbf{p}_i = 0,$$

so the kinetic term can be written as

$$\frac{1}{2M} \left(\sum_{i=1}^Z \mathbf{p}_e \right)^2 + \frac{1}{2m} \sum_{i=1}^Z \mathbf{p}_i^2 = \frac{1}{2\mu} \sum_{i=1}^Z \mathbf{p}_i^2 + \frac{1}{M} \sum_{i < j} \mathbf{p}_i \mathbf{p}_j,$$

where M and m are the mass of the nucleus and of the electron, respectively, and

$$\mu = \frac{mM}{m+M}$$

is the reduced mass.

In the case of a system with two electrons, therefore, the effective Hamiltonian takes the form

$$H = \frac{1}{2\mu} (\mathbf{p}_1^2 + \mathbf{p}_2^2) + V + \frac{1}{M} \mathbf{p}_1 \cdot \mathbf{p}_2. \quad (10.26)$$

Compared to the case of fixed force center, there are two corrections:

- The reduced mass has replaced the electron mass. We have done the preceding calculations in atomic units, where the mass entered

the definition of the atomic unit, $1 \text{ a.u.} \propto m$. Therefore in order to take into account this type of correction it suffices to multiply the preceding result by μ/m . Of course, the energy of the ionized helium must also be calculated with the reduced mass, where the corrections under question enter in the same fashion. In short corrections of this first type can be summarized by

$$\Delta_1 E_0 = \left(\frac{\mu}{m} - 1 \right) E_0 , \quad \Delta_1 J = \left(\frac{\mu}{m} - 1 \right) J .$$

Note that $\mu/m - 1 \sim -m/M < 0$: the correction tends to diminish the ionization potential, which goes in the right direction.

- The second type of correction, due to the last term of eqn (10.26), is known as *mass polarization*. This is a small correction, proportional to m/M , and can be treated by perturbation theory. Its contribution is

$$\Delta_2 E_0 = \frac{m}{M} \frac{1}{\langle \psi | \psi \rangle} \left\langle \psi \left| \frac{1}{m} \mathbf{p}_1 \mathbf{p}_2 \right| \psi \right\rangle \equiv \frac{m}{M} \frac{1}{N} \mathcal{K} . \quad (10.27)$$

The mass polarization would not contribute if the wave function has a factorized form, $f(r_1)f(r_2)$: the matrix element would factorize and each term would vanish by, e.g., parity. Equation (10.27), after integration by parts gives

$$\Delta_2 E_0 = \frac{m}{M} \frac{1}{N} \int (\nabla_1 \psi) \cdot \nabla_2 \psi ,$$

where N is the quadratic form defined earlier. Also this new form can be expressed in terms of the variables s, t, u , with the result

$$\begin{aligned} \mathcal{K}(\varphi) = & \int_0^\infty ds \int_0^s du \int_0^u dt \\ & \left\{ (s^2 + t^2 - 2u^2) \left[\left(\frac{\partial \varphi}{\partial s} \right)^2 - \left(\frac{\partial \varphi}{\partial t} \right)^2 \right] u - (s^2 - t^2)u \left(\frac{\partial \varphi}{\partial u} \right)^2 \right. \\ & \left. - 2 \frac{\partial \varphi}{\partial u} \left[\frac{\partial \varphi}{\partial s} (u^2 - t^2) + \frac{\partial \varphi}{\partial t} t(s^2 - u^2) \right] \right\} . \end{aligned}$$

The corresponding matrix elements K_{ij} are given in the notebooks. The final corrections are the second and the third terms of eqn (10.24):

$$\Delta_1 J = -27.18 \text{ cm}^{-1} , \quad \Delta_2 J = -4.78 \text{ cm}^{-1} .$$

These corrections, added to the preceding result, yield the final answer

$$J_{\text{ours}} = J + \Delta_1 J + \Delta_2 J = 198\,312.55 \text{ cm}^{-1} , \quad J_{\text{exp}} = 198\,310.67 ,$$

which is fairly good. There is still a small discrepancy, of the order of $\Delta J/J \sim 10^{-6}$, but in a sense, the result is perhaps too good: in fact, we have so far neglected relativistic corrections, analogous to the fine structure of the hydrogen atom. *A priori* we would expect corrections for the energy of the order of $(Z\alpha)^2 \sim 10^{-4}$, while our result appears to be correct up to corrections of 10^{-5} .

It turns out that for the ground state the fine-structure corrections almost cancel out exactly³, leaving a correction which is smaller than expected. The dominant effect is due to the Lamb shift. The computation, which is rather complicated, of the two contributions yields a further shift of -1.90 cm^{-1} of the ionization potential.

With these corrections taken into account, we find that

$$J_{\text{th}} = J + \Delta_1 J + \Delta_2 J + \Delta_{\text{rel}} = 198\,310.65 \text{ cm}^{-1}; \quad J_{\text{exp}} = 198\,310.67;$$

and the agreement is excellent.

The same procedure can be repeated for other elements. Note also that this improved treatment allows us to get a reasonable result for the bound H^- ion.

The results up to Be^{++} are indicated in the following table:

	H^-	He	Li^+	Be^{++}
J_{exp}	$6\,100 \pm 100$	$198\,310.669 \pm 0.001$	$610\,079 \pm 1$	$1\,241\,242.0 \pm 5$
J	6082.99	198310.65	610076.03	1241247.06
δJ_{rel}	-0.31	-1.90	8.86	75.00

³Calculation of the relativistic corrections is done in the exercises at the end of this chapter.

Guide to the Supplements

Several supplements complete the discussion in this chapter. A brief account is given of some numerical methods such as the spectral and pseudospectral techniques for the solution of differential equations and the Gauss integration method. These techniques are used to develop numerical tools for solving Schrödinger's equation using the basis constructed with several kinds of polynomials (Laguerre, Hermite, Chebyshev, Fourier). As an example of the power and flexibility of the method we quote the result of notebook NB-10.10 where we show how to

compute the eigenvalues of an anharmonic oscillator with 50-digit precision (or more).

There are seven notebooks on the variational problem for the helium, which present a few computational techniques: the classical one by Hylleraas and a more recent one by Pekeris. In the last case we show how to compute the energy levels with an accuracy of one part in 10^7 with respect to the experimental data.

A brief guide to these notebooks can be found in the file: [Guide_to_NB.pdf](#).

Problems

- (10.1) Apply a variational method with hydrogenoid wave functions to the computation of the ground-state energy of helium. Use the Temple method to give an estimate of the error.
- (10.2) Let us interpret the scale parameter α used in the

variational computations of an anharmonic oscillator as a variational frequency. Show that the choice used in the test is the one suggested by the Bohr-Sommerfeld quantization conditions.

- (10.3) Compute the corrections m/M to the helium Hamiltonian by an explicit coordinate transformation in Schrödinger's equation.
 (10.4) Perform the following change of variables for the Hylleraas coordinates in helium:

$$s = r_1 + r_2; \quad t = r_1 - r_2 - 2; \quad u = r_{12}.$$

Write Schrödinger's equation for a rotationally invariant state in these coordinates.

- (10.5) Write the mean energy of the Hamiltonian on a spherically symmetric state in terms of the Hylleraas variables. Write Schrödinger's equation resulting from the variational principle and compare it with the result of the previous problem.
 (10.6) Write the effective Hamiltonian for the relativistic corrections to the S states of helium. Compute

the effect on the ground state using the simplest variational wave function. (For the general atomic Hamiltonian see the supplements of chapter 14).

- (10.7) Consider a generic interval $[a, b]$ and a measure $\mu(x) dx$ on this interval. Assume that all moments exist, i.e. x^n are integrable. In the Hilbert space $L^2[\mu, a, b]$ one can define a complete base of polynomials (Weierstrass' theorem).
 (a) Show that the basis can be made orthogonal and that multiplication by the variable x on a polynomial of degree n can be expressed as a linear combination of polynomials of degrees $n+1, n, n-1$.
 (b) Interpret this relation as a Hilbert-space realization (matrix realization) of the x operator and show that by considering a finite-dimensional approximation of this representation one can prove Gauss' summation formulas, i.e., the approximations of integrals by means of abscissas and weights of the relative polynomial class.

Numerical analyses

- (10.1) Use the Mathematica function `NVariationalBound` to study the variational method in systems like the harmonic oscillator, the anharmonic oscillator, the hydrogen atom and the helium atom.
 (10.2) Use the Mathematica function `NVariationalBound` to give an estimate of the S -state energies for He and Li .
 (10.3) Study Gauss' integration formulas by using Mathematica .
 (10.4) With the help of a book on numerical analysis and using the Mathematica Help study the pseudospectral method for solving differential equations.
 (10.5) Study the connection between discretization method and the variational principle.
 (10.6) Use a basis of the Laguerre polynomials to solve radial problems with the variational method.
 (10.7) Study the stability and the precision of the variational results using a basis of Laguerre polynomials. In particular compute numerically with 20-
- digit precision the ground-state energy for a radial potential $-V_0/\cosh(\alpha r)^2$.
 (10.8) Study the pseudospectral method in conjunction with Laguerre polynomials.
 (10.9) Study the variational method using Hermite polynomials.
 (10.10) Solve numerically the anharmonic oscillator problem using Hermite polynomials. Study the double well. Try to compute the eigenvalues with 50-digit precision.
 (10.11) Study the effect of an external linear potential (electric field) on a double-well system. Verify the Feynman-Hellmann theorem.
 (10.12) Use a Fourier basis to study variational problems.
 (10.13) Use the Chebyshev polynomials to implement a variational calculation. Study the pseudospectral method with this basis.
 (10.14) Study the variational procedure for a two-

dimensional problem with potential

$$V(x, y) = \frac{1}{2}x^2 + \frac{1}{2}y^2 + x^2y^2.$$

Apply the same method to the study of a regularization of the Hénon potential

$$V[x, y] = \alpha(x^2 + y^2)^2 + \beta(x^2 + y^2) + \gamma(x^3 - 3xy^2). \quad (10.19)$$

(10.15) Study the Hylleraas and Pekeris coordinate systems for helium.

(10.16) Study analytically the variational problem for the s-states of helium with a low dimensional basis. Use both the Hylleraas and Pekeris coordinates.

(10.17) Study numerically the ground-state of helium using Hylleraas coordinates.

(10.18) Extend the variational calculation to excited states of helium atoms.

(10.19) Compute the relativistic corrections for S-states levels of the helium atom.

(10.20) Compute S-states levels of helium using the triangular (Pekeris) variables.

(10.21) Compute the relativistic corrections to the helium atom using triangular coordinates.

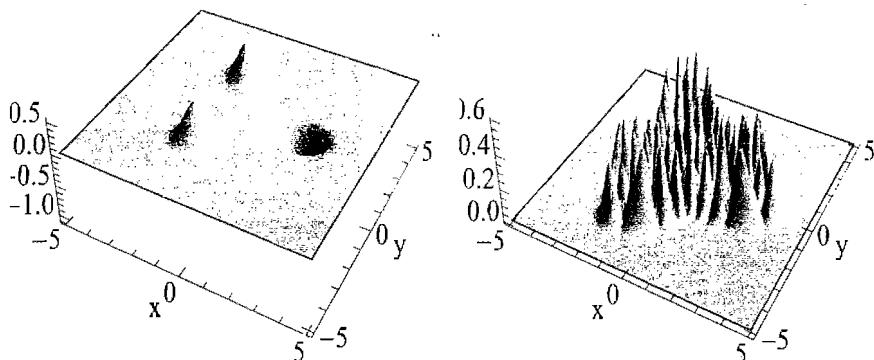


Fig. 10.2 The wave function and the density for a low and an high excited level in the Henon potential, NB-10.14.

The semi-classical approximation

11

In this chapter we study the limit $\hbar \rightarrow 0$ of quantum mechanics. The passage from quantum mechanics to classical mechanics involves precisely this limit, and the approximation schemes developed for small \hbar are known as the *semi-classical approximation*. The semi-classical approximation has a predecessor: the so-called old quantum theory. Many of the questions concerning the connection between the quantum and classical mechanics were already raised during the years of foundation of quantum mechanics, 1900–1927, but satisfactory answers have not always been obtained.

Until the second half of the last century, the semi-classical method made progress as an approximate treatment of Schrödinger's equations, but without really significant steps from the point of view of principles. The new facts which changed the perspectives are many. On the one hand, a re-discovery of some old results by Einstein allowed a much deeper understanding of the quantization of classically integrable systems; on the other, the formulation of the KAM (Kolmogorov, Arnold, Moser) theorem opened the way to understanding new phenomena which are classically non-integrable. As a consequence of these investigations, together with further progress in the study of asymptotic expansions in general and some new results in variational calculus, it has become possible to explore the semi-classical quantization of classically non-integrable systems as well, and, possibly, chaotic systems.

In this chapter, for obvious reasons of space, only the elementary aspects of the problem will be discussed. Some more details will be given in the supplement of this chapter.

11.1 The WKB approximation	265
11.2 The Bohr–Sommerfeld quantization condition	271
11.3 The tunnel effect	283
11.4 Phase shift	295
Further reading	300
Guide to the Supplements	300
Problems	301
Numerical analyses	302

11.1 The WKB approximation

WKB stands for Wentzel, Kramers, and Brillouin, who at the same time as some other authors proposed a scheme for studying the limit $\hbar \rightarrow 0$. The approximation is similar to the approximation of geometrical optics for the Maxwell equation: for small variations of the wavelengths as compared to the distance traveled by light, it makes sense to describe the propagation of electromagnetic waves in terms of the ray and wavefront, of which evolution (iconal equation) constitutes the basis of geometrical optics.

Consider the one-dimensional Schrödinger equation for a particle moving in a potential $V(x)$:

$$-\frac{\hbar^2}{2m} \psi'' + V(x) \psi = E \psi. \quad (11.1)$$

It is clear that the limit $\hbar \rightarrow 0$ is a singular one: in this limit the order of the differential equation changes and therefore the classes of the functions which satisfy it. Actually in this particular case one passes from a differential to an algebraic equation.

The hint for the correct procedure comes from the simplest of cases: free particles. In these cases the eigenfunction of Schrödinger's equation is also an eigenfunction of the momentum, and has the form of a plane wave,

$$\psi(x) = e^{ipx\hbar}.$$

For $\hbar \rightarrow 0$, at fixed p , the function oscillates more and more rapidly, the wavelength $\lambda = h/p$ tending to zero. It is this rapid oscillation which produces the factor \hbar^{-1} each time the derivative acts, and cancels the factor \hbar^2 in front of the kinetic term. We can talk about the limit $\hbar \rightarrow 0$ of a more general wave function, only by considering the corrections to such a behavior, forced upon us by the structure of Schrödinger's equation, eqn (11.1).

It is therefore natural to seek for an approximation by setting

$$\psi(x) = \exp\left(i\frac{\sigma}{\hbar}\right), \quad (11.2)$$

and assuming that σ , and not ψ itself, is a function expandable in \hbar :

$$\sigma(x) = \sum_{k=0}^{\infty} \left(\frac{\hbar}{i}\right)^k \sigma_k = \sigma_0 + \frac{\hbar}{i} \sigma_1 + \left(\frac{\hbar}{i}\right)^2 \sigma_2 + \dots. \quad (11.3)$$

The factor $1/i$ in eqn (11.3) is introduced conventionally, to simplify the expressions somewhat. Substituting eqn (11.2) into eqn (11.1), one finds that

$$(\sigma')^2 - i\hbar\sigma'' = p^2(x), \quad (11.4)$$

where we have defined the "classical momentum"

$$p^2(x) = 2m(E - V(x)),$$

which for $E > V(x)$ indeed represents the classical momentum of the particle. Equation (11.3) is equivalent to the original equation (11.1): it is an equation of the first order¹ but non-linear, in $y = \sigma'$. One of the two integration constants of eqn (11.1) is just the integration constant appearing in the passage from y to σ . Substituting the expansion (11.3) in eqn (11.4) we find, to the 0-th order, that

$$(\sigma'_0)^2 = p^2; \sigma_0 = \pm \int p(x) dx; p(x) = +\sqrt{2m(E - V(x))}.$$

¹ This procedure of substituting the function ψ by an unknown function y related to the former by

$$\psi = \exp\left(\int^x y(\xi) d\xi\right)$$

is quite a standard one. The resultant equation is known as Riccati's equation.

Two possible signs of the square roots correspond to two linearly independent solutions. To the order \hbar^n , we find that

$$\sum_{k=0}^n \sigma'_k \sigma'_{n-k} + \sigma''_{n-1} = 0 , \quad (11.5)$$

by setting the coefficients of each power of \hbar to zero. Equation (11.5) gives a recursive expression for σ_n ; indeed σ'_n appears only in two terms, multiplied by σ'_0 :

$$\sigma'_1 = -\frac{1}{2\sigma'_0} \sigma''_0 \Rightarrow \sigma_1 = -\frac{1}{2} \log(p) ; \quad (11.6a)$$

$$\sigma'_n = -\frac{1}{2\sigma'_0} \left(\sum_{k=1}^{n-1} \sigma'_k \sigma'_{n-k} + \sigma''_{n-1} \right) ; \quad n \geq 2 . \quad (11.6b)$$

By choosing, for instance, the solution $\sigma'_0 = +p(x)$, one finds explicitly that

$$\begin{aligned} \sigma'_2 &= -\frac{1}{2p} \left[\sigma'^2_1 + \sigma''_1 \right] = \frac{1}{4} \frac{p''}{p^2} - \frac{3}{8} \frac{p'^2}{p^3} = -\frac{1}{2p^{1/2}} \frac{d^2}{dx^2} p^{-1/2} ; \\ \sigma'_3 &= -\frac{1}{2p} (2\sigma'_1 \sigma'_2 + \sigma''_2) = -\frac{1}{2} \frac{d}{dx} \frac{\sigma'_2}{p} . \end{aligned}$$

To the order \hbar or \hbar^2 we have, respectively,

$$\begin{aligned} e^{i \frac{x}{\hbar}} &\simeq \frac{1}{\sqrt{p(x)}} \exp \left(i \int_{x_0}^x \left[\frac{1}{\hbar} p(x) \right] dx \right) ; \\ e^{i \frac{x}{\hbar}} &\simeq \frac{1}{\sqrt{p(x)} e^{-\hbar^2 \frac{\sigma'_2}{p}}} \exp \left(i \int_{x_0}^x \left[\frac{1}{\hbar} p(x) + \hbar \frac{1}{2p^{1/2}} \frac{d^2}{dx^2} p^{-1/2} \right] dx \right) . \end{aligned}$$

From eqn (11.6b) it follows that:

- 1) The terms σ_n with even n are odd in p , and eqn (11.3) implies that for real $p(x)$ it contributes to the *phase* of the wave function.
- 2) The odd terms σ_n are even in p , and contribute to the amplitude of ψ .

The WKB approximation consists in keeping the dominant terms of the expression,

$$\psi(x) = b_1 \frac{1}{\sqrt{p}} e^{i \frac{1}{\hbar} \int_{x_0}^x p(x) dx} + b_2 \frac{1}{\sqrt{p}} e^{-i \frac{1}{\hbar} \int_{x_0}^x p(x) dx} ; \quad (11.7)$$

x_0 is an arbitrary reference point, and the coefficients b_1 and b_2 vary with x_0 . If the approximation were uniformly (in x) valid, we would have found an approximate solution of the problem.

To see the condition of validity of the formula, let us rewrite it as

$$\exp \left(i \int_{x_0}^x \sigma' \right) = \exp \left(i \int_{x_0}^x (\sigma'_0 - i\hbar\sigma'_1 - \hbar^2\sigma'_2 + \dots) \right) .$$

The approximation is good if the inequalities

$$\hbar^2 \frac{|\sigma'_2|}{|\sigma'_0|} \ll \hbar \frac{|\sigma'_1|}{|\sigma'_0|} \ll 1,$$

are met. The second inequality can be rewritten, by using eqn (11.6), as (let us assume real p)

$$\frac{1}{2} \hbar \frac{p'}{p^2} \ll 1 \Rightarrow \frac{1}{4\pi} \frac{d\lambda}{dx} \ll 1; \quad \lambda = \frac{\hbar}{p}; \quad (11.8)$$

λ is de Broglie's wavelength. Inequality (11.8) tells that the approximation is good when the variation of the wavelength is small compared to itself (i.e., it has a well-defined wavelength for many oscillations). To interpret the condition from the particle point of view, we write

$$p' = \frac{d}{dx} \sqrt{2m(E - V(x))} = \frac{1}{2} 2m \frac{V'}{p} = -m \frac{F}{p},$$

where F is the classical force. Equation (11.8) then imposes the condition

$$m \hbar \frac{F}{p^3} \ll 1,$$

which is certainly violated at the points where either F is too large or p is too small, in particular, at the classical turning points where $p = 0$.

Analogous considerations can also be made for the first of inequalities (11.8). Let us note that inequalities (11.8) impose local constraints, but the conditions on σ_2 may not be sufficient. In classically allowed regions (where p is real), σ_0 and σ_2 both form the phase of the function ψ , which is defined modulo 2π . It can therefore happen that even if $\sigma'_2 \ll \sigma'_0$ the effects due to σ'_2 are more important than those due to σ'_0 . The validity of the WKB approximation therefore requires that

$$\int_{x_0}^x \hbar^3 \sigma'_2 dx \ll 1,$$

quite independently of the classical turning points or the singularities of the potential.

The presence of the classical turning points in general, near which the WKB approximation breaks down, introduces a partition of the region of the coordinates, in each of which approximate formulas such as (11.3) are valid. Precisely because these formulas cannot be extrapolated up to near the partition points, the problem of establishing the correct *connection formulas* between expressions (11.7) valid in the neighboring regions is a nontrivial one.

11.1.1 Connection formulas

Let us consider first the case of a single turning point. Let $x = a$ be a root of the equation $E - V(x) = 0$. To fix the idea, let us suppose that $V(x) > E$ for $x > a$. The situation is schematically illustrated in

Figure 11.1. The region $x < a$ will be called *classically allowed* while the region where $x > a$ is the *classically forbidden* one. For $x < a$ the two linearly independent solutions are

$$\frac{1}{\sqrt{p}} \cos(|w|) ; \quad \frac{1}{\sqrt{p}} \sin(|w|) , \quad (11.9)$$

with

$$w(a, x) = \frac{1}{\hbar} \int_a^x p(x) dx , \quad p(x) = \sqrt{2m(E - V)} ;$$

whereas for $x > a$ it is

$$\frac{1}{\sqrt{|\tilde{p}|}} e^{-\tilde{w}} ; \quad \frac{1}{\sqrt{\tilde{p}}} e^{\tilde{w}} , \quad (11.10)$$

where

$$\tilde{w}(a, x) = \frac{1}{\hbar} \int_a^x \tilde{p}(x) dx , \quad \tilde{p}(x) = \sqrt{2m(V - E)} .$$

A possible method to find the connection formula is to solve the problem exactly with the linearized potential near $x = a$, and to match the asymptotic form of such a solution to the semi-classical wave functions valid far from the turning point, $|x - a| \gg 0$, on both sides of a . Near a , in fact, we can approximate as $2m\hbar^{-2}(E - V(x)) \simeq \beta^2(a - x)$, so eqn (11.1) becomes

$$\psi'' + \beta^2(a - x)\psi = 0 .$$

After setting $(x - a) = \beta^{-2/3}z$ we see that the equation is

$$\frac{d^2}{dz^2}\psi - z\psi = 0 , \quad (11.11)$$

whose solutions are the Airy functions: $\text{Ai}(z), \text{Bi}(z)$. The reader can find a brief summary of the properties of Airy functions in Supplement 24.1.3. At large values of z they behave as

$$\frac{|z|^{-\frac{1}{4}}}{\sqrt{\pi}} \cos\left(\frac{2}{3}|z|^{3/2} - \frac{\pi}{4}\right) \xrightarrow[z \rightarrow -\infty]{} \text{Ai}(z) \xrightarrow[z \rightarrow \infty]{} \frac{1}{\sqrt{\pi}} \frac{1}{2} z^{-1/4} e^{-\frac{2}{3}|z|^{3/2}} ; \quad (11.12a)$$

$$-\frac{|z|^{-\frac{1}{4}}}{\sqrt{\pi}} \sin\left(\frac{2}{3}|z|^{3/2} - \frac{\pi}{4}\right) \xrightarrow[z \rightarrow -\infty]{} \text{Bi}(z) \xrightarrow[z \rightarrow \infty]{} \frac{1}{\sqrt{\pi}} z^{-\frac{1}{4}} e^{+\frac{2}{3}|z|^{3/2}} . \quad (11.12b)$$

Let us write the momentum and the phase w in terms of z :

$$p = \hbar\beta(a - x)^{\frac{1}{2}} = \hbar\beta^{\frac{1}{3}}\sqrt{-z} ; \quad w(a, x) = -\frac{2}{3}\beta(a - x)^{\frac{3}{2}} = -\frac{2}{3}|z|^{\frac{3}{2}} ;$$

$$\tilde{p} = \hbar\beta(x - a)^{\frac{1}{2}} = \hbar\beta^{\frac{1}{3}}\sqrt{z} ; \quad \tilde{w}(a, x) = \frac{2}{3}\beta(x - a)^{\frac{3}{2}} = \frac{2}{3}|z|^{\frac{3}{2}} .$$

From eqn (11.12) it follows that the two independent solutions are

$$\frac{1}{\sqrt{p}} \cos\left(|w(a, x)| - \frac{\pi}{4}\right) \xrightarrow[x \rightarrow -\infty]{} \psi \xrightarrow[x \rightarrow \infty]{} \frac{1}{2} \frac{1}{\sqrt{\tilde{p}}} e^{-|\tilde{w}|} ; \quad (11.13a)$$

$$-\frac{1}{\sqrt{p}} \sin\left(|w(a, x)| - \frac{\pi}{4}\right) \xrightarrow[x \rightarrow -\infty]{} \psi \xrightarrow[x \rightarrow \infty]{} \frac{1}{\sqrt{\tilde{p}}} e^{+|\tilde{w}|} . \quad (11.13b)$$

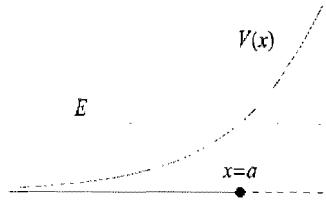


Fig. 11.1 A classical turning point. $x < a$ is the classically allowed region, $x > a$ the region the particle cannot penetrate into classically.

A generic linear combination of the solutions is therefore given by

$$\frac{1}{\sqrt{p}} \cos \left(|w(a, x)| - \frac{\pi}{4} + \alpha \right) \leftarrow \psi(x) \rightarrow \frac{\sin \alpha}{\sqrt{p}} e^{|\bar{w}|} + \frac{1}{2} \frac{\cos \alpha}{\sqrt{p}} e^{-|\bar{w}|}. \quad (11.14)$$

The formulas above also remain valid when the classically allowed region is $x > a$. Equations (11.13), (11.14) will be sufficient to cover all the cases discussed in this chapter. Obviously these and some of the subsequent formulas must be used *cum grano salis*: a small variation in the phase α in the classically allowed region induces an exponentially large correction in the forbidden region; vice versa, one needs to know with an exponential precision ψ in the forbidden region to get the correct phase α . In principle eqn (11.14) is an exact asymptotic expression, but for the reasons stated it must be applied with some care.

In many cases one is interested in the solution with a particular boundary condition: this allows us to use eqn (11.13) in an unambiguous way. For instance, if the whole region $\infty > x > a$ is classically forbidden, the exponentially growing component must be set strictly zero there ($\alpha = 0$), and one finds that

$$\frac{1}{\sqrt{p}} \cos \left(|w(a, x)| - \frac{\pi}{4} \right) \leftarrow \psi(x) \rightarrow \frac{1}{2} \frac{1}{\sqrt{p}} e^{-|\bar{w}|}. \quad (11.15)$$

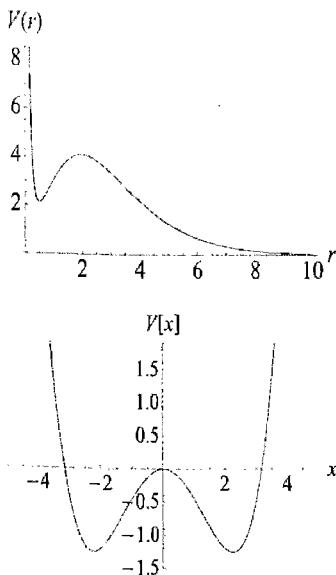


Fig. 11.2 Potentials with three and four inversion points.

The main applications of eqn (11.13) are: the derivation of the Bohr-Sommerfeld quantization condition, the semi-classical estimation of tunnel effect, and the theory of α decay. These and some other applications are discussed in the following.

Parabolic interpolation

The connection formula (11.14) was obtained by approximating the region near the turning point by a linearized potential. In the following this formula will be used repeatedly to obtain the tunneling amplitude, etc. In some cases, the two turning points may be so close to each other that a better approximation is provided by a quadratic potential. Namely, in the region near the double turning points, Schrödinger's equation can be approximated by

$$\psi'' + (b - ax^2) \psi = 0;$$

its solutions are the so-called parabolic-cylinder functions, and in this context play an analogous role to the Airy functions, used in the case of the linearized potential.

Below we cite the connection formula for cases in which there are classically forbidden regions on both sides of the small classically allowed region with two turning points, see [Berry and Mount (1972)] for the

derivation.

$$\frac{1}{\sqrt{|p|}} \exp(-|w(a_L, x)|) \xrightarrow{x \rightarrow -\infty} \psi \xrightarrow{x \rightarrow +\infty} \frac{1}{\sqrt{|p|}} \left[\left(\frac{2}{\pi} \right)^{1/2} \right. \\ \left. \left(\frac{e}{\tilde{J}} \right)^{\tilde{J}} \Gamma \left(\tilde{J} + \frac{1}{2} \right) \cos(\pi \tilde{J}) \exp(|w(a_R, x)|) + \sin(\pi \tilde{J}) \exp(-|w(a_R, x)|) \right]. \quad (11.16)$$

a_L, a_R are the two turning points, which limit the classical region. \tilde{J} indicates the action variable, in units of \hbar :

$$\tilde{J} = \frac{J}{\hbar} = \frac{1}{\hbar} \frac{1}{2\pi} \oint p(x) dx = \frac{1}{\hbar} \frac{1}{\pi} \int_{a_L}^{a_R} p(x) dx. \quad (11.17)$$

In eqn (11.16) the term with the cosine is exponentially increasing in the classically prohibited region, while the term with the sine is the decreasing one. We note that

$$\lim_{\tilde{J} \rightarrow \infty} \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{e}{\tilde{J}} \right)^{\tilde{J}} \Gamma \left(\tilde{J} + \frac{1}{2} \right) = 2. \quad (11.18)$$

11.2 The Bohr–Sommerfeld quantization condition

Let us consider a one-dimensional potential of the type shown in Fig. 11.3.

We expect that Schrödinger's equation gives a series of bound states with E_n and $\psi_n, \psi_n \in \mathbb{L}^2$. The semi-classical treatment of the problem starts with the identification of the classical turning points,

$$p(x) = 0, \text{ i.e., } E = U(x).$$

Let a and b be the roots. We shall use the notation

$$w(c, x) = \frac{1}{\hbar} \int_c^x \sqrt{2m(E - V)} dx \quad \sigma(c, x) = \frac{1}{\hbar} \int_c^x \sqrt{2m(V - E)} dx.$$

In the classically accessible regions $x < a$ and $x > b$ the asymptotic expansion of the solution must be

$$\psi \sim \exp(\pm \frac{1}{\hbar} \int |p(x)| dx).$$

The request $\psi \in \mathbb{L}^2$ imposes that asymptotically only the exponentially decreasing functions be present; for instance in $x > b$ the acceptable solution is of the form

$$\frac{C}{2} \frac{1}{\sqrt{|p|}} \exp(-\sigma(b, x)). \quad (11.19)$$

The connection formula, eqn (11.13), tells us that the wave function in the region $x < b$ is

$$\frac{C}{2} \frac{1}{\sqrt{|p|}} \exp(-\sigma(b, x)) \rightarrow \frac{C}{\sqrt{|p|}} \cos \left(w(x, b) - \frac{\pi}{4} \right). \quad (11.20)$$

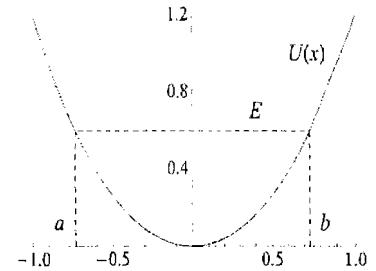


Fig. 11.3 A one-dimensional potential. a, b are the classical turning points.

Note that this formula fixes the phase of the wave function but in itself does not select any particular value of the energy.

The same argument, applied at the left turning point imposes the condition that

$$\frac{D}{2} \frac{1}{\sqrt{|p|}} \exp(-\sigma(x, a)) \rightarrow \frac{D}{\sqrt{|p|}} \cos\left(w(a, x) - \frac{\pi}{4}\right). \quad (11.21)$$

The quantization condition arises from the requirement that the two determinations of the wave function in the classically allowed region, $a \leq x \leq b$, coincide. The amplitude must be the same, implying that $|C| = |D|$. We can always choose a real wave function: $D = \pm C$. To compare the phase, let us write eqn (11.21) in the form

$$\begin{aligned} \cos\left(w(a, x) - \frac{\pi}{4}\right) &= \cos\left(w(a, b) - w(x, b) - \frac{\pi}{4}\right) \\ &= \cos\left(w(x, b) - w(a, b) + \frac{\pi}{4}\right). \end{aligned}$$

This determination can differ from eqn (11.20) only for $n\pi$, with n even or odd, according to the relative sign between C and D . Therefore

$$-\frac{\pi}{4} = n\pi + \left(-w(a, b) + \frac{\pi}{4}\right) \Rightarrow w(a, b) = \left(n + \frac{1}{2}\right)\pi. \quad (11.22)$$

Corresponding to the value of n , even or odd, one has $D = (-1)^n C$. By using the classical definition of the action variable, J , defined as the integral of $p(x)$ over a full period, in this case along the trajectory, $a \rightarrow b \rightarrow a$, we can write eqn (11.22) in the form

$$J \equiv \frac{1}{2\pi} \oint p(x) dx = \left(n + \frac{1}{2}\right)\hbar. \quad (11.23)$$

This is the Bohr–Sommerfeld quantization condition, apart from a small (but important) difference of an additional $\hbar/2$ term on the right-hand side. Equation (11.23) can be solved for E , giving the different levels as n is varied.

As x increases from a to b , the phase of the cosine,

$$\frac{C}{\sqrt{p}} \cos\left(\frac{1}{\hbar} \int_a^x p(x) dx - \frac{\pi}{4}\right),$$

varies between $-\pi/4$ and $n\pi - \pi/4$, that is, it has n zeros. The corresponding wave function is that of the n -th excited state, with $E_0 \leq E_1 \dots$, in accordance with the oscillation theorem (Subsection 3.2.3).

As has been said already, the semi-classical approximation corresponds to the limit of geometric optics of electromagnetism, i.e., the limit of small wavelength with respect to the characteristic length of the problem. In our case the typical length is the size of the classically accessible region, $L = b - a$, so we expect that the better the approximation becomes, the larger n is, that is the smaller $\lambda = h/p \sim L/n$ is. We should be able to recover the classical limit in the limit $n \rightarrow \infty$.

For the complete determination of the wave function one needs to fix the constant C . Normally the overall constant in front of the wave function is determined by the normalization condition $\mathbb{L}^2 = 1$. As the wave function is exponentially small outside the classical region, one may write

$$1 = \int_{-\infty}^{\infty} |\psi|^2 dx \simeq \int_a^b |\psi|^2 dx = C^2 \int_a^b \frac{dx}{p} \cos^2 \left(\frac{1}{\hbar} \int_x^b p(x) dx - \frac{\pi}{4} \right).$$

As the semi-classical approximation is good when the cosine oscillates many times, in a first approximation we could replace $\cos^2(\varphi)$ by $\frac{1}{2}$, obtaining

$$\frac{C^2}{2} \int_a^b \frac{dx}{p} \simeq 1. \quad (11.24)$$

The period of oscillation is defined by

$$T = 2 \int_a^b \frac{dx}{v} = 2m \int_a^b \frac{dx}{p},$$

and therefore

$$\frac{C^2}{2} \frac{T}{2m} = 1 \Rightarrow C = 2\sqrt{\frac{m}{T}} = \sqrt{\frac{2m\omega}{\pi}}; \quad \omega = \frac{2\pi}{T}. \quad (11.25)$$

We have obtained estimate (11.24) for C^2 assuming that $n \gg 1$; actually these formulas are often used for small n also, and in particular for the ground state. In Problem 11.15 the reader can find a proof² of eqn (11.25) which does not use the condition $n \gg 1$.

²The proof is due to W. H. Furry [Furry (1947)].

11.2.1 Counting the quantum states

The quantization condition, eqn (11.23),

$$\frac{1}{2\pi} \oint p dq = \hbar \left(n + \frac{1}{2} \right) \quad (11.26)$$

has obvious geometrical meaning. A classical periodic motion corresponds to a closed trajectory in phase space: the left-hand side of eqn (11.26) is the area (in a one-dimensional case) enclosed by a closed curve in the (q, p) plane. Relation (11.26) asserts that for each quantum state there is an associated area $2\pi\hbar$ of phase space. Equivalently, if we consider a macroscopic portion of phase space, $\Delta p \Delta q$, the number of quantum states included in it would be

$$n = \frac{\Delta p \Delta q}{2\pi\hbar}. \quad (11.27)$$

As is well known the most important application of this formula is in statistical physics, in which the counting of the states is an important element. For the case of a particle in a box, eqn (11.27) reduces to the classical counting of the vibrational modes of a cavity: $p/\hbar = k = 2\pi/\lambda$

is the wave number, and the quantization condition amounts to the statement that the size of the box is an integer multiple of half the wavelength, and in this case there is no need to invoke the semi-classical approximation. Still, the present formulation has the advantage that the answer does not depend on the detail of the potential.

Equation (11.26) provides another interesting relation which helps to understand the connection between classical and quantum mechanics. If we consider a system with $n \gg 1$ it is possible to estimate the difference between two adjacent levels. Let $\Delta E = E_{n+1} - E_n$ be such a difference; one has approximately (by using $p = \sqrt{2m(E - U)}$)

$$\Delta n = 1 = \frac{1}{2\pi\hbar} \Delta E \frac{\partial}{\partial E} \oint pdx = \frac{1}{2\pi\hbar} \Delta E \oint \frac{mdx}{p} = \frac{1}{2\pi\hbar} \Delta E T,$$

where T is the period of the classical motion. Calling $\omega = 2\pi/T$ the angular frequency of the motion, we have

$$\Delta E \simeq \hbar\omega. \quad (11.28)$$

This means that for large values of n the levels are equally spaced and the difference between two energy levels, corresponding to the frequency of the transition between them, is an integer multiple of the basic frequency of the classical oscillation. In the semi-classical approximation the evolution of a state is then

$$\psi(x, t) \sim \sum_k \psi_k(x) e^{-ik\omega t},$$

which is just the form expected for a function periodic with period T , in other words just the Fourier series.

We expect that the classical description of a system corresponds to a precise localization in phase space; in other words the characteristic quantum number n must be large to have a classical limit, but the distribution of the values must be sufficiently narrow that the volume $\Delta p \Delta q$ is well defined and at the same time much larger than the quantum granularity $2\pi\hbar$. In other words the classical state corresponds to the situation

$$1 \ll \Delta n \ll n.$$

If we expand a state of this sort in terms of the semi-classical eigenfunctions

$$\Psi = \sum_n c_n \psi_n,$$

³Here we shall follow the discussion in [Landau and Lifshitz (1976 c)].

we would have the coefficients c_n distributed in a narrow range of n , around some $\bar{n} \gg 1$. Let us consider now the time evolution of an observable f ,³

$$\bar{f}(t) = \langle \Psi(t) | f | \Psi(t) \rangle = \sum_{m,n} c_n^* c_m f_{mn} e^{\frac{i}{\hbar}(E_m - E_n)t}.$$

For all levels appearing in the sum we can apply eqn (11.28), and hence $E_m - E_n \simeq (m-n)\hbar\omega$. By changing the variable and writing $m = n+k$ we have

$$\tilde{f}(t) = \sum_n \sum_k c_{n+k}^* c_n f_{n+k,n} e^{ik\omega t} = \sum_k \tilde{f}_k e^{ik\omega t}.$$

Such an evolution is exactly what is expected of a classical motion with periodicity $T = 2\pi/\omega$. We see that the Fourier components of the classical evolution correspond to the matrix elements of the quantum observables.

Historically an exactly opposite route was taken by Heisenberg to arrive at quantum mechanics. The Fourier components of a classical observable are to be related to the quantum jumps, that is, are to be associated to a quantity $F(n+k, n)$, which for Heisenberg, was the main quantity to be studied. An analogy with Ritz's combination rule in spectroscopy then led Heisenberg to a multiplication rule for the quantity F , which was finally recognized as the multiplication rule for matrices, infinite-dimensional in general.

11.2.2 Potentials defined for $x > 0$ only

In various applications it is useful to generalize the preceding analysis to those cases in which the particle is bound to move on a half-line, for instance the case of a radial motion of a particle moving in a spherically symmetric potential, $V(r)$, in an s wave. The situation is illustrated in Figure 11.4. In this case the wave function must satisfy the constraint $\psi(0) = 0$. It is easy to find the quantization condition for these cases by formally extending the region of the space to $x < 0$ with the potentially defined for negative x as $V(x) = V(|x|)$. The classical turning points are then $\pm a$; the constraints at $x = 0$ are automatically satisfied by the odd states of this new potential, and therefore it must be the case that

$$\begin{aligned} w(-a, a) &= 2w(0, a) = \left[(2n+1) + \frac{1}{2} \right] \pi \\ &= \left(2n + \frac{3}{2} \right) \pi \Rightarrow w(0, a) = \left(n + \frac{3}{4} \right) \pi. \end{aligned} \quad (11.29)$$

In other words, in terms of the action integral J

$$J = \frac{1}{2\pi} \oint p(x) dx \equiv \frac{1}{2\pi} 2 \int_0^a p(x) dx = \left(n + \frac{3}{4} \right) \hbar. \quad (11.30)$$

It is instructive to get the same result directly anyway. The condition of matching and the requirement $\psi \in L^2$ in this case reduce to

$$\frac{C}{2\sqrt{|p|}} \exp(-\sigma(a, x)) \rightarrow \frac{C}{\sqrt{|p|}} \cos \left(w(x, a) - \frac{\pi}{4} \right).$$

The vanishing of the function at $x = 0$ imposes the condition

$$w(0, a) - \frac{\pi}{4} = n\pi + \frac{\pi}{2} \rightarrow w(0, a) = n\pi + \frac{3\pi}{4},$$

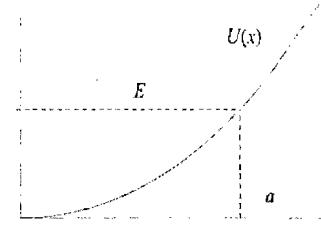


Fig. 11.4 A one-dimensional potential limited to the region $x > 0$. $0, a$ are the turning points.

which is again the condition (11.29).

11.2.3 On the meaning of the limit $\hbar \rightarrow 0$

No doubt the careful reader will have asked the following question at some point or other: what does it mean to consider the limit $\hbar \rightarrow 0$, since \hbar is a dimensional quantity. It has the dimension of an action, and the question of the validity of the WKB approximation depends on a comparison between the typical action involved in the problem and \hbar . In view of the form of the quantization condition, eqn (11.23), the approximation will in general be good if $\hbar/J \ll 1$, that is, for large n , as we have already argued on the base of an analogy with the geometric optics. Formally the semi-classical limit is thus defined by $\hbar \rightarrow 0$ at constant J , or a power expansion in $1/n$. We expect that the corrections to the WKB approximation will be of the form

$$\frac{J}{\hbar} = \frac{1}{2\pi\hbar} \oint p(x) dx = n + \frac{1}{2} + \frac{c_1}{n} + \dots$$

Equation (11.23) is to be interpreted as the dominant and the first sub-dominant terms of an expansion in $1/n$, and any question about the terms suppressed with respect to it in the WKB approximation must be considered as part of the analysis of successive terms of such an expansion. For instance we shall see in a moment that the WKB approximation exactly reproduces the spectrum of the harmonic oscillator and of the hydrogen atom. These statements do not mean much in themselves, unless the vanishing of the corrections to them is not verified.

Another point to be kept in mind is the following. It can happen that \hbar appears in the Hamiltonian in places other than the terms with the derivatives such as the kinetic term, $\hbar^2 d^2/dx^2$, i.e., in the potential. In the spirit of the semi-classical approximation, an approximation based on small wavelengths, the terms of the potential should be neglected.

Exceptions to this rule arise when there are also singularities of the potential present, such as a potential term of the form \hbar/x . This term will be negligible except near the singular point $x = 0$. In such points the WKB approximation fails and the particular form of the wave function reflects the nature of the singularity: it is analogous to the fact that the phase α in the general formula, eqn (11.14), depends on the behavior of the wave function near the turning point. This sort of problem arises for instance in the treatment of angular variables, as is studied in the next section.

11.2.4 Angular variables

Let us consider the case in which Schrödinger's equation refers to angular variables. The simplest case is associated with L_z . For azimuthal motion, Schrödinger's equation takes the form

$$-\hbar^2 \frac{\partial^2 f}{\partial \varphi^2} = \lambda f, \quad (11.31)$$

where φ stands for the azimuthal angle, f the wave function, and λ the eigenvalue. Equation (11.31) can obviously be solved exactly; however in the spirit of the semi-classical approximation it can be treated as a one-dimensional Schrödinger equation for a particle of mass $\frac{1}{2}$ and energy λ . The classical momentum conjugate to φ is $p_\varphi = \pm\sqrt{\lambda}$. The two possible determinations for p_φ correspond to two semi-classical solutions,

$$f = C \exp \left[\pm \frac{i}{\hbar} \int_0^\varphi p_\varphi d\varphi \right] = C \exp \left(\pm \frac{i}{\hbar} p_\varphi \varphi \right). \quad (11.32)$$

The interesting point is that φ being periodic and p_φ constant and non-vanishing, there are no turning points, and the semi-classical solution (11.32) is everywhere valid. The quantization condition arises from the periodicity condition for φ :

$$f(\varphi + 2\pi) = f(\varphi); \Rightarrow p_\varphi = \hbar m; \quad m \in \mathbb{Z},$$

which is the exact solution of the system.

We note that in this case the quantization condition has no half-integer correction, in contrast to the oscillatory case. These two types of motions correspond, in the old quantum theory, to the rotational and oscillatory motions, and indeed it was known there that the appropriate quantization condition (with or without $\hbar/2$) had to be used.

The normalized expression of the WKB wave function is

$$f(\varphi) = \frac{C}{\sqrt{|p_\varphi|}} \exp(im\varphi) = \frac{1}{\sqrt{2\pi}} \exp(im\varphi).$$

The normalization constant here differs from eqn (11.25) as here we are considering complex exponential functions instead of the real trigonometric functions.

A slightly more complicated case than this is that of the three-dimensional angular variables,

$$-\hbar^2 \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\} \psi = \Lambda \psi. \quad (11.33)$$

We know from the theory of angular momentum that the exact solution of this has $\Lambda = \hbar^2 \ell(\ell+1)$ as the eigenvalue. Let us try to see how this problem can be attacked in a semi-classical approach. For simplicity let us consider the case of $m = 0$, i.e., by eliminating the derivative term with respect to φ . The exact solution of eqn (11.33) is

$$\psi(\theta) = P_\ell(\cos \theta); \quad \ell \in \mathbb{N}; \quad \psi(0) = 1. \quad (11.34)$$

By making a change of variables $\psi(\theta) = f(\theta)/\sqrt{\sin \theta}$ we see that eqn (11.33) can be brought to the form

$$\hbar^2 \left[\frac{d^2 f}{d\theta^2} + \left(\frac{1}{4} + \frac{1}{4 \sin^2 \theta} \right) f \right] + \Lambda f = 0; \quad 0 \leq \theta \leq \pi. \quad (11.35)$$

The “classical momentum” is

$$p_\theta = \sqrt{\Lambda + \frac{\hbar^2}{4} + \frac{\hbar^2}{4 \sin^2 \theta}}. \quad (11.36)$$

The condition for the validity of the semi-classical approximation in eqn (11.35) is violated near the boundaries of the domain. In fact, the de Broglie wavelength at $\theta \sim 0$ is of the order of $\lambda_\theta = \hbar/p_\theta \sim \theta$ and $d\lambda_\theta/d\theta \sim 1$, and similarly for the region $\theta \sim \pi$. Far from these neighborhoods, and for finite Λ and for $\hbar \rightarrow 0$, we may neglect terms in $1/\sin^2 \theta$, and, setting $\lambda = \sqrt{\Lambda + \hbar^2/4}$, we can write the semi-classical solution

$$f(\theta) = A \cos(\lambda\theta - \alpha); \quad (11.37)$$

with

$$\frac{\hbar}{\sin \theta} \ll \lambda; \quad \text{i.e. } \theta \gg \frac{\hbar}{\lambda}; \quad \text{and } \theta \ll \pi - \frac{\hbar}{\lambda}.$$

The phase α is usually determined from the condition of matching but in this case one cannot directly use eqn (11.15) as we are in the presence of a singularity: the matching must be done by finding an exact solution near the singularity and connecting it to eqn (11.37). For $\theta \ll 1$ eqn (11.35) becomes

$$\frac{d^2 f}{d\theta^2} + \left(\frac{\lambda^2}{\hbar^2} + \frac{1}{4\theta^2} \right) f = 0, \quad (11.38)$$

which has as a regular solution

$$f(\theta) \sim \sqrt{\theta} J_0\left(\frac{\lambda}{\hbar}\theta\right); \quad \theta \ll 1. \quad (11.39)$$

J_0 is a Bessel function of order 0. The normalization in eqn (11.39) has been chosen so as to satisfy eqn (11.34), as $J_0(0) = 1$. For $\lambda \gg 1$ eqn (11.39) has a region of overlap with eqn (11.37) around $\hbar/\lambda \ll \theta \ll 1$. In this domain one can use the asymptotic expansion⁴

$$J_0\left(\frac{\lambda}{\hbar}\theta\right) \sim \sqrt{\frac{2\hbar}{\pi\lambda\theta}} \cos\left(\frac{\lambda}{\hbar}\theta - \frac{\pi}{4}\right), \quad (11.40)$$

and this fixes the two constants A, α in eqn (11.37):

$$f(\theta) \simeq \sqrt{\frac{2\hbar}{\pi\lambda}} \cos\left(\frac{\lambda}{\hbar}\theta - \frac{\pi}{4}\right).$$

Let us note that, in accordance with the cases already seen, the procedure does not fix the value of λ , which must follow from the single-valuedness of the function $f(\theta)$. The estimate made for small θ can be repeated for the region near the second singularity $\theta = \pi$: it suffices to make a change of variables and set $x = \pi - \theta$. This way we find the second expression for f :

$$\sqrt{\frac{2\hbar}{\pi\lambda}} \cos\left(\frac{\lambda}{\hbar}(\pi - \theta) - \frac{\pi}{4}\right) = \sqrt{\frac{2\hbar}{\pi\lambda}} \cos\left(\frac{\lambda}{\hbar}(\theta - \pi) + \frac{\pi}{4}\right).$$

⁴ This expansion can be obtained by using the saddle point method in the integral representation

$$J_0(z) = \frac{1}{\pi} \int_0^\pi d\theta \cos(z \sin \theta).$$

The two determinations must coincide apart from a sign, thus

$$\left(\frac{\lambda}{\hbar}\theta - \frac{\pi}{4}\right) - \left(\frac{\lambda}{\hbar}(\theta - \pi) + \frac{\pi}{4}\right) = \pi\ell \Rightarrow \lambda = \hbar\left(\ell + \frac{1}{2}\right); \quad \ell \in \mathbb{N},$$

from which $\Lambda = \lambda^2 - \hbar^2/4 = \hbar^2\ell(\ell+1)$ and, for the wave function

$$P_\ell(\cos\theta) \simeq J_0\left(\left(\ell + \frac{1}{2}\right)\theta\right) \simeq \sqrt{\frac{2}{\pi\ell\theta}} \cos\left(\left(\ell + \frac{1}{2}\right)\theta - \frac{\pi}{4}\right). \quad (11.41)$$

Let us note that the condition $\lambda/\hbar \gg 1$ is equivalent, in terms of ℓ , to $\ell \gg 1$.

The fact that we have obtained the exact answer for the eigenvalues of L^2 involves a little bit of cheating: it comes from having retained the term $\hbar^2/4$ in eqn (11.36). In the limit $\hbar \rightarrow 0$ at fixed Λ , which is the semi-classical limit we are studying, this is an arbitrary procedure: strictly speaking we are not entitled to keep such terms, and the standard semi-classical approximation consists in discarding all terms proportional to \hbar which do not multiply the derivatives. The rest of the argument is the same and one would have obtained $\Lambda = \hbar^2(\ell + \frac{1}{2})^2$ which, in the limit of large ℓ , coincides with what we found above anyway.

The question arises when one wants to apply the formula found to smaller values of ℓ , in particular to the S waves. In this case the quality of the approximation appears to depend on the system: in the case of the Coulomb potential in three dimensions we shall see that the substitution $\Lambda \rightarrow \hbar^2(\ell + \frac{1}{2})^2$ gives a better approximation.

11.2.5 Radial equations

Analogous considerations apply in general, in the presence of singularities in the potential. If the turning points either coincide or stay near such a singularity, the connection formulas found earlier must be appropriately modified. We have already considered the case of the radial equation where the particle “lives” on a half-line $r \geq 0$, and seen how the quantization condition is modified from eqn (11.23) to eqn (11.30). The problem becomes relevant for potentials singular at $r = 0$ such as the Coulomb potential, or more generally in the presence of the centrifugal potential, in which the potential behaves as $1/r^2$.

Let us consider a particle moving in a spherically symmetric potential $U(r)$. The radial Schrödinger equation for the reduced wave function $\varphi = R(r)/r$ has the form

$$\hbar^2 \frac{d^2\varphi}{dr^2} + \left[2m(E - U) - \frac{L^2}{r^2}\right] \varphi = 0; \quad L^2 = \hbar^2\ell(\ell+1). \quad (11.42)$$

The condition for the validity of the semi-classical approximation is, in general,

$$\frac{d}{dr}\left(\frac{\hbar}{|p|}\right) \ll 1; \quad p = \sqrt{2m\left((E - U) - \frac{\hbar^2}{2mr^2}\ell(\ell+1)\right)}.$$

For a singular potential of the form, $V \sim C r^{-\alpha}$, for $r \rightarrow 0$, one has $|p| \sim \sqrt{2mV} \sim r^{-\alpha/2}$, that is

$$\frac{d}{dr} \left(\frac{\hbar}{|p|} \right) \sim \frac{\alpha \hbar}{2\sqrt{2mC}} r^{\alpha/2-1} \ll 1.$$

The semi-classical condition is certainly violated for $\alpha < 2$, in particular for the Coulomb potential in the S wave, while the case $\alpha = 2$ (e.g. a Coulomb potential for $\ell \neq 0$), we are on the borderline. This is also a general situation where the centrifugal potential is dominant, in which

$$\frac{d}{dr} \left(\frac{\hbar}{|p|} \right) \sim \frac{1}{\sqrt{\ell(\ell+1)}}.$$

The approximation is good, as expected, only for $\ell \gg 1$.

Let us analyze the particularly interesting case of the Coulomb potential $U = -Ze^2/r$. We shall consider the two problems separately:

(a) *Semi-classical estimate of the spectrum.*

In this case we consistently apply the Bohr-Sommerfeld quantization condition. The angular part, according to this procedure, has quantization of the type $\tilde{L} = \hbar(\ell + \frac{1}{2})$. One uses this expression to calculate the radial momentum p_r :

$$p_r(r) = \sqrt{2m \left(E + \frac{Ze^2}{r} - \frac{\hbar^2}{2mr^2} (\ell + \frac{1}{2})^2 \right)},$$

and apply the quantization condition (11.23). The equation $p_r = 0$ has two roots for $E < 0$, giving rise to two turning points r_1, r_2 :

$$\frac{1}{r_{1,2}} = \frac{(\ell + \frac{1}{2})^2}{a_0} \left(1 \pm \sqrt{1 - \frac{2|E|}{\varepsilon_0} (\ell + \frac{1}{2})^2} \right),$$

with

$$a_0 = \frac{\hbar^2}{Zme^2}; \quad \varepsilon_0 = \frac{Ze^2}{a_0}.$$

Condition (11.23) can be written as

$$J_r = \frac{1}{2\pi} \oint p_r(r) dr = \frac{1}{\pi} \int_{r_1}^{r_2} p_r(r) dr = \hbar(n_r + \frac{1}{2}), \quad (11.43)$$

and by performing the integration we find that

$$J_r = \hbar \sqrt{\frac{\varepsilon_0}{2|E|}} - \hbar(\ell + \frac{1}{2}) = \hbar(n_r + \frac{1}{2}) ; n_r = 0, 1, \dots;$$

the energy levels follow:

$$E_n = -|E| = -\frac{\varepsilon_0}{2n^2}; \quad n = n_r + \ell + 1 = 1, 2, \dots,$$

which coincides with the exact result. For details see Problem 11.3.

(b) *Semi-classical approximation for the wave function.*

In particular we want to recover the quantization condition for p_r and the energy levels. In this case the problem is to find a good approximation for the wave function which is plagued by the problems mentioned above. For example we note that for $\ell > 0$ the region $r \sim 0$ is in the classically forbidden zone and the WKB prescription dictates the behavior in the action

$$\frac{1}{\sqrt{|p|}} e^{-\int |p(r)| dr} \sim \frac{1}{\sqrt{|p|}} e^{\pm \sqrt{\ell(\ell+1)} \int^r \frac{dr}{r}} = r^{1/2} e^{\pm \sqrt{\ell(\ell+1)}},$$

while the regular behavior which follows from eqn (11.42) is $\varphi \sim r^{\ell+1}$. We leave it to the reader to verify that for $L^2 \rightarrow \hbar^2 \ell(\ell+1)$ the quantization rule (11.23) does not reproduce the correct result. A method to consistently treat the limit $\hbar \rightarrow 0$ in the radial equation (11.42) has been proposed in [Langer (1937)]. Basically the idea is to make a change of variables so that the singular point is sent to infinity, so as to make the WKB formulas applicable everywhere on the real axis. The result will again be the substitution $\ell(\ell+1) \rightarrow (\ell + \frac{1}{2})^2$, which in this context takes the name of the Langer correction.

Langer corrections

Set

$$r = e^x; \quad \varphi = e^{x/2} u(x); \quad (11.44)$$

substituting these in eqn (11.42) gives

$$\frac{\hbar^2}{2m} \frac{d^2 u}{dx^2} - \frac{\hbar^2}{2m} \left(\ell(\ell+1) + \frac{1}{4} \right) u + (Ee^{2x} + Ze^2 e^x) u = 0.$$

The effective momentum for $E < 0$ is

$$p(x) = e^x \sqrt{2m \left(Ze^2 e^{-x} - |E| - \frac{\hbar^2 (\ell + \frac{1}{2})^2}{2m} e^{-2x} \right)}.$$

With this substitution the WKB approximation is applicable along the whole real axis, except near the turning points, the singularity of the potential having been sent away to infinity. The turning points are the same as the preceding case, with e^{-x} replacing $1/r$ and the Bohr-Sommerfeld quantization condition:

$$\hbar(n_r + \frac{1}{2}) = \frac{1}{\pi} \int_{x_1}^{x_2} p(x) dx = \hbar(\ell + \frac{1}{2}) \int_{x_1}^{x_2} e^x \sqrt{(e^{-x} - \frac{1}{r_2})(\frac{1}{r_1} - e^{-x})} dx,$$

which is identical to eqn (11.43) after the change of variable $r = e^x$, and therefore yields the correct hydrogenoid spectrum.

For $x \rightarrow -\infty$ the momentum behaves as $|p(x)| \rightarrow \hbar(\ell + \frac{1}{2})$, so for small r one finds that

$$u \sim \frac{1}{\sqrt{|p|}} e^{\int \frac{|p|}{\hbar} dx} \rightarrow e^{(\ell + \frac{1}{2})x},$$

and the reduced wave function,

$$\varphi = e^{x/2} u \rightarrow e^{(\ell+1)x} = r^{\ell+1},$$

which is the correct behavior at $r \rightarrow 0$.

The Langer correction can be applied in the case of any spherically symmetric potential.

11.2.6 Examples

The harmonic oscillator

As is well known the application of the WKB formula to the harmonic oscillator gives

$$\hbar \left(n + \frac{1}{2} \right) = \frac{1}{\pi} \sqrt{2mE} a \int_0^1 \sqrt{1 - z^2} dz = \frac{2E}{\omega \pi} \frac{\pi}{2} = \frac{E}{\omega},$$

as the exact answer for the energy levels. The details are left to the reader as an exercise.

Less known perhaps is the result for the wave function. Figure 11.5 shows a comparison between the exact wave function and the semi-classical one, for the ground state and for the state $n = 10$: it is evident that the approximation is surprisingly good for $n = 10$ already, except, of course, near the turning points.

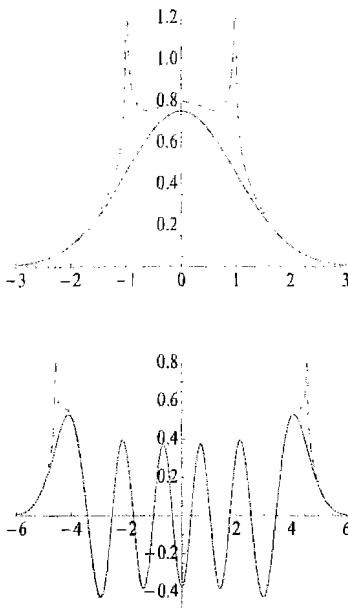


Fig. 11.5 The WKB wave function (full curve) and the exact wave function (dashed line) for the $n = 0$ and $n = 10$ states of a harmonic oscillator.

For reference, here is the explicit form of the WKB wave function:

$$C = \sqrt{\frac{4m}{T}}; \quad a = \sqrt{\frac{2E}{m\omega^2}}; \quad E = \hbar\omega \left(n + \frac{1}{2} \right); \quad p(x) = \sqrt{2mE} \sqrt{1 - \frac{x^2}{a^2}},$$

and

$$\begin{aligned} 0 < x < a : \quad \psi(x) &= \frac{C}{\sqrt{p(x)}} \cos \left(\frac{1}{\hbar} \int_{-a}^x p(x) dx - \frac{\pi}{4} \right) \\ &= \frac{C}{\sqrt{p(x)}} \cos \left(\frac{2\pi}{4} \left(n + \frac{1}{2} \right) - \frac{\pi}{4} + \int_0^x \frac{p(x)}{\hbar} dx \right) \\ &= \frac{C}{\sqrt{p(x)}} \cos \left(\frac{n\pi}{2} + \frac{E}{\hbar\omega} \left[\arcsin \left(\frac{x}{a} \right) + \frac{x}{a} \sqrt{1 - \frac{x^2}{a^2}} \right] \right); \\ a < x : \quad \psi(x) &= \frac{C}{2\sqrt{p(x)}} \exp \left(-\frac{E}{\hbar\omega} \left[\frac{x}{a} \sqrt{\frac{x^2}{a^2} - 1} - \operatorname{argcosh} \left(\frac{x}{a} \right) \right] \right). \end{aligned}$$

eqn (11.8).

The discontinuities at the classical turning points reflect the general constraint. A more refined (uniform) approximation can be performed; see notebook NB-11.9. In this uniform approximation the WKB approximation uniformly approximate the wave function, even at the classical transition points. An example for a quartic oscillator is given in Figure 11.6.

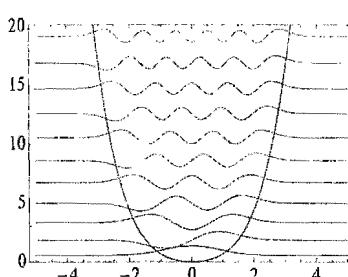


Fig. 11.6 A uniform WKB approximation for the first few states of an anharmonic oscillator.

The quartic potential

A less trivial case concerns the quartic potential, $U = \frac{g}{2}x^4$:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}gx^4\psi = E\psi. \quad (11.45)$$

By making a transformation $x = \lambda z$, with $\lambda = (\hbar^2/mg)^{1/6}$ we see that eqn (11.45) transforms into

$$-\frac{1}{2} \frac{d^2\psi}{dz^2} + \frac{1}{2}z^4\psi = \frac{\epsilon}{2}\psi; \quad \frac{\epsilon}{2} = E \left(\frac{m}{\hbar^2}\right)^{2/3} g^{-1/3}. \quad (11.46)$$

The eigenvalues of eqn (11.46) do not depend on any parameter, and hence it suffices to study it and put at the end

$$E_n = \left(\frac{\hbar^2}{m}\right)^{2/3} g^{1/3} \frac{\epsilon}{2}. \quad (11.47)$$

For eqn (11.46) the turning points are $z = \pm a = \pm \varepsilon^{1/4}$ and the quantization condition can be written as⁵

⁵ $B(p, q)$ is Euler's beta function.

$$\begin{aligned} n + \frac{1}{2} &= \frac{1}{2\pi} \sqrt{\varepsilon} 2 \int_{-a}^a \sqrt{1 - \left(\frac{z}{a}\right)^4} dz = \frac{2}{\pi} a \sqrt{\varepsilon} I, \\ I &= \frac{1}{4} B\left(\frac{1}{4}, \frac{3}{2}\right) = \frac{\sqrt{\pi} \Gamma\left(\frac{1}{4}\right)}{8 \Gamma\left(\frac{7}{4}\right)} = 0.8740192\dots, \end{aligned}$$

from which

$$\varepsilon_n = \left[\frac{\pi}{2I} \left(n + \frac{1}{2}\right)\right]^{4/3}.$$

A comparison between the WKB results here and the exact levels (which can be found by the variational method discussed in the previous chapter) is shown below:

n	ε_n	ε_n^{WKB}	$\delta\varepsilon/\varepsilon$
0	1.06036	0.86715	0.18222
1	3.79967	3.75192	0.01257
2	7.45570	7.41399	0.00559
3	11.64475	11.61153	0.00285
4	16.26183	16.23361	0.00173
5	21.23837	21.21365	0.00116

As may be seen, the approximation steadily improves for large n but is already quite reasonable even for the ground state.

11.3 The tunnel effect

One of the most characteristic phenomena in quantum mechanics is the tunnel effect: in classical terms, this is the transition of a particle between two zones separated by a portion of space which is classically

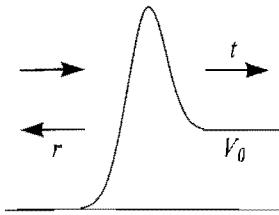


Fig. 11.7 Schematic illustration of the tunnel effect. An incident wave from the left gives rise to the transmitted and reflected waves t, r , respectively.

from the left gives rise to the transmitted and reflected waves t, r , respectively.

forbidden. A typical situation is illustrated in Figure 11.7: a particle incident from the left, with energy less than the maximum height of the potential, hits the potential barrier. Classically the only possibility is for it to be bounced back; quantum mechanically the particle penetrates through the barrier, with a non-vanishing amplitude.

These processes have been discussed in a simple one-dimensional context in Chapter 3; here a semi-classical description of the phenomena will be presented. The stationary wave function which describes the process is, asymptotically,

$$\psi(x) = \begin{cases} \frac{1}{\sqrt{k}} [e^{ikx} + r e^{-ikx}] & x \rightarrow -\infty \\ \frac{1}{\sqrt{k'}} t e^{ik' x} & x \rightarrow +\infty \end{cases}; \quad (11.48)$$

k and k' are the wave numbers of the incident and outgoing particle:

$$p = \hbar k; \quad p' = \hbar k';$$

we shall assume that the limiting values for $x \rightarrow \pm\infty$ of the potential are respectively 0 and V_0 , and that the momentum is given by

$$p = \sqrt{2mE}; \quad p' = \sqrt{2m(E - V_0)}.$$

From the expression of the current density

$$j = \frac{\hbar}{2mi} \left(\psi^* \frac{d}{dx} \psi - \psi \frac{d}{dx} \psi^* \right),$$

it follows that the wave function (11.48) corresponds to a unit incident flux, to the flux $|r|^2$ of the reflected particles, and to the flux $|t|^2$ that penetrates through the potential barrier. In other words, the probabilities of reflection and tunneling are $|r|^2$ and $|t|^2$, respectively.

Coming back to our problem of Figure 11.7, we consider $V_0 \leq E \leq V_{\max}$. The simplest case corresponds to $V_0 = 0$ and the following formulas will refer to this last case.

There are two turning points, a, b ($a < b$), which are solutions of the equation $p(x) = 0$. By imposing the boundary condition that only the penetrated waves are present at $x = +\infty$ (particle incident from the left), the semi-classical wave functions in the regions $x < a$ and $x > b$ have the forms, in the respective domains,

$$\psi(x) = \frac{1}{\sqrt{p}} e^{iw(a,x)} + R(E) \frac{1}{\sqrt{p}} e^{-iw(a,x)}, \quad \psi(x) = T(E) \frac{1}{\sqrt{p}} e^{iw(b,x)},$$

where the phases w are defined in eqn (11.10). The result for coefficients R and T is:

$$T(E) = \frac{e^{-i\tilde{w}(a,b)} e^{-i\delta(E)}}{(1 + e^{-2\tilde{w}(a,b)})^{1/2}}, \quad R(E) = \frac{e^{-i\delta(E)}}{(1 + e^{-2\tilde{w}(a,b)})^{1/2}}, \quad (11.49)$$

where

$$\tilde{w}(a, b) = \frac{1}{\hbar} \int_a^b |p(x)| dx .$$

$|T|^2$ gives the probability for tunneling:

$$P^{(\text{tunnel})} = |T|^2 = \frac{e^{-2\tilde{w}(a,b)}}{1 + e^{-2\tilde{w}(a,b)}} \simeq e^{-\frac{2}{\hbar} \int_a^b |p(x)| dx} \quad (11.50)$$

This famous quantum-mechanical formula asserts that the tunneling probability is exponentially suppressed, the exponent being the twice the “reduced action” of the classically forbidden region (in the unit of \hbar), $\tilde{w}(a, b)$.

The phase $\delta(E)$ can also be determined:

$$\delta(E) = \frac{\tilde{w}}{\pi\hbar} \log \left| \frac{\tilde{w}}{\pi\hbar e} \right| + \arg \Gamma \left(\frac{1}{2} - i \frac{\tilde{w}}{\pi\hbar} \right) . \quad (11.51)$$

Γ is Euler's gamma function. We shall not make much use of this result, but note that the value of this phase is always rather small, as in Figure 11.8. The proof of eqn (11.50) is a simple application of the connection formulas. Starting from the right of the potential we have indeed

$$\begin{aligned} e^{i(w(b,x)-\frac{\pi}{4})} &= \left[\cos \left(w(b,x) - \frac{\pi}{4} \right) + i \sin \left(w(b,x) - \frac{\pi}{4} \right) \right] \rightarrow \\ &\left[\frac{1}{2} e^{-\tilde{w}(x,b)} - i e^{\tilde{w}(x,b)} \right] \\ &\simeq -i e^{\tilde{w}(x,b)} = -i e^{\tilde{w}(a,b)} e^{-\tilde{w}(a,x)} \rightarrow -i e^{\tilde{w}(a,b)} 2 \cos \left(w(x,a) - \frac{\pi}{4} \right) \\ &= e^{-i\frac{\pi}{2}} e^{\tilde{w}(a,b)} \left[e^{i(w(x,a)-\frac{\pi}{4})} + e^{-i(w(x,a)-\frac{\pi}{4})} \right] \\ &= e^{-i\frac{\pi}{2}} e^{\tilde{w}(a,b)} \left[e^{i(-w(a,x)-\frac{\pi}{4})} + e^{i(w(a,x)+\frac{\pi}{4})} \right] . \end{aligned}$$

From the ratio of the two sides we find for $\tilde{w} \gg 1$ that

$$\begin{aligned} T &= \frac{e^{-i\frac{\pi}{4}}}{e^{-i\frac{\pi}{2}} e^{\tilde{w}(a,b)} e^{i\frac{\pi}{4}}} = e^{-\tilde{w}(a,b)} ; \\ \frac{R}{T} &= \frac{e^{-i\frac{\pi}{2}} e^{\tilde{w}(a,b)} e^{-i\frac{\pi}{4}}}{e^{-i\frac{\pi}{4}}} = -i e^{\tilde{w}(a,b)} \Rightarrow R = -i , \end{aligned}$$

which coincides with eqn (11.49) (note that in this limit $\delta(E) = 0$). For the sake of illustration the comparison between the WKB formula and the exact (numerical) result is shown in Figure 11.9 (see NB-11.5 in this chapter.)

11.3.1 The double well

One of the most interesting examples of the elementary application of quantum mechanics is the study of the energy levels in a deep double well potential, as in Figure 11.10. The interest arises due to the fact that



Fig. 11.8 $\delta(E)$ as a function of \tilde{w}/π .

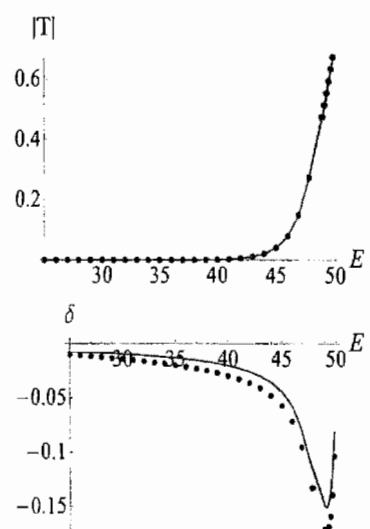


Fig. 11.9 $|T|$ and $\delta(E)$ as a function of the energy, for the potential $V_0 e^{-x^2/\Delta^2}$. The full curve is the result of the WKB approximation, while the points are the exact (numerical) results.

the semi-classical approximation allows us to see neatly how a symmetry can manifest themselves differently in classical and quantum mechanics. In this particular case, what is in question is the symmetry under the reflection $x \leftrightarrow -x$ (a sort of one-dimensional parity). Classically the particle will move in one of the potential minima, and the symmetry of the system under the parity is, so to speak, broken by the actual solution. A particle oscillating in the right-hand well has no chance of being found in the left-hand well, or vice versa.

Quantum mechanically the situation is *qualitatively* different. From what we have seen in Chapters 2,3 we know that

- (i) The system has only discrete spectrum: all energy eigenstates correspond to bound states;
- (ii) Owing to the “no-degeneracy theorem” (3.4), valid for one-dimensional discrete levels, each bound state is non-degenerate.
- (iii) Each non-degenerate energy eigenstate ψ must be eigenstate of the symmetry of the Hamiltonian

$$H = \frac{p^2}{2m} + U(x),$$

i.e., an eigenstate of parity, even or odd;

- (iv) The oscillation theorem (3.5) tells us that these parity eigenstates must alternate as the energy is increased: the ground state must be parity even (no nodes), the first excited state odd, the second excited state again even, and so on.

On the other hand, for a deep double well, with the central barrier high compared to the energy, the physical situation for the lower-lying levels must somehow be close to that of a particle moving in one of the separated wells, and indeed, the classical situation sketched above must be recovered in the $\hbar \rightarrow 0$ limit.

How can these two apparently contradictory requirements be reconciled?

The crucial effect is the tunneling between the two wells. Let us consider the ground state and the first excited state, corresponding to the two localized wave functions ϕ_+ and ϕ_- , centered in the right-hand and left-hand wells, respectively. ϕ_+ and ϕ_- are such that they would describe the ground state of the single well, right or left, in the limit of the central barrier going to infinity. If the higher levels are neglected, the system can be qualitatively described as a two-level system, described by an effective Hamiltonian

$$H = \begin{pmatrix} E_0 & -\epsilon \\ -\epsilon & E_0 \end{pmatrix},$$

written in the basis of ϕ_+, ϕ_- . ϵ is the tunneling amplitude, $\propto e^{-\bar{w}}$, between the two wells. Diagonalization of such a Hamiltonian immediately gives the true ground state and the first excited state,

$$\psi_1 = \frac{1}{\sqrt{2}}(\varphi_+ + \varphi_-), \quad \psi_2 = \frac{1}{\sqrt{2}}(\varphi_+ - \varphi_-),$$

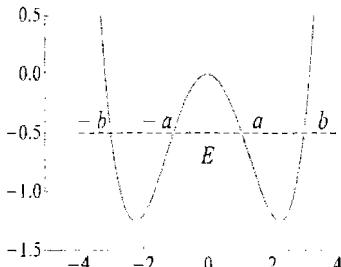


Fig. 11.10 A “double-well” potential. The two pairs of turning points are at $x = \pm a$ and $x = \pm b$.

which is consistent with the general quantum-mechanical results mentioned above. For the difference in the energy, one finds $\Delta E = E_2 - E_1 \propto \epsilon$.

If the particle is at time $t = 0$ in the right-hand well, then

$$\varphi_+(t) = \frac{1}{\sqrt{2}} (\psi_1(0)e^{-E_1 t/\hbar} + \psi_2(0)e^{-E_2 t/\hbar}), \quad (11.52)$$

from which

$$|\langle \varphi_- | \varphi_+(t) \rangle|^2 = \sin^2 \frac{\Delta Et}{2\hbar}.$$

After an interval of $T \sim \pi\hbar/\Delta E$ the particle will be in the other well, beyond the barrier. This simple calculation shows that the particle can be localized for short period of time, $t \ll T$, while for longer periods of time the tunnel effects can no longer neglected. $\epsilon \propto e^{-S/\hbar}$ where S is the “classical action” in the forbidden region, and therefore if $S \gg \hbar$ a particle localized in one well could survive a very long time. For a stationary state, however, the relevant time can be considered infinitely long, and thus the particle is not localized at all, and we find a symmetric (or antisymmetric) wave function.

Let us be more quantitative. Consider a symmetric potential $U(-x) = U(x)$, and let ψ_1, ψ_2 be two eigenstates,

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_1 + U(x)\psi_1 &= E_1 \psi_1, \\ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_2 + U(x)\psi_2 &= E_2 \psi_2, \end{aligned}$$

corresponding to two nearly degenerate levels. We find that

$$E_{1,2} = E_0 \pm \frac{\Delta E}{2}, \quad \Delta E = E_2 - E_1 = \frac{\hbar\omega}{\pi} e^{-\frac{1}{\hbar} \int_a^b df |p(x)|}, \quad (11.53)$$

where the classical (angular) frequency $\omega = \frac{2\pi}{T}$, $T = m \int_a^b dx / |p(x)|$, has been introduced.

There are several ways to show eqn (11.53). Here we follow a simple method using the connection formulas. Let us write

$$w(x_1, x_2) = \frac{1}{\hbar} \int_{x_1}^{x_2} |p(x)| dx.$$

For $x > b$ the semi-classical wave function must be exponentially decreasing:

$$\psi = \frac{1}{\sqrt{|p|}} e^{-w(b,x)}.$$

We now successively apply the connection formulas, being careful to change each time the turning points appropriately to the particular tran-

sition considered, to get:

$$\begin{aligned} \frac{1}{\sqrt{|p|}} e^{-w(b,x)} &\rightarrow \frac{2}{\sqrt{|p|}} \sin(w(x,b) + \frac{\pi}{4}) = \frac{2}{\sqrt{|p|}} \sin(w(a,b) - w(a,x) + \frac{\pi}{4}) = \\ \frac{2}{\sqrt{|p|}} \{ \sin(w(a,b)) \cos(w(a,x) - \frac{\pi}{4}) &- \cos(w(a,b)) \sin(w(a,x) - \frac{\pi}{4}) \} = \\ \frac{2}{\sqrt{|p|}} \{ \sin(w(a,b)) \cos(w(a,x) - \frac{\pi}{4}) &+ \cos(w(a,b)) \cos(w(a,x) + \frac{\pi}{4}) \} \rightarrow \\ \frac{1}{\sqrt{|p|}} \{ \sin(w(a,b)) e^{-w(x,a)} &+ 2 \cos(w(a,b)) e^{w(x,a)} \} = \\ \frac{1}{\sqrt{|p|}} \{ \sin(w(a,b)) e^{-w(0,a)+w(0,x)} &+ 2 \cos(w(a,b)) e^{w(0,a)-w(0,x)} \}. \end{aligned} \quad (11.54)$$

This must be an even or odd function for the ground-state and the first-excited state, respectively: it must reduce to $\cosh(w(0,x))$ and $\sinh(w(0,x))$ in the two cases. Therefore for the ground state the relation

$$\frac{\cos(w(a,b))}{\sin(w(a,b))} \equiv \frac{1}{2} K,$$

must hold, where

$$K \equiv e^{-2w(0,a)} = e^{-w(-a,a)}$$

is precisely the tunneling amplitude in the WKB approximation. For $K \rightarrow 0$ (small tunneling rate) $w(a,b)$ must approach $\pi/2$. Writing then $w(a,b) = \pi/2 - \mu$ we find that

$$\sin \mu \simeq \mu = \frac{1}{2} K.$$

We therefore have the quantization condition

$$w(a,b) = \frac{1}{\hbar} \int_a^b \sqrt{2m(E-U)} dx = \frac{\pi}{2} - \frac{1}{2} K.$$

For $K = 0$ one has the equation for a semi-classical approximation for E_0 ; by setting $E = E_0 + \delta E$ for $K \neq 0$ and expanding in small quantities, we find that

$$\frac{1}{2} 2m \delta E \frac{1}{\hbar} \int_a^b \frac{1}{\sqrt{2m(E-U)}} dx = \delta E \frac{T}{2\hbar} = -\frac{1}{2} K,$$

where T is the classical period of oscillation in one of the wells. Thus we find that

$$\delta E = -\frac{\hbar\omega}{2\pi} K \quad E_1 = E_0 - \frac{\hbar\omega}{2\pi} K,$$

and similarly

$$E_2 = E_0 + \frac{\hbar\omega}{2\pi} K,$$

which gives the result (11.53) for $\Delta E = E_2 - E_1$.⁶

⁶Another method can be found in §50 of the book [Landau and Lifshitz (1976 c)]. Actually, a more precise determination of the pre-exponential factor in ΔE , which depends on the details of $U(x)$, requires a little more careful consideration. A good discussion on this problem can be found in Coleman's Erice lectures [Coleman (1979)]; see also the note below.

Note on the pre-exponential factor

To get a more precise estimate of the pre-exponential factor K , it is necessary to use a more sophisticated connection formula such as the one in eqn (11.16), rather than using eqn (11.14) twice. The two formulas connecting the left and right forbidden regions are

$$\frac{1}{\sqrt{|p|}} e^{-w(b,x)} \leftrightarrow \frac{1}{\sqrt{|p|}} \left\{ \sin(w(a,b)) e^{-w(x,a)} + 2 \cos(w(a,b)) e^{w(x,a)} \right\},$$

$$\frac{1}{\sqrt{|p|}} e^{-w(b,x)} \leftrightarrow \left\{ \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{e}{\tilde{J}} \right)^{\tilde{J}} \Gamma(\tilde{J} + \frac{1}{2}) \cos(\pi \tilde{J}) e^{w(x,a)} + \sin(\pi \tilde{J}) e^{-w(x,a)} \right\},$$

where the second refers to the formula obtained by using the parabolic approximation in the region with two turning points. In a deep well, there are highly excited states for which $J \rightarrow \infty$, and limit (11.18) can be taken, and we recover eqn (11.53). For the lowest-lying states and for small values of K , $w(a,b) = \pi \tilde{J} = \pi/2 - \mu$ and in the first order in μ we can use

$$\left(\frac{2}{\pi} \right)^{1/2} \left(\frac{e}{\tilde{J}} \right)^{\tilde{J}} \Gamma(\tilde{J} + \frac{1}{2}) \cos(\pi \tilde{J}) \rightarrow 2 \sqrt{\frac{e}{\pi}} \sin \mu,$$

which leads to

$$\Delta E = \sqrt{\frac{\pi}{e}} \frac{\hbar \omega}{\pi} K.$$

As $\sqrt{\pi/e} \sim 1.075$ this amounts to some 7% correction in the result.

11.3.2 The semi-classical treatment of decay processes

Many interesting systems in physics are only approximately stable: they are metastable. For a certain amount of time these systems behave as stationary states, at some instant they decay into different states. Typical examples of such processes are the decay of excited atoms, unstable nuclei, or particles (resonances), into the final states, their decay products. An excited atom can decay into an atom of lower energy by emitting one or more photons; a nucleus can disintegrate producing various nuclei, by fission, by emitting α particles (helium nuclei), beta rays (electrons), gamma rays (photons), and neutrinos.

Some of these problems have been considered in the context of perturbation theory (see Chapter 9), and furthermore will be investigated in Chapter 13: here we shall study the problem from the semi-classical point of view.

As already seen in Chapter 9, if the system is in a metastable state $|i\rangle$ at time 0, the probability of finding the system in the same state after

the time interval t is given by

$$P_i(t) = e^{-\gamma t}. \quad (11.56)$$

The quantity $\tau = 1/\gamma$ is called the *mean lifetime*. Often the notation $\Gamma = \hbar\gamma \equiv \hbar/\tau$ is used: Γ has the dimension of energy and is known as the level *width*.

As an application of our semi-classical formulas, let us consider the α decay of nuclei. The α particle is the helium nucleus composed of two protons and two neutrons:

$$m(\alpha)c^2 - 2(m_p + m_n)c^2 \simeq -26.06 \text{ MeV}. \quad (11.57)$$

In atomic mass units, $u \simeq 931.494 \text{ MeV}/c^2$:

$$m_p = 1.007\,276\,470 u; \quad m_n = 1.008\,664\,904 u; \quad m(\alpha) \simeq 4.003\,90 u.$$

In a crude approximation one can consider a model of the nucleus in which a particle α moves in a mean field due to other nucleons (protons and neutrons). The latter may be approximated by a spherically symmetric square potential of depth $-U_0$ and width r_0 , of the order of the range of the nuclear forces. Besides the nuclear forces there are repulsive Coulomb forces between the α particle and the rest of the nucleus of charge $Z-2$. The situation is sketched in Figure 11.11. A look at the figure shows that the α particle can be bound inside such a nucleus with $E > 0$ thanks to the Coulomb barrier. These states can, however, only be meta-stable: the α particle can tunnel through the Coulomb barrier and the nucleus will disintegrate. The decay rate can be estimated by using the semi-classical approximation as follows. If P is the tunneling probability through the barrier, the probability of decay per unit time will be

$$\gamma = \mathcal{N} \times P,$$

where \mathcal{N} is the number of times α hits the barrier per second. A stationary state can be seen classically as a periodic motion with period T : a particle hits one of the box walls with frequency $1/T$, so that

$$\Gamma = \hbar\gamma = \frac{\hbar}{T} P. \quad (11.58)$$

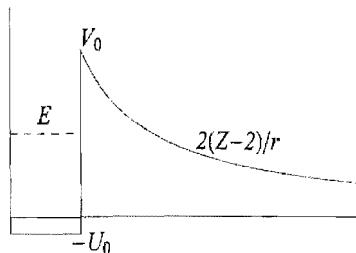


Fig. 11.11 Potential for an α particle, schematized as a spherical well plus the Coulomb repulsion.

A more formal but equivalent demonstration of $\mathcal{N} = 1/T$ is the following. Consider an S wave (reduced) radial function $\chi = A \sin(kr)$. Using the normalization to fix A ,

$$1 = \int_0^{r_0} A^2 \sin^2(kr) \sim \frac{A^2}{2} r_0 \quad \Rightarrow \quad A^2 = \frac{2}{r_0}$$

we see that the complete function is

$$\psi = \frac{1}{\sqrt{4\pi}} \frac{A}{r} \sin(kr) = \frac{1}{\sqrt{4\pi}} \frac{A}{2ir} [e^{ikr} - e^{-ikr}]. \quad (11.59)$$

This solution describes expanding and contracting spherical waves. The flux density is

$$\mathbf{j} = \frac{\hbar}{2m i} [\psi^* \nabla \psi - \psi \nabla \psi^*].$$

By using the expanding wave in eqn (11.59) we find that the flux through a surface of radius r_0 is

$$j_r = \frac{\hbar k}{m} \frac{1}{4\pi} \frac{A^2}{4r^2}, \quad \Phi = 4\pi r^2 j_r = \frac{\hbar k}{m} \frac{A^2}{4} = \frac{\hbar k}{m} \frac{1}{2r_0} = \frac{v}{2r_0},$$

where $\hbar k/m = v$ is the velocity of the particle. Finally $v/2r_0 = 1/T$.

Z(A)	$T_{1/2}$	E(MeV)	Z(A)	$T_{1/2}$	E(MeV)
Po(212)	3.0×10^{-7} s	8.95	Th(219)	0.11×10^{-6} s	9.34
Po(214)	1.5×10^{-4} s	7.83	Th(220)	$10. \times 10^{-6}$ s	8.79
Po(215)	1.8×10^{-3} s	7.50	Th(221)	2.810^{-3} s	7.98
Po(216)	0.158 s	6.89	Th(224)	1.05 s	7.085
Th(212)	0.03 s	7.92	Th(225)	8.72 m	6.47
Th(213)	0.14	7.69	Th(226)	30.6 m	6.28
Th(214)	0.10 s	7.68	Th(227)	18.72 d	5.92
Th(215)	1.2 s	7.46	Th(228)	1.91 y	5.38
Th(217)	0.25×10^{-3} s	9.25	Th(229)	7340 y	4.91
Th(218)	0.11×10^{-6} s	9.67	Th(230)	77×10^3 y	4.65
			Th(232)	14.1×10^9 y	3.98

Table 11.1 Examples of α decays. Listed in the Table are the parent nuclei, half-decay time (s = seconds, m = minutes, d = days, y = years), and the energy of α in MeV. For some nuclei the average energy is given.

The tunneling probability P in eqn (11.58) is the transmission coefficient through the barrier. The turning points are r_0 and r_1 , where

$$\frac{2(Z-2)e^2}{r_1} = E = \frac{p^2}{2m}, \quad \Rightarrow \quad r_1 = \frac{2(Z-2)e^2}{E},$$

and P is given by

$$P = \exp[-2\sigma(r_0, r_1)] = \exp \left[-\frac{2}{\hbar} \int_{r_0}^{r_1} \sqrt{2m \left(\frac{2(Z-2)e^2}{r} - E \right)} dr \right].$$

To simplify this further let us write the Coulomb interaction as C/r , where

$$C = 2(Z-2)e^2.$$

By changing the variable as $r = r_1 x$ and noting that $\sqrt{2mC}r_1 = 2C/v$, we see that the integral becomes

$$I = \sqrt{r_1 2mC} \int_{\frac{r_0}{r_1}}^1 dx \sqrt{\frac{1}{x} - 1} = \frac{2C}{v} \left[\arccos\left(\sqrt{\frac{r_0}{r_1}}\right) - \sqrt{\frac{r_0}{r_1}} \left(1 - \frac{r_0}{r_1}\right) \right].$$

As $r_0/r_1 \ll 1$ in many applications, let us expand this as follows:

$$I \simeq \frac{2C}{v} \left(\frac{\pi}{2} - 2\sqrt{\frac{r_0}{r_1}} \right) = \frac{\pi C}{v} - 2\sqrt{2Cmr_0},$$

and one finds that

$$P = \exp\left(-\frac{2\pi C}{\hbar v} + 4\frac{\sqrt{2Cmr_0}}{\hbar}\right).$$

Denoting by q_1, q_2 the charges in units of e and the fine-structure constant by $\alpha = e^2/\hbar c$, the dependence is of the type

$$P \propto \exp\left[-\frac{2\pi\alpha q_1 q_2}{v/c}\right]. \quad (11.60)$$

The strong (exponential) dependence on the velocity, and hence on the energy of the α particle, is characteristic of this type of decay. This means that a small variation of the energy corresponds to a considerable difference in the life-time. This prediction is met by the experimental data shown in Table 11.1.

Figure 11.12 shows as an illustration the quantity $\log(\Gamma)$ as a function of $2\pi C/\hbar v$ for the two families of polonium (Po) and of thorium (Th): the agreement is quite reasonable.

In the following section eqn (11.58) will be obtained from a more formal approach, due to Gamow and Siegert.

11.3.3 The Gamow–Siegert theory

Equation (11.56) would be satisfied if a stationary state ψ with a complex energy eigenvalue $E - i\Gamma/2$ existed. In this case the probability of survival would be given as

$$P(t) = |\langle \psi | \psi(t) \rangle|^2 = \left| \langle \psi | e^{-iEt/\hbar - \Gamma t/2\hbar} | \psi \rangle \right|^2 = e^{-\Gamma t/\hbar}, \quad (11.61)$$

which reproduces exactly eqn (11.56).

Of course, H is self-adjoint and all its eigenvalues are real; on the other hand, the states in which we are interested are not really stable. Mathematically H is self-adjoint in the space of functions, which remains bounded at $r \rightarrow \infty$; if we lose this condition, H can formally have complex eigenvalues. We shall see in Chapter 13 what such a choice means: for the moment we follow a more intuitive approach due to Gamow and Siegert.

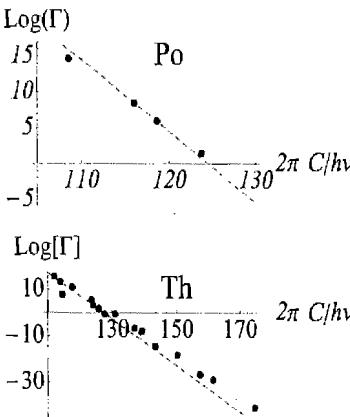


Fig. 11.12 $\log(\Gamma)$ as a function of $2\pi C/\hbar v$ for polonium and thorium. The dashed line represents the slope deduced from eqn (11.60).

A metastable state should be described by a spherical wave of type $\exp(ikr)/r$; we shall therefore look for a solution of Schrödinger's equation

$$H\psi = E\psi,$$

with the boundary condition that it is regular at the origin and with the behavior e^{ikr}/r at infinity. For simplicity let us limit ourselves to the case of a spherically symmetric potential and to an *S* wave function. For the reduced radial function $\varphi = r\psi$ we consider the problem

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2}\varphi + V(r)\varphi = E\varphi; \quad \varphi(0) = 0; \quad \varphi \xrightarrow[r \rightarrow \infty]{} \exp(ikr); \quad (11.62)$$

$k = \sqrt{2mE}$. Equation (11.62) does not in general allow for a solution with real E . It has two independent solutions which can be chosen real, as $V(r)$ is real, and by forcing the boundary condition at the origin ($\varphi = 0$) and by choosing the phase of the regular solution to be real, one would have an asymptotic form $\cos(kr + \delta)$.

There would be a solution, if we allow for a complex value for E , of the type $E = E_0 - i\Gamma/2$. In this case there are no conditions of reality of the wave function and eqn (11.62) can admit a solution. To see how the complex eigenvalue is determined, imagine solving eqn (11.62) starting from $r = 0$ with an arbitrary normalization, e.g., $\varphi(0) = 0, \varphi'(0) = 1$. For each E it is a Cauchy problem and it has a unique solution φ_L . Repeat the same procedure starting from $r \rightarrow +\infty$ with the boundary condition, again with an arbitrary normalization,

$$\varphi - Ae^{ikr} \rightarrow 0; \quad \varphi' - ikAe^{ikr} \rightarrow 0,$$

which gives a solution, φ_R . The compatibility between the two solutions at an intermediate point is given by

$$\frac{\varphi'_L}{\varphi_L} = \frac{\varphi'_R}{\varphi_R}.$$

This equation, independent of the normalization, determines the (complex) value of E .

Equation (11.62) can be solved numerically following the procedure just sketched. The states thus determined are called *resonances*. An example with the potential $V(r) = 7.5r^2e^{-r}$ (see problems) gives a resonance at

$$E = 3.4264, \quad \Gamma = 0.0255. \quad (11.63)$$

The Gamow–Siegert theory in the WKB approximation

We shall find below the solution of the Gamow–Siegert problem in the context of WKB approximation.

First of all let us note that multiplying eqn (11.62) by φ^* and subtracting from it its complex conjugate yields

$$2i\text{Im}(E)|\varphi|^2 = -\frac{\hbar^2}{2m} \frac{d}{dr} \left(\varphi^* \frac{d}{dr} \varphi - \varphi \frac{d}{dr} \varphi^* \right).$$

Integrating this from 0 to r and using the boundary condition $\varphi(0) = 0$ one finds that

$$2 \operatorname{Im}(E) \int_0^r |\varphi|^2 dr = -\frac{\hbar^2}{2m i} \left(\varphi^* \frac{d}{dr} \varphi - \varphi \frac{d}{dr} \varphi^* \right). \quad (11.64)$$

If for large r we write $\varphi \equiv |\varphi| \exp(i\theta)$, we obtain

$$2 \operatorname{Im}(E) \int_0^r |\varphi|^2 dr = -\frac{\hbar^2}{2m} 2 \frac{d}{dr} \theta(r).$$

Thus an increasing phase corresponds to $\operatorname{Im}(E) < 0$, consistently with boundary condition (11.62).

By writing $\varphi = \varphi_1 + i\varphi_2$, $E = E_1 + iE_2$, we find that eqn (11.62) takes the form

$$-\frac{\hbar^2}{2m} \varphi_1'' + V(r) \varphi_1 = E_1 \varphi_1 - E_2 \varphi_2; \quad (11.65a)$$

$$-\frac{\hbar^2}{2m} \varphi_2'' + V(r) \varphi_2 = E_2 \varphi_1 + E_1 \varphi_2. \quad (11.65b)$$

If there were no tunnel effects we would find $E_2 = 0$ and $\varphi_2 = 0$. The wave function would be concentrated in a region around the origin and would simply have a decreasing behavior in the classically forbidden region. The idea we use in solving eqn (11.65) approximately is that for $E_2 \ll E_1$ the situation just sketched does not change much. We can then choose the phases such that in the classically forbidden region the real part decreases while the imaginary part increases. The situation is illustrated in Figure 11.13. The function φ_2 starts to be of the same order of magnitude as φ_1 near the second turning point, $r = b$.

If one neglected the tunnel effect, the WKB solution of eqn (11.62) in the region $a < r < b$ would have the form

$$\frac{C}{2\sqrt{|p|}} \exp(-\tilde{w}(a, r)) \equiv \frac{C}{2\sqrt{|p|}} \exp(-\tilde{w}(a, b) + \tilde{w}(r, b)), \quad (11.66)$$

where

$$\tilde{w}(a, x) = \frac{1}{\hbar} \int_a^x \tilde{p}(x) dx, \quad \tilde{p}(x) = \sqrt{2m(V - E)}$$

is the "action" in the classically forbidden region as before. Usually $C \sim \mathcal{O}(1)$ is determined by the normalization condition of the bound state. In the presence of a small imaginary part, increasing with r , we shall have

$$\varphi = \frac{C}{2\sqrt{|p|}} \exp(-\tilde{w}(a, b) + \tilde{w}(r, b)) + i \frac{D}{\sqrt{|p|}} \exp(-\tilde{w}(r, b)). \quad (11.67)$$

The continuation to the region $r > b$ can be found from the general connection formulas (11.13):

$$\frac{1}{\sqrt{|p|}} \left[-\frac{C}{2} e^{-\tilde{w}(a, b)} \sin \left(w(b, r) - \frac{\pi}{4} \right) + i 2D \cos \left(w(b, r) - \frac{\pi}{4} \right) \right] \quad (11.68)$$

$$= i 2D \frac{1}{\sqrt{|p|}} \left[\cos \left(w(b, r) - \frac{\pi}{4} \right) + i \frac{C}{4D} e^{-\tilde{w}(a, b)} \sin \left(w(b, r) - \frac{\pi}{4} \right) \right].$$

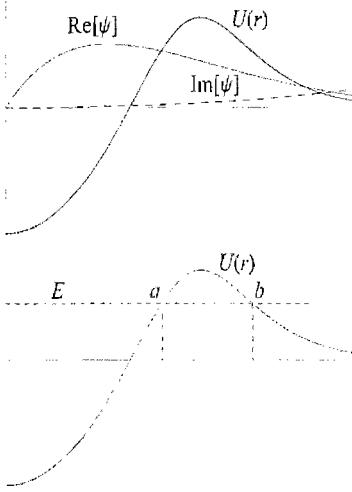


Fig. 11.13 Qualitative behavior of the real and imaginary parts of the semi-classical solution describing the decay.

Requiring a solution $\exp(+iw(b, r))$ corresponding to an increasing phase gives the condition

$$4D = C \exp(-\tilde{w}(a, b)), \quad (11.69)$$

and for $r \geq b$ the solution (11.68) becomes

$$\varphi = i \frac{C}{2\sqrt{|p|}} e^{-\tilde{w}(a, b)} e^{i(w(b, r) - \frac{\pi}{4})}.$$

Using eqn (11.64) for $r \geq b$ and remembering that $w' = p/\hbar$ we have

$$2 \operatorname{Im}(E) \int_0^r |\varphi|^2 dr = -\frac{\hbar^2}{2m} \frac{C^2}{4p} e^{-2\tilde{w}(a, b)} 2i w' = -\frac{\hbar}{4m} C^2 e^{-2\tilde{w}(a, b)}. \quad (11.70)$$

Apart from exponentially suppressed terms, the function φ is concentrated in the classically allowed region, for $r < b$, and therefore the integration in the first term can be extended to infinity, keeping, however, the semi-classical expression for φ without the transmitted piece; therefore the integration gives just the normalization of the function. There still remains the problem of determining C : this can be done by connecting the solution to the one inside the well, $r < a$. In that region the imaginary part of φ is negligible, and the wave function reduces to the form of eqn (11.66). The connection to the wave function inside the region $r < a$ is already known:

$$r < a : \quad \varphi = \frac{C}{\sqrt{p}} \cos\left(w(r, a) - \frac{\pi}{4}\right).$$

Also, we know (recall eqn (11.30)) that such a wave function leads to the semi-classical energy levels

$$J = \frac{1}{2\pi} \oint p(r) dr = \hbar \left(n + \frac{3}{4} \right); \quad n = 0, 1, \dots,$$

which gives the real part of the energy levels. Normalizing the wave function φ inside the potential well, we have as in Section 11.2:

$$1 = \int_0^a \frac{C^2}{p} \cos^2(w) dx \simeq \frac{C^2}{2} \int_0^a \frac{dx}{p} = \frac{C^2}{4m} T \Rightarrow C^2 = \frac{4m}{T}$$

where T stands for the classical period of motion. From eqn (11.70) it follows that:

$$2 \operatorname{Im}(E) \equiv -\Gamma = -\frac{\hbar}{T} \exp(-2\tilde{w}(a, b))$$

(11.71)

This formula coincides with the one obtained earlier by a more qualitative argument.

11.4 Phase shift

We next consider the effects of the resonances (metastable states) in the scattering processes in the semi-classical approximation, although a more general discussion of the scattering processes will be given later, in Chapter 16.

General remarks

To be concrete, let us consider a particle moving in a spherically symmetric potential, $V(r)$, such that $V(r) \rightarrow 0$ at $r \rightarrow \infty$. The spectrum of H will be given by the continuous spectrum at $E \geq 0$ (improper eigenvalues) and, possibly, bound states with $E < 0$. For the latter, the eigenvalues and eigenfunctions are determined from the radial Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\chi}{dr^2} + \left[V(r) + \frac{\hbar^2 \ell(\ell+1)}{2m r^2} \right] \chi(r) = E \chi(r). \quad (11.72)$$

This equation, being a differential equation of second degree, has two linearly independent solutions. The requirement of regularity at the origin $\chi(0) = 0$ fixes the combination, the regular solution, apart from the normalization. If the potential $V(r)$ decreases more rapidly than $1/r^2$ at infinity (which we shall assume), then at large r the equation becomes that of a free particle: the regular solution will behave as a linear combination of the two such solutions. For the S wave, for simplicity, the asymptotic form of the solution is then

$$\chi(r) = A(E) \exp\left(-\frac{\sqrt{-2mE}}{\hbar} r\right) + B(E) \exp\left(\frac{\sqrt{-2mE}}{\hbar} r\right). \quad (11.73)$$

This solution is in general non-normalizable; a normalizable solution will occur for $E_0 < 0$ at the zeros of the coefficient $B(E)$. This of course corresponds to the usual fact that the requirement $\chi \in L^2$ is a constraint on the asymptotic behavior of the wave function.

⁷For completeness we note that the asymptotic form (11.73) is valid everywhere on the physical sheet only if the terms neglected, for instance, $V(r) \exp(\sqrt{-2mE}r/\hbar)$, are small. This is the case if V has a finite support. If, for instance, V decreases exponentially then the asymptotic form is valid in a strip which includes the real axis, which is sufficient for our purpose here.

Let us now consider the continuous spectrum, $E > 0$. Differential equation (11.72) is analytic in E , and therefore by the general result on the differential equations the solution must also be analytic, and in particular, single-valued in E , which is regarded as a complex variable. The function $\sqrt{-E}$ has a cut along the positive real axis: therefore the coefficients $A(E), B(E)$ must also have the cut for $E > 0$, so that the solution χ is analytic. The Riemann surface of the function $\sqrt{-E}$ is a doubly sheeted complex plane sewed together along the branch cut $E > 0$. The asymptotic behavior of χ^7 provides the functions A and B on the same Riemann surface, the first sheet will be called in this context the *physical sheet*. For $E \in \mathbb{R}; E < 0$, we can always choose a real solution: this means that for $E < 0$ the functions $A(E), B(E)$ are real. The continuation to the complex plane of A, B can then be performed by using the principle of the Schwarz reflection:

$$A(E^*) = A^*(E) \quad B(E^*) = B^*(E).$$

If one starts from a real negative value of E , $E = -|E|$ and moves clockwise along a semi-circle, one reaches the upper edge of the cut, at $E = |E|$, and since

$$\sqrt{-E} = \sqrt{|E|} \rightarrow \sqrt{e^{-i\pi}|E|} = -i\sqrt{|E|} \equiv -ik; k^2 = 2mE; \text{ (for } E > 0\text{)},$$

the function takes the value on the upper side of the cut

$$\chi = A(E + i\varepsilon) e^{ikr} + B(E + i\varepsilon) e^{-ikr}. \quad (11.74a)$$

Vice versa, reaching the lower side of the cut along an anti-clockwise route, one gets

$$\chi = A(E - i\varepsilon) e^{-ikr} + B(E - i\varepsilon) e^{ikr}. \quad (11.74b)$$

Therefore in order to assure the single-valuedness of the wave function on the cut, A and B must be such that

$$\lim_{\varepsilon \rightarrow 0} A(E + i\varepsilon) = \lim_{\varepsilon \rightarrow 0} B(E - i\varepsilon) = \lim_{\varepsilon \rightarrow 0} B^*(E + i\varepsilon), \quad (11.75)$$

which means that $A(E)$ will be complex with the imaginary part related to B , which in turn is determined from the regularity of the function at the origin.

For $E > 0$ the asymptotic behavior is

$$\chi(r) = C \sin(kr + \delta).$$

The constant C depends on the normalization of the wave function; the phase δ is fixed since one has chosen a particular solution, regular at $r = 0$. Rewriting the sine function as in eqn (11.74a) one finds that

$$-\frac{A}{B} = \exp(2i\delta). \quad (11.76)$$

Equation (11.76) confirms that δ does not depend on the normalization of the wave function and is indeed consistent with eqn (11.75), which implies that $|A| = |B|$ on the positive real axis. δ is known as the *phase shift* or the *scattering phase*. Comparing this with the solution for the free particle, $\sin(kr)$, one sees that that δ indeed describes the shift in the phase of the asymptotic wave function, as compared to the free case. We will see in the chapter on elastic scattering (Chapter 16) that $\sin \delta$ is directly related to an observable quantity: the scattering cross section.

So far the discussion has been general: we shall now specialize to the situation in which some resonances (metastable, quasi-bound states) are present. The Gamow–Siegert theory associates a resonance state to a wave, a purely expanding spherical wave, corresponding to a complex eigenvalue of the form, $E_0 - i\Gamma/2$. From eqn (11.74a) it follows that such an eigenvalue corresponds to a zero of $B(E)$, more precisely a zero in the second Riemann sheet:

$$B(E_0 - i\frac{\Gamma}{2}) = 0.$$

The occurrence of the zero in the second sheet follows from the fact that for $\text{Im}E < 0$ in the first sheet, the B part of the wave function behaves on the first sheet, by the reflection principle, as $B^* e^{+ikr}$, that is, as an expanding spherical wave (which should be present). The Gamow–Siegert theory instead requires the contracting part of the spherical wave

to vanish at the resonance. We recall that the region $\text{Im}E < 0$ on the second sheet is the region immediately adjacent to the upper edge of the cut on the positive real axis in the first sheet.

Suppose now that there exists a resonant state and $\Gamma \ll E$. The zero of B means that one can write $B = b(E - (E_0 - i\frac{\Gamma}{2}))$, with a nonzero b in the neighborhood of the resonance. The single-valuedness of the wave function, eqn (11.75), imposes the condition that

$$\chi(r) = b^* \left[E - \left(E_0 + i\frac{\Gamma}{2} \right) \right] e^{ikr} + b \left[E - \left(E_0 - i\frac{\Gamma}{2} \right) \right] e^{-ikr}.$$

For E far from the resonance, $E - E_0 \gg \Gamma$, and it follows from eqn (11.76) that

$$e^{2i\delta^0(E)} = -\frac{b^*}{b}, \quad (11.77)$$

which is a function "regular" in E .

Near the resonance, the phase shift changes abruptly. From eqns (11.76) and (11.77) it follows that

$$e^{2i\delta} = e^{2i(\delta^0 + \delta_R)} = -\frac{b^*}{b} \frac{E - (E_0 + i\frac{\Gamma}{2})}{E - (E_0 - i\frac{\Gamma}{2})} = -\frac{b^*}{b} \frac{1 + i\frac{\Gamma}{2(E_0 - E)}}{1 - i\frac{\Gamma}{2(E_0 - E)}}.$$

By using the identity

$$e^{2i\arctan \alpha} = \frac{e^{i\arctan \alpha}}{e^{-i\arctan \alpha}} = \frac{1 + i\alpha}{1 - i\alpha},$$

one finds that

$$\boxed{\delta = \delta^0 + \arctan \frac{\Gamma}{2(E_0 - E)}} \quad (11.78)$$

The phase shift δ therefore undergoes an increase of π , as the energy increases through the resonance energy, and this change of δ occurs in a narrow region if $\Gamma \ll E_0$. The situation is even clearer if the derivative of $\delta(E)$ is considered: near the resonance one has

$$\delta'(E) = \delta^{(0)'} + \frac{\Gamma/2}{\frac{\Gamma^2}{4} + (E - E_0)^2}. \quad (11.79)$$

For example, we report in Figure 11.14 the result of a numerical calculation of $\delta'(E)$ for the potential

$$V(r) = V_0 r^2 e^{-r}; \quad V_0 = 7.5, \text{ (atomic unit)}. \quad (11.80)$$

The abrupt change of the phase shift is clearly seen, around $k \sim 2.5$, which signals the presence of a resonance. In the second figure the derivative $\delta'(E)$ is plotted, from which (by using eqn (11.79)) the parameters

$$E_0 = 3.4266; \quad \Gamma = 0.026$$

can be obtained. These numbers are in nice agreement with what was found before by the Gamow-Siegert method, eqn (11.63).

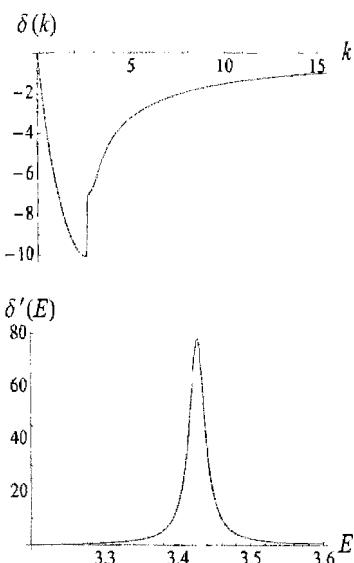


Fig. 11.14 The scattering phase shift as a function of k for potential (11.80).

In the second figure the derivative with respect to the energy $\delta'(E)$ is shown, near the resonance.

The WKB approximation for $\delta(E)$

It is quite instructive to see how the preceding formulation manifests itself in the semi-classical approximation. To be concrete, let us consider potential (11.80) in an S wave. According to whether we use the Langer correction or not we get the two graphs shown in Figure 11.15. In the first case there is a turning point $r = c$ due to the centrifugal potential. Whichever potential is used, there are two turning points $r = a, b$ for the energy lying between the local minimum of V and the local maximum, $\min(V) < E < \max(V) = E_{\max}$.

Let us consider, for example, the WKB approximation with the Langer correction. It is not difficult to get, by systematically using the connection formula, eqn (11.14):

$$E > E_{\max} : \frac{1}{\sqrt{p}} \cos \left(w_{cr} - \frac{\pi}{4} \right); \quad (11.81a)$$

$$E_{\min} < E < E_{\max} : \quad (11.81b)$$

$$\begin{cases} \frac{1}{\sqrt{p}} \cos \left(w_{cr} - \frac{\pi}{4} \right); & c < r < a \\ \frac{1}{\sqrt{|p'|}} \left\{ \sin \left(\frac{\pi}{2} - w \right) e^{\sigma_{ar}} + \frac{1}{2} \cos \left(\frac{\pi}{2} - w \right) e^{-\sigma_{ar}} \right\}; & a < r < b \\ \frac{1}{\sqrt{p}} \left\{ 2 \cos(w) e^{\sigma} \cos \left(w_{br} - \frac{\pi}{4} \right) \right. \\ \left. - \frac{1}{2} \sin(w) e^{-\sigma} \sin \left(w_{br} - \frac{\pi}{4} \right) \right\}; & b < r \end{cases}$$

$$E < E_{\min} : \frac{1}{\sqrt{p}} \cos \left(w_{br} - \frac{\pi}{4} \right). \quad (11.81c)$$

For compactness of writing we have indicated various turning points as indices, e.g.,

$$w_{cr} \equiv w(c, r) = \frac{1}{\hbar} \int_c^r p(r) dr, \quad \sigma_{ar} \equiv \tilde{w}(a, r) = \frac{1}{\hbar} \int_a^r |p(r)| dr,$$

and so on, and furthermore:

$$w = \frac{1}{\hbar} \int_c^a p(r) dr; \quad \sigma = \frac{1}{\hbar} \int_a^b |p(r)| dr.$$

For a sufficiently high barrier, $\sigma \gg 1$, and from eqn (11.81) it follows that the asymptotic phase of the wave function is always fixed by the factor $\cos(w - \pi/4)$. By indicating the external turning point by b and subtracting the corresponding phase for the free particle, one finds the phase shift (with $k^2 = 2mE/\hbar^2$):

$$\delta = \int_b^\infty \sqrt{k^2 - \frac{2mV(r)}{\hbar^2} - \frac{(\ell + \frac{1}{2})^2}{r^2}} dr - \int_{b_0}^\infty \sqrt{k^2 - \frac{(\ell + \frac{1}{2})^2}{r^2}} dr. \quad (11.82)$$

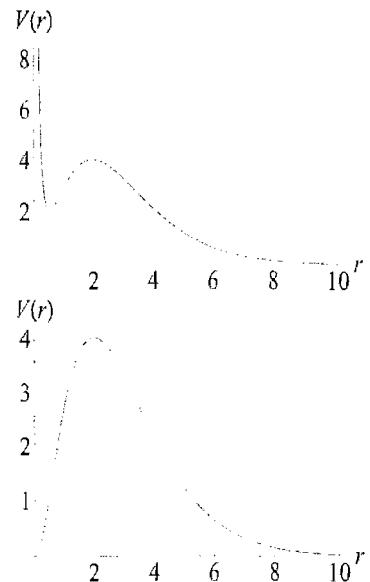


Fig. 11.15 The potential (11.80) with and without the Langer correction ($1/8r^2$ in S wave)

We have written the formula for a generic angular momentum. Note that the turning point for the free particle is at $b_0 = k/(\ell + \frac{1}{2})$, and approximately equal to b only for large energies.

The exception to the formula occurs for $w = \pi(n + \frac{1}{2})$, which corresponds exactly to the Bohr-Sommerfeld quantization condition. In this case the asymptotic phase can be written as

$$w(b, r) - \frac{\pi}{4} + \arctan\left(\frac{e^{-2\sigma}}{4} \tan(w)\right),$$

in which the jump of π occurring at the passage of the resonance is displayed.

In Figure 11.16 the semi-classical calculation of the phase shift for potential (11.80), by using eqn (11.82), is shown. The agreement is quite satisfactory, with or without Langer correction. From eqn (11.81) it is also evident what the signal of the existence of the resonance is in our semi-classical treatment. For almost all values of the energy the ratio between the probability density outside and inside the well (in which the particle is confined) is of the order of

$$\frac{|\psi_{\text{out}}|^2}{|\psi_{\text{in}}|^2} \sim \cos^2(w) e^{2\sigma} \sim e^{2\sigma},$$

and this means intuitively that the particle is not confined (non-resonating state). At precisely the resonance energy, $\cos(w) = 0$, and the above ratio is now

$$\frac{|\psi_{\text{out}}|^2}{|\psi_{\text{in}}|^2} \sim e^{-2\sigma},$$

which corresponds to the particle confined inside the internal region of the potential.

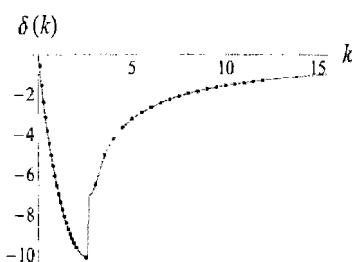


Fig. 11.16 The semi-classical phase shift (points) and the exact result (continuous curve) for potential (11.80). The second figure is obtained from the standard WKB without the Langer correction.

Further reading

There is a vast literature on the subject. A good starting point for a deeper understanding of the subject is the article [Berry and Mount (1972)]. Lectures of M.V. Berry

at Les Houches [Berry (1983)] are also recommended. At a more advanced level the book [Gutzwiller (1990)] gives an idea of more recent developments.

Guide to the Supplements

In Supplement 21.5 we give a brief account of the generalization of the semi-classical approximation to systems

with n degrees of freedom. We shall limit ourselves to integrable systems, exposing the so-called EKB (Einstein, Keller, Brillouin) quantization procedure. A few remarks are added to the semi-classical quantization of general systems, mostly for quasi-integrable systems. The problem is closely related to classical mechanics, and we provide a short account of the necessary ideas. The reader can find a couple of examples of EKB-type quantization for non-integrable systems in notebook NB-11.10 while some example of caustics are presented in NB-11.11.

Some more technical details on the WKB approximation are distributed among the notebooks and the problems in this chapter. On the accompanying CD the reader

will find a short file, `WKBresults.nb`, where the essential aspects of uniform approximation are presented (see also notebook NB-11.9). A related aspect, the computation of the phase for the transmission coefficient (see eqn (11.51)) is in Problem 11.14.

In Problems 11.9 and 11.11 a quite detailed analysis of the small-coupling behavior of the level splitting in a double-well potential is given, while in 11.12 an analogous problem for an inverted potential is solved. This calculation is relevant for instantons (see Chapter 8) and for the computation of the high-order behavior of perturbation theory.

Higher orders in \hbar are computed in Problem 11.10.

Problems

- (11.1) Write the semi-classical quantization conditions for the case with two turning points using Cauchy's theorem. Assume that $p(x)$ has only one cut, between the two turning points, and no essential singularities in the complex plane.
- (11.2) Write the semi-classical quantization conditions for a harmonic oscillator. Generalize the results for a pure x^N oscillator, with N even.
- (11.3) Write the semi-classical quantization conditions for a central field. In particular find the hydrogen spectrum using the Bohr-Sommerfeld quantization conditions.
- (11.4) Solve the harmonic oscillator problem in the lowest-order WKB approximation.
- (11.5) Compute the spectrum for a potential x^N in the lowest-order WKB approximation, assuming N is even. Study the limit of large quantum numbers.
- (11.6) Consider a particle of mass m in a one-dimensional potential
- $$V(x) = g\delta(x - a) + g\delta(x + a).$$
- Compute in the semi-classical approximation the energy and width of the metastable states. Compare the results with the solution of Schrödinger's equation with the Gamow-Siegert boundary conditions. Solve the same problem for a "radial" barrier, i.e. defined in the semi-space $x > 0$.
- (11.7) Compute the spectrum of an anharmonic oscillator $\frac{1}{2}(\lambda_2 x^2 + \lambda_4 x^4)$ in the lowest WKB approximation.
- λ_2 is positive. Compare the results with that of perturbation theory.
- (11.8) Consider a generic even potential $V(x)$ with two degenerate absolute minima. Show that for small tunneling amplitudes the splitting between the ground state and the first excited state can be obtained by a variational technique based on the two semi-classical solutions built on the two minima.
- (11.9) Compute in the lowest WKB approximation the energy splitting between the two lowest-lying states in a double well.
- (11.10) Consider the Schrödinger equation for a potential $V(x)$. Let us suppose that $V(x)$ is analytic, then the equation can be extended in the complex domain. Set
- $$\psi(x) = \exp\left(i\frac{\sigma(x)}{\hbar}\right),$$
- $\sigma(x)$ in general will have branch points at the classical turning points. Let us suppose that there are only two of them. The monodromy requirement on ψ implies the constraint
- $$\frac{1}{\hbar} \oint \sigma(x) dx = 2\pi n.$$
- Show that this leads, to leading order, to the Bohr-Sommerfeld quantization condition, and allows one to compute higher-order corrections in \hbar in the WKB quantization procedure.

- (11.11) Compute the energy splitting between the two lowest-lying states in a double well, in the limit $g \rightarrow 0$.

- (11.12) Compute in the limit $g \rightarrow 0$ the imaginary part $\text{Im}[E]$ for the potential

$$V(x) = \frac{1}{2}x^2 - \frac{1}{2}g x^4; \quad g > 0.$$

- (11.13) Compute exactly the reflection and the transmission coefficients for a potential $V(x) = -F|x|$.

- (11.14) Compute exactly the reflection and the transmission coefficients for the potential $V(x) = -\frac{1}{2}\beta x^2$.

- (11.15) Show that the normalization condition $C = 2\sqrt{m/T}$ for a semi-classical bound state in one dimension is valid also for low-lying quantum states if the quantization condition holds.

- (11.16) (a) Study the transformation properties of

$$I_1 = \oint p_i dq_i; \quad I_2 = \sum_i \oint p_i dq_i.$$

under coordinate transformations and general canonical transformations.

- (b) Show that in a system with n degrees of freedom there exist at most n functionally independent integrals of motion.

- (c) Show that in the hypothesis of Liouville's theorem for integrable systems there are n tangent vectors tangent to the torus and construct them. Show that the involution property of the integrals of motion implies the local existence of S such that $\nabla S = p$.

- (d) Consider an $n-1$ parameter family of trajectories in an integrable system. Show that the envelopes of the family coincide with caustics.

- (11.17) Perform the $\hbar \rightarrow 0$ limit in Schrödinger's equation with the substitution

$$\psi = A \exp\left(\frac{i}{\hbar} S\right).$$

Numerical analyses

- (11.1) Study numerically the energy levels and wave functions for harmonic and anharmonic potentials in the WKB approximation.

- (11.2) Study the double-well anharmonic oscillator in the WKB approximation; compare the results with variational computations. Study in particular the small coupling limit.

- (11.3) Study the WKB approximation for an anharmonic potential by writing the solution in terms of elliptic integrals.

- (11.4) Use the WKB approximation to study the presence of metastable states in the potential,

$$V(x) = \frac{1}{2}x^2 - \frac{g}{2}x^4; \quad g > 0.$$

- (11.5) Study in the WKB approximation the problem of transmission and reflection coefficients, in particular consider the cases

$$V_1(x) = \frac{V_0}{2} \left(1 + \cos\left(2\pi \frac{x}{\Delta}\right)\right) \theta\left(\frac{\Delta}{2} + x\right) \theta\left(\frac{\Delta}{2} - x\right),$$

$$V_2(x) = V_0 \exp(-x^2/\Delta^2).$$

- (11.6) Study in the WKB approximation the metastable states for the radial potential

$$V(r) = V_0 r^2 \exp(-r); \quad V_0 = 7.5.$$

- (11.7) Compute the S-wave scattering phase as a function of energy for the radial potential

$$V(r) = V_0 r^2 \exp(-r); \quad V_0 = 7.5.$$

Compare the results with the WKB approximation.

- (11.8) Study numerically the time evolution of metastable states in the radial potential

$$V(r) = V_0 r^2 \exp(-r); \quad V_0 = 7.5.$$

- (11.9) Apply the method of uniform approximation to a quartic oscillator.

- (11.10) Study the EKB quantization procedure for the potentials

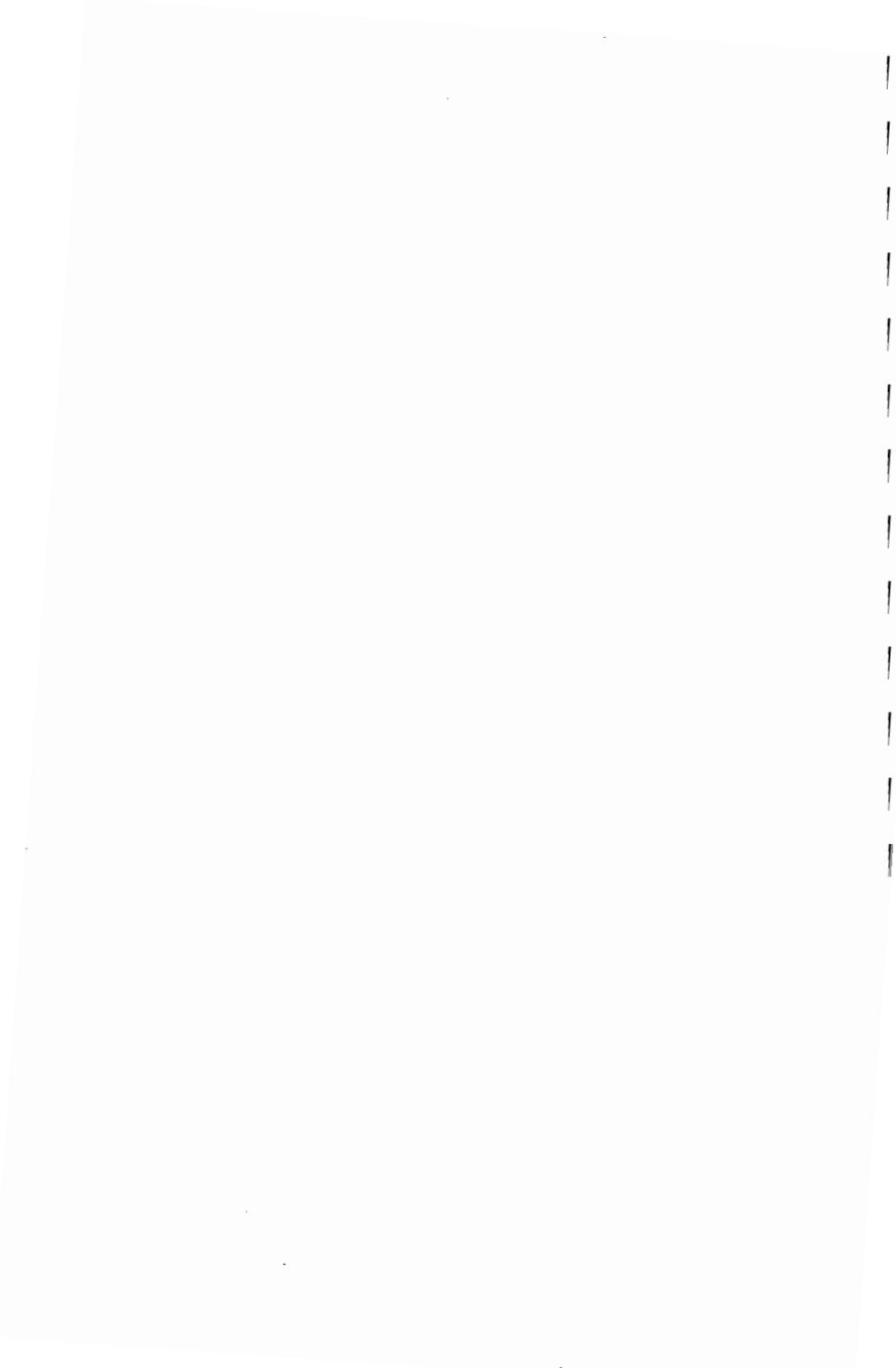
$$V(x, y) = \frac{1}{2} (\omega_1 x^2 + \omega_2 y^2) + \lambda x (y^2 + \eta x^2);$$

$$V(x, y) = \frac{\omega^2}{2} (x^2 + y^2) + \frac{g}{2} x^2 (x^2 + y^2).$$

- (11.11) Study the caustic curves for a uniform gravitational field and for the two body gravitational problem.

Part III

Applications



Part III of this book is dedicated to various applications of the formalism and methods developed in Parts I and II. Topics discussed include systems with general time-dependent Hamiltonians, general aspects of electromagnetic interactions with matter, atoms, and rather briefly, elastic scattering theory, and nuclei and elementary particles.



12

Time evolution

In a system with a time-independent Hamiltonian H , the evolution of a state $|\psi\rangle$ is given by $|\psi(t)\rangle = e^{-iHt/\hbar} |\psi(0)\rangle = \sum_k a_k e^{-iE_k t/\hbar} |k\rangle$, where $|k\rangle$ are the eigenstates of H . When the Hamiltonian depends on time, but is such that the time-dependent part of the Hamiltonian is small as compared to the dominant, unperturbed Hamiltonian (whose eigenvalue problem is assumed to be exactly solvable), the problem can be dealt with by using perturbation theory, as was done in Chapter 9.

There is a vast class of interesting physical problems, however, which involve time-dependent Hamiltonians and which are not accessible to perturbative treatment. In this chapter, we discuss some of these systems.

12.1 General features of time evolution	307
12.2 Time-dependent unitary transformations	309
12.3 Adiabatic processes	311
12.4 Some nontrivial systems	320
12.5 The cyclic harmonic oscillator: a theorem	331
Guide to the Supplements	341
Problems	341
Numerical analyses	342

12.1 General features of time evolution

The time evolution of a system is in general described by Schrödinger's equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H(t) |\psi(t)\rangle \Rightarrow -i \frac{d}{dt} \langle \psi(t)| = \langle \psi(t)| H^\dagger(t). \quad (12.1)$$

In terms of a complete set of (fixed) vectors $|i\rangle$ of the Hilbert space any vector can be expanded as

$$|\psi(t)\rangle = \sum_i a_i(t) |i\rangle \quad (12.2)$$

and eqn (12.1) is equivalent to the system

$$i\hbar \frac{da_i}{dt} = \sum_j (i|H(t)|j\rangle) a_j \equiv H_{ij}(t) a_j. \quad (12.3)$$

The solution of this system is uniquely determined once the initial state $|\psi(t_0)\rangle$ hence the coefficients $a_i(t_0)$, are specified.

The Hermiticity of the Hamiltonian $H = H^\dagger$ implies that (eqn (12.1))

$$\begin{aligned} i \frac{d}{dt} \langle \varphi(t) | \psi(t) \rangle &= \langle \varphi | H^\dagger | \psi \rangle - \langle \varphi | H | \psi \rangle = 0 \\ \Rightarrow \langle \varphi(t) | \psi(t) \rangle &= \langle \varphi(t_0) | \psi(t_0) \rangle, \end{aligned}$$

that is, the time evolution conserves the scalar products among the states. In other words, the time evolution is described by a unitary

operator,

$$|\psi(t)\rangle = U(t, t_0)|\psi(0)\rangle, \quad U^\dagger = U^{-1}. \quad (12.4)$$

The evolution operator U satisfies

$$i\hbar \frac{d}{dt} U(t, t_0) = H(t)U(t, t_0), \quad (12.5)$$

as can be easily verified by substituting eqn (12.4) into eqn (12.1). The initial condition is translated into the condition

$$\lim_{t \rightarrow t_0} |\psi(t)\rangle = |\psi(t_0)\rangle \quad \Rightarrow \quad \lim_{t \rightarrow t_0} U(t, t_0) = \mathbf{1},$$

where $\mathbf{1}$ is the identity operator.

To solve eqn (12.5) let us first observe that it is equivalent to the following integral equation

$$U(t, t_0) = \mathbf{1} - \frac{i}{\hbar} \int_{t_0}^t H(t_1)U(t_1, t_0)$$

which can be solved iteratively. Starting from the zeroth approximation, $U^0 = \mathbf{1}$, we find that

$$\begin{aligned} U(t) &= \mathbf{1} + \frac{-i}{\hbar} \int_{t_0}^t dt_1 H(t_1) + \dots \\ &+ \left(\frac{-i}{\hbar}\right)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{n-1}} dt_n H(t_1) \dots H(t_n) + \dots \end{aligned} \quad (12.6)$$

Note that in eqn (12.6) the ordering of the operators is important: each $H(t)$ acts after (i.e., on the left of) all other Hamiltonian operators in preceding times. In fact, a convenient way to express this is to introduce the T -ordered operator products,

$$T[H(t_1) \dots H(t_n)] = \sum_P \theta(t_{P_1}, \dots, t_{P_n}) H(t_{P_1}) \dots H(t_{P_n}),$$

where

$$\theta(t_1, t_2, \dots, t_n) = \theta(t_1 - t_2)\theta(t_2 - t_3) \dots \theta(t_{n-1} - t_n).$$

In terms of the T -ordered product, or simply T -product, eqn (12.6) can be rewritten as

$$\sum_n \frac{1}{n!} \left(\frac{-i}{\hbar}\right)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^t dt_n T[H(t_1) \dots H(t_n)].$$

In terms of such T products, the last expression can be formally written as an exponential:

$$U(t, t_0) = T \exp \left(-\frac{i}{\hbar} \int_{t_0}^t dt H(t) \right). \quad (12.7)$$

The Heisenberg picture

It is also possible to define the Heisenberg picture for systems in which H explicitly depends on time. The unitary transformation

$$|\psi(t)\rangle \rightarrow |\psi_H\rangle = U^\dagger(t)|\psi(t)\rangle$$

makes $|\psi_H\rangle$ constant in time:

$$i\hbar \frac{d}{dt}|\psi_H\rangle = -U^\dagger(t)H|\psi(t)\rangle + U^\dagger(t)[H|\psi(t)\rangle] = 0.$$

The time evolution is transferred to the dynamical variables:

$$A_H \equiv U^\dagger(t)AU(t).$$

The operator A (in the Schrödinger picture) can itself depend on time through some external, time-dependent parameter. The equation of motion for the corresponding Heisenberg operator is

$$\begin{aligned} i\hbar \frac{dA_H}{dt} &= -U^\dagger(t)H(t)AU(t) + i\hbar U^\dagger(t) \frac{\partial A}{\partial t}U(t) + U^\dagger(t)AH(t)U(t) = \\ &= [A_H, H_H] + i\hbar \frac{\partial A_H}{\partial t}. \end{aligned} \quad (12.8)$$

Equation (12.8) is formally identical to eqn (7.56) provided that the partial derivative in the second line is correctly interpreted. More explicitly, let λ_i be the time-dependent parameters appearing in A ; then the last term of eqn (12.8) means

$$\frac{\partial A_H}{\partial t} \equiv \sum_k \dot{\lambda}_k U^\dagger \frac{\partial A}{\partial \lambda_k} U.$$

In particular, for the Hamiltonian

$$i\hbar \frac{dH_H}{dt} = i\hbar \frac{\partial H_H}{\partial t} \equiv i\hbar \sum_k \dot{\lambda}_k U^\dagger \frac{\partial H}{\partial \lambda_k} U.$$

12.2 Time-dependent unitary transformations

The definition of H as the infinitesimal generator of time translation $U(t)$ (see eqn (12.5)) allows us to understand how the Hamiltonian itself changes by a time-dependent unitary transformation. Let $S(t)$ be a unitary operator depending on t and

$$|\psi_S(t)\rangle = S(t)|\psi(t)\rangle. \quad (12.9)$$

Comparison of the two expressions

$$|\psi_S(t)\rangle = U_S(t, t_0)|\psi_S(t_0)\rangle; |\psi_S(t)\rangle = S(t)|\psi(t)\rangle = S(t)U(t, t_0)|\psi(t_0)\rangle$$

tells us that the evolution operator in the new representation is given by

$$U_S(t, t_0) = S(t) U(t, t_0) S^\dagger(t_0).$$

Taking the derivative with respect to t one gets

$$\begin{aligned} H_S(t) U_S(t) &= i \hbar \frac{d}{dt} U_S = \\ &i \left[\hbar \frac{dS}{dt} S^\dagger(t) \right] S(t) U(t, t_0) S^\dagger(t_0) + S(t) H(t) U(t, t_0) S^\dagger(t_0) \\ &= i \left[\hbar \frac{dS}{dt} S^\dagger(t) \right] U_S(t, t_0) + S(t) H(t) S^\dagger(t) U_S(t, t_0). \end{aligned}$$

Thus the Hamiltonian effectively transforms as

$$H_S(t) = S(t) H(t) S^\dagger(t) - K, \quad i \hbar \frac{dS}{dt} S^\dagger(t) \equiv -K. \quad (12.10)$$

Consideration of the time derivative of eqn (12.9),

$$i \hbar \frac{d}{dt} |\psi_S(t)\rangle = i \hbar \frac{dS}{dt} |\psi(t)\rangle + S(t) H \psi(t) = \left[i \hbar \frac{dS}{dt} S^\dagger(t) + S H S^\dagger \right] |\psi_S(t)\rangle,$$

leads to the same conclusion.

A particularly useful case of eqn (12.10) is the one in which H_S turns out to be independent of time, in which case

$$U(t, t_0) = S^\dagger(t) e^{-iH_S t/\hbar} S(t_0). \quad (12.11)$$

Spin in a time-dependent magnetic field

As an application of the preceding formulas let us consider the case of a spin- $\frac{1}{2}$ particle in a variable magnetic field. A constant magnetic field is in the z direction and a variable magnetic field lies in the x, y plane. An example of such a system is

$$H = \frac{1}{2} g \mu \sigma_z B_z + \frac{1}{2} g \mu \sigma_x B_x \cos \omega t$$

corresponding to, for instance, a linearly polarized electromagnetic field of radio frequency. This system does not have a simple analytic solution; we shall instead consider a variation of the problem, with a rotating magnetic field:

$$H = \frac{1}{2} g \mu \sigma \cdot \mathbf{B}, \quad \mathbf{B} = B_0 \hat{\mathbf{z}} + \mathbf{B}_\perp(t), \quad \mathbf{B}_\perp(t) \equiv B_1 (\hat{\mathbf{x}} \cos \omega t + \hat{\mathbf{y}} \sin \omega t).$$

By setting

$$\hbar \omega_0 = \mu g B_0, \quad \hbar \omega_1 = \mu g B_1,$$

we see that the Hamiltonian is

$$H = \frac{\hbar}{2} \begin{pmatrix} \omega_0 & \omega_1 e^{-i\omega t} \\ \omega_1 e^{i\omega t} & -\omega_0 \end{pmatrix} \equiv \frac{1}{2} [\omega_0 \sigma_3 + \omega_1 \sigma_1 \cos(\omega t) + \omega_1 \sigma_2 \sin(\omega t)].$$

If one recalls the Larmor's theorem it should not be too surprising that the problem is solvable in a closed form. In fact, perform a time-dependent unitary transformation,

$$S(t) = e^{i\omega t \frac{\sigma_3}{2}} = \cos\left(\frac{\omega t}{2}\right) \mathbb{1} + i \sin\left(\frac{\omega t}{2}\right) \sigma_3; \quad i\hbar \frac{dS}{dt} S^\dagger = -\frac{\hbar\omega}{2} \sigma_3.$$

By multiplication of the matrices one finds that

$$SHS^\dagger = \frac{\hbar}{2} \begin{pmatrix} \omega_0 & \omega_1 \\ \omega_1 & -\omega_0 \end{pmatrix} = \frac{\hbar}{2} (\omega_0 \sigma_3 + \omega_1 \sigma_1),$$

and therefore

$$H_S = SHS^\dagger + i\hbar \frac{dS}{dt} S^\dagger = \frac{\hbar}{2} ((\omega_0 - \omega)\sigma_3 + \omega_1 \sigma_1).$$

H_S is independent of time, so the evolution operator can be found immediately:

$$U_S = \exp\left[-i\frac{t}{2} ((\omega_0 - \omega)\sigma_3 + \omega_1 \sigma_1)\right]$$

and from eqn (12.11) it follows, by setting $t_0 = 0$, that

$$U(t, 0) = e^{-it\frac{\omega}{2}\sigma_3} e^{-i\frac{t}{2}((\omega_0 - \omega)\sigma_3 + \omega_1 \sigma_1)}. \quad (12.12)$$

This system has important applications, the most famous of them being magnetic resonance. When the magnetic field is static and in the fixed direction \hat{z} the spin precesses around the z axis: the probability of finding $s_z = +\frac{1}{2}$, P_\uparrow , remains constant. When an oscillating magnetic field $\mathbf{B}_\perp(t)$ is applied, with a small amplitude ($\omega_1 \ll \omega_0$) but with the frequency near the precession frequency, the system enters into resonance and the absorption of radiation by the system (whose spin flips from \uparrow to \downarrow with unit probability) obeys the Breit-Wigner curve

$$W \sim \frac{1}{\omega_1^2 + (\omega - \omega_0)^2}$$

(see [Abragam (1961)]).

12.3 Adiabatic processes

Many interesting physical systems are characterized by a Hamiltonian which contains parameters varying slowly with time. For instance, a microscopic system can be subjected to an external field (electric or magnetic) varying slowly with time. When the rate of change of external parameter(s) is sufficiently slow with respect to the characteristic time scale of the quantum system, one talks about an *adiabatic variation* of the external¹ parameters.

One of the most important results concerning these systems is the so-called *adiabatic theorem*. Given a Hamiltonian with a non-degenerate, discrete spectrum, suppose that the system is initially in one of the discrete levels, $|n\rangle$. Then the following theorem holds:

¹More precisely if $\lambda(t)$ is the varying parameter, a variation in an interval T is adiabatic if $\dot{\lambda} \rightarrow 0$ while $\lambda \cdot T \rightarrow \text{const.}$ as $T \rightarrow \infty$.

Theorem 12.1. (The adiabatic theorem) *The transition rate from $|n\rangle$ to other states during a time evolution vanishes in the limit of adiabatic variation of the external parameters, if it is assumed that none of the other levels becomes degenerate with $|n\rangle$ during the evolution.*

Proof The idea of the proof is to consider the “instantaneous” eigenstates of H as the basis of the evolution of the states. Let λ be generically the set of the parameters which appear in the Hamiltonian. Let $H(\lambda)$ be diagonalized by the states, $|s(\lambda)\rangle$:

$$H(t)|s(\lambda)\rangle = E_s(t)|s(\lambda)\rangle. \quad (12.13)$$

A system which at $t = 0$ is in the state $|n\rangle$ will evolve into the state $|\psi(t)\rangle$ which can always be written as

$$|\psi(t)\rangle = \sum_k c_k(t) e^{-\frac{i}{\hbar} \int_0^t E_k(t') dt'} |s(\lambda)\rangle. \quad (12.14)$$

The factor

$$\delta_s = \frac{1}{\hbar} \int_0^t E_s(t') dt' \quad (12.15)$$

is the usual variation of the phase of the state, which is present also for a constant Hamiltonian. δ_s is sometimes called the *dynamical* phase of the state.

Substituting eqn (12.14) into Schrödinger’s equation one finds that

$$\begin{aligned} & \sum_s \left[i \hbar \dot{c}_s(t) |s(\lambda)\rangle + E_s(t) |s(\lambda)\rangle + c_s(t) i \hbar \frac{\partial}{\partial t} |s(\lambda)\rangle \right] e^{-\frac{i}{\hbar} \int_0^t E_s(t') dt'} \\ &= \sum_k E_k(t) c_k(t) e^{-\frac{i}{\hbar} \int_0^t E_k(t') dt'} |s(\lambda)\rangle. \end{aligned} \quad (12.16)$$

By multiplying eqn (12.16) by $\langle k(\lambda) |$ and using the orthogonality of the eigenstates of H , we get

$$\frac{d}{dt} c_k(t) = - \sum_s c_s(t) e^{\frac{i}{\hbar} \int_0^t (E_k(t') - E_s(t')) dt'} \langle k(\lambda) | \frac{\partial}{\partial t} |s(\lambda)\rangle. \quad (12.17)$$

The scalar product on the right-hand side of eqn (12.17) can be calculated by taking a derivative with respect to the time of eqn (12.13):

$$\frac{\partial H}{\partial t} |s(\lambda)\rangle + H \frac{\partial}{\partial t} |s(\lambda)\rangle = E_s(t) \frac{\partial}{\partial t} |s(\lambda)\rangle + \frac{\partial E_s}{\partial t} |s(\lambda)\rangle.$$

For $k \neq s$ multiplication from the left by $\langle k(\lambda) |$ yields

$$\langle k(\lambda) | \frac{\partial}{\partial t} |s(\lambda)\rangle = \frac{1}{E_s - E_k} \langle k(\lambda) | \frac{\partial H}{\partial t} |s(\lambda)\rangle. \quad (12.18)$$

The diagonal term instead is certainly a phase. Indeed from the normalization condition $\langle k|k\rangle = 1$ it follows that

$$0 = \left\langle \frac{\partial}{\partial t} k \middle| k \right\rangle + \left\langle k \middle| \frac{\partial}{\partial t} k \right\rangle \quad \Rightarrow \quad \left\langle k \middle| \frac{\partial}{\partial t} k \right\rangle = i \gamma_k. \quad (12.19)$$

Finally we find by substituting equations (12.18), (12.19) into eqn (12.17) that

$$\frac{d}{dt}c_k(t) = - \sum_{s \neq k} \frac{c_s(t) e^{\frac{i}{\hbar} \int_0^t (E_k(t') - E_s(t')) dt'}}{E_s - E_k} \langle k(\lambda) | \frac{\partial H}{\partial t} | s(\lambda) \rangle - i\gamma_k(t) c_k(t). \quad (12.20)$$

Let us now assume that our system is initially in the state $|n\rangle$. This means that at $t = 0$ we have $c_k(0) = 0$ for $k \neq n$, $c_n(0) = 1$. This initial condition can be substituted on the right-hand side of eqn (12.20), the only surviving term being $s = n$, yielding

$$k \neq n : \frac{d}{dt}c_k \simeq \frac{c_s(t) e^{\frac{i}{\hbar} \int_0^t (E_k(t') - E_n(t')) dt'}}{E_n - E_k} \langle k(\lambda) | \frac{\partial H}{\partial t} | n(\lambda) \rangle$$

from which one gets the estimate

$$c_k(T) \simeq i\hbar \frac{e^{\frac{i}{\hbar}(E_k - E_n)T} - 1}{(E_k - E_n)^2} \langle k(\lambda) | \frac{\partial H}{\partial t} | n(\lambda) \rangle \sim \mathcal{O}(\lambda). \quad (12.21)$$

We have made use here of $\partial H/\partial t = \mathcal{O}(\lambda)$.

□

Formula (12.21) shows that the general criterion for the validity of the adiabatic theorem is

$$\left| \left(\frac{\partial H}{\partial t} \right)_{kn} \right| \ll \frac{(E_k - E_n)^2}{\hbar}, \quad \forall k \neq n. \quad (12.22)$$

Note that the condition of non-degeneracy is indeed necessary: if $E_k \rightarrow E_n$ the factor of $\partial H/\partial t$ in eqn (12.21) produces a term proportional to T which does not vanish in the adiabatic limit.

The concrete application of these conditions sometimes requires certain care. For instance, consider the case of a particle confined inside moving walls, discussed below in Section 12.4.1. Suppose that one of the walls moves slowly with a constant velocity, v , away from the other wall. How small should v be for the adiabatic approximation to be valid? The problem is that the (instantaneous) energy levels themselves depend on the distance $L(t)$ between the walls, as $\Delta E \propto 1/L(t)^2$. As a consequence, however small v may be chosen, there will be a time when the criterion (12.22) eventually fails, and the process ceases to be adiabatic. This example shows that it is not only the parameters of the initial system and the parameter entering the variation $\partial H/\partial t$ that determine the validity of the adiabatic approximation. Sometimes also the real time t enters as a part of condition.

12.3.1 The Landau–Zener transition

The adiabatic theorem in general will fail when during a time evolution two or more levels come close to each other. In such a case there is

a finite probability that the system jumps from an adiabatic level to another. A simple model of this sort has been analyzed and solved by Landau and Zener.

Consider a two-level system, described by the Hamiltonian

$$H = \begin{pmatrix} E_1(t) & F \\ F^* & E_2(t) \end{pmatrix}, \quad (12.23)$$

such that $E_2(0) = E_1(0)$. For concreteness let us assume a linear dependence,

$$E_2(t) - E_1(t) = \nu t, \quad \nu > 0,$$

while the non-diagonal element F will be taken to be a constant. We wish to find out, given the system in the ground state of eqn (12.23) at time $t = -\infty$, the probability that the system is in the higher level, at $t = \infty$. Even if $E_2(0) = E_1(0)$ the two levels are never actually degenerate. This is an example of a well-known phenomenon of "level repulsion" in quantum mechanics. The instantaneous energy eigenvalues are in fact

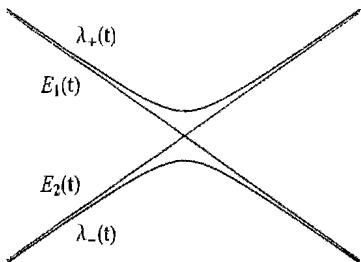


Fig. 12.1

The eigenvalues $\lambda_{\pm}(t)$ are plotted against t , together with $E_{1,2}(t)$, in Figure 12.1. In the adiabatic limit (i.e., in the limit $\nu \rightarrow 0$), if the system at $t = -\infty$ is in the state $|\psi_-\rangle$ corresponding to the ground state, it will remain in the instantaneous eigenstates $|\psi_-(t)\rangle$ corresponding to $\lambda_-(t)$ as they vary with time: at $t = +\infty$ it will still find itself in the ground state. Of course, the state $|\psi_-\rangle$ is not an eigenstate of the time evolution operator, (12.7), and in general the system has a finite probability of ending up in the excited state $|\psi_+\rangle$. In a relatively slow variation process such a result may be interpreted as a jump from the state $|\psi_-\rangle$ to $|\psi_+\rangle$: it is a non-adiabatic effect. This phenomenon is often called the *Landau-Zener transition*.²

To evaluate the probability for the transition let us set

$$\psi = \begin{pmatrix} A(t) e^{-\frac{i}{\hbar} \int_{-\infty}^t dt' E_1(t')} \\ B(t) e^{-\frac{i}{\hbar} \int_{-\infty}^t dt' E_2(t')} \end{pmatrix},$$

where the base states are taken as in eqn (12.23). By substituting this into Schrödinger's equation

$$i\hbar \frac{\partial}{\partial t} \psi = H \psi,$$

one finds that

$$i\hbar \dot{A} = BF e^{-i \int_{-\infty}^t \omega(t') dt'}, \quad i\hbar \dot{B} = AF^* e^{i \int_{-\infty}^t \omega(t') dt'}, \quad (12.24)$$

where

$$\omega(t) \equiv \frac{E_2 - E_1}{\hbar} = \frac{\nu}{\hbar} t. \quad (12.25)$$

²The Landau-Zener transition or related phenomena appear in a vast number of physical problems: in nuclear, molecular or atomic collision processes, optics, neutrino oscillation, Bose-Einstein condensation, cosmology, and so on.

By considering another time derivative and using eqn (12.24) to simplify the equations one arrives at

$$\ddot{A} + i\omega(t)\dot{A} + \frac{|F|^2}{\hbar^2}A = 0; \quad \ddot{B} - i\omega(t)\dot{B} + \frac{|F|^2}{\hbar^2}B = 0. \quad (12.26)$$

The problem is to solve eqn (12.26) or eqn (12.24), with the boundary condition

$$A(-\infty) = 0; \quad B(-\infty) = 1. \quad (12.27)$$

To solve these equations we follow the simple method due to Wittig [Wittig (2005)]. Consider the equation for B , with $\omega(t) = (\nu/\hbar)t$. Dividing it by B itself and integrating it with dt/t over the range $t = (-\infty, \infty)$ gives

$$i\frac{\nu}{\hbar} \log B(\infty) = \frac{|F|^2}{\hbar^2} \int_{-\infty}^{\infty} \frac{dt}{t} + \int_{-\infty}^{\infty} \frac{dt}{t} \frac{\ddot{B}(t)}{B(t)}. \quad (12.28)$$

where the initial condition $B(-\infty) = 1$ has been used. The integration contour is taken as in Figure 12.2 to avoid the singularity at $t = 0$. The contribution of the first term on the right-hand side is

$$\frac{|F|^2}{\hbar^2} \log \frac{R}{Re^{-i\pi}} = \frac{i\pi |F|^2}{\hbar^2}.$$

The second term may be evaluated by further modifying the contour as in Figure 12.3: as $\dot{B}(0)/B(0) = -|F|^2/\hbar^2$ as can be seen from eqn (12.26) and eqn (12.25), the last terms gives $-2\pi i|F|^2/\hbar^2$, yielding the sum

$$i\frac{\nu}{\hbar} \log B(\infty) = -i\pi \frac{|F|^2}{\hbar^2},$$

and therefore

$$P_{excited}(\infty) = |B(\infty)|^2 = e^{-2\pi|F|^2/\nu\hbar}. \quad (12.29)$$

Actually a more careful consideration of the choice of the integration contour is necessary. Either a clockwise or anti-clockwise small semi-circle around the origin can be used, but the large semi-circle must be taken in the anti-clockwise direction, in order to get a result compatible with the perturbative consideration [Wittig (2005)]. The same result, eqn (12.29), is found with both choices of the contour. Note that with the second choice the entire contribution comes from the first term on the right-hand side of eqn (12.28).

As $E_2 > E_1$ and $|E_{1,2}| \gg F$ at $t \rightarrow +\infty$, the coefficient $B(\infty)$ indeed gives the probability that the system finds itself in the *excited* level, at the very end of the evolution. The result, eqn (12.29), is exact.

12.3.2 The impulse approximation

Before proceeding with some interesting results valid in the adiabatic regimes, let us consider briefly the extreme opposite of the adiabatic

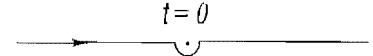


Fig. 12.2

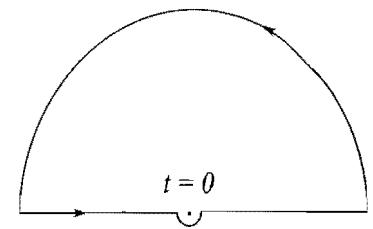


Fig. 12.3

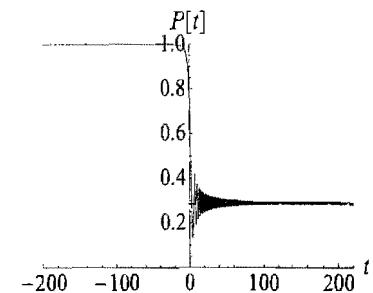


Fig. 12.4 Numerical solution of the evolution equations for $F/\hbar = 0.2$, $\nu/\hbar = 0.2$. The probability $P(t)$ is plotted against t , whose asymptotic value reproduces eqn (12.29).

variations: *an almost instantaneous change of the Hamiltonian*. Suppose that the Hamiltonian changes abruptly around $t = 0$, such that

$$H = \begin{cases} H_0, & t \leq -\epsilon; \\ H_1 (\neq H_0), & t \geq 0. \end{cases}$$

If the interval of time ϵ during which the change occurs is sufficiently small, with respect to the typical time scale $|1/\omega_{fi}|$ associated with transition among the states, the wave function does not have enough time to “adjust itself” and will remain unchanged. In fact, the evolution operator $U(t)$ reduces in such a situation to the unit operator, and at $t \rightarrow 0$

$$\psi(0) = U(\epsilon)\psi(-\epsilon) \simeq \psi(-\epsilon). \quad (12.30)$$

On the other hand, the energy levels change instantaneously according to the change of H . The probability of finding the system, $\psi_i^{(0)}$ before the variation of the Hamiltonian, in one of the new eigenstates at $t > 0$ is then simply

$$P_{i \rightarrow f} \simeq \left| \int dq \psi_f^* \psi_i^{(0)} \right|^2 \quad (12.31)$$

(known as the impulse approximation or sudden approximation).

This discussion is without doubt over-simplified, and the applicability of a formula such as (12.30) must be checked in each case. For example, in the case of a particle confined between two moving walls (Section 12.4.1), the impulse approximation is never valid in the case of contraction, however quickly the walls contract.

12.3.3 The Berry phase

One of the most remarkable results about the adiabatic variation of quantum systems, due to M. Berry, concerns *cyclic* variation of the parameters in the Hamiltonian. Let us consider a system with external parameters $\{\lambda(t)\}$ which vary adiabatically and after a period T go back to the original values $\{\lambda(T)\} = \{\lambda(0)\}$. Suppose that the system is initially in a stationary state, $|n\rangle$: according to the adiabatic theorem, the state remains in the instantaneous eigenstate while the system varies, and eqn (12.17) simplifies:

$$\frac{d}{dt} c_n(t) = -\gamma_n(t) c_n, \quad \gamma_n(t) \equiv -i \langle n(\lambda) | \frac{\partial}{\partial t} | n(\lambda) \rangle$$

(γ_n real), which has the solution (with $c_n(0) = 1$, $c_k(0) = 0$, $k \neq n$)

$$c_n(t) = \exp \left(-i \int_0^t \gamma_n(t') dt' \right) \equiv \exp(-i\Gamma(t)).$$

The state ends up being

$$|\psi(t)\rangle = e^{-i\delta_n(t)} e^{-i\Gamma(t)} |n\rangle, \quad \delta_s = \frac{1}{\hbar} \int_0^t E_s(t') dt'.$$

In addition to the “dynamical” phase δ_n which is there even for the constant Hamiltonian, there is another phase Γ . At first sight it might seem that such an additional phase can be always eliminated, absorbed by a redefinition of the wave function,

$$|n(\lambda)\rangle \rightarrow |n(\lambda)\rangle' = e^{i\mu} |n(\lambda)\rangle; \quad \mu_n(t) = - \int_0^t \gamma_n(t') dt'.$$

Or equivalently,

$$i\gamma'_n = \langle n' | \frac{\partial}{\partial t} | n' \rangle = i\gamma_n + i \frac{d}{dt} \mu_n = 0. \quad (12.32)$$

This is certainly so for sufficiently small values of t .

A crucial observation by Berry was that eliminating the extra phase this way is not always possible globally. Let us indeed consider a cyclic variation $\{\lambda(T)\} = \{\lambda(0)\}$: after time T the system returns to be the same as the original one. As t varies $\{\lambda\}$ travels along a closed curve, and according to the adiabatic theorem, the state vector also goes around in the Hilbert space and goes back to the same state. The wave function can, however, acquire an *observable* phase in doing so.

The situation becomes clearer if we write

$$A_i = -i \langle \lambda | \frac{\partial}{\partial \lambda_i} | \lambda \rangle \quad \gamma_n(t) = A_i(\lambda) \dot{\lambda}_i.$$

Then

$$\Gamma(T) = \int_0^T \gamma_n dt \equiv \oint A_i d\lambda^i. \quad (12.33)$$

Note that in the last expression the dynamical details of variation of λ has disappeared. The phase Γ has a purely geometrical meaning in the space of the parameters.

The phase change (12.32) can be seen as a kind of “gauge transformation”

$$A_i \rightarrow A_i + \frac{\partial \mu}{\partial \lambda_i},$$

depending on the coordinates $\{\lambda\}$ of the parameter space. Equation (12.33) accordingly represents the line integral of a “vector potential”, A_i . To further enforce the analogy with the electromagnetic vector potential, let us consider the case of three-dimensional parameter space,³ $\{\lambda\} = (X_1, X_2, X_3)$: eqn (12.33), by the Stokes theorem transforms into the flux of the “magnetic field”

$$\Phi = \int dS_{ij} F_{ij}, \quad F_{ij} = \frac{\partial A_j}{\partial X_i} - \frac{\partial A_i}{\partial X_j}, \quad (12.34)$$

through the surface enclosed by the (closed) trajectory in (X_1, X_2, X_3) . As the magnetic field is invariant under gauge transformations the phase $\Gamma(T)$ in general cannot be reabsorbed by a change of phase (gauge transformation) of the basis vectors. We conclude that in general the wave function acquires, after a cyclic variation of the external parameters, an extra phase, $\Gamma(T)$ (the *Berry phase*).

³This is just for the sake of illustration. Stokes’ theorem is valid in any dimension, and a formula analogous to (12.34) can be written in the parameter space of any dimension larger than one: see below.

To convince ourselves that such a phase is indeed observable, suppose that a beam of particles with spin is sent to a beam splitter: one part goes through a cavity with a rotating (real) magnetic field, the other through an empty cavity. At the exit the two beams are made to converge. It is clear that this way the phase difference can be measured by studying the interference fringes.

The most important aspect in the Berry phase (12.33) is that it depends on the global (geometrical) property of the parameter space. This feature can be better expressed by modifying (12.33) as

$$\begin{aligned}\Gamma(T) &= \oint_C \mathbf{A} \cdot d\mathbf{X} = \int_{\partial C} d\mathbf{S} \cdot (\nabla_{\mathbf{R}} \times \mathbf{A}) = -i \int_{\partial C} d\mathbf{S} (\nabla_{\mathbf{R}} \langle n |) \times (\nabla_{\mathbf{R}} |n \rangle) \\ &= \text{Im} \int_{\partial C} d\mathbf{S} \sum_{m \neq n} \langle \nabla_{\mathbf{R}} n | m \rangle \times \langle m | \nabla_{\mathbf{R}} | n \rangle,\end{aligned}\quad (12.35)$$

and by utilizing the following identity:

$$\langle m | \nabla_{\mathbf{R}} | n \rangle = \frac{\langle m | (\nabla_{\mathbf{R}} H) | n \rangle}{E_n - E_m}, \quad m \neq n. \quad (12.36)$$

The final result is

$$\begin{aligned}\Gamma(T) &= \int_{\partial C} d\mathbf{S} \cdot \mathbf{V}(\mathbf{R}), \\ \mathbf{V}(\mathbf{R}) &= \text{Im} \sum_{m \neq n} \frac{\langle n | (\nabla_{\mathbf{R}} H) | m \rangle \times \langle m | (\nabla_{\mathbf{R}} H) | n \rangle}{(E_n - E_m)^2}.\end{aligned}$$

Stokes' theorem is valid in any dimension: this formula can be used in cases where the parameter space $\{\lambda(t)\}$ has any dimension. In the following we shall see some concrete examples in simple systems. The Aharonov–Bohm effect, discussed in Chapter 14, can be thought of as an example (in this case A_i is truly the electromagnetic vector potential).⁴

⁴ **Exercise.** Verify the equalities in (12.35); show the identity (12.36) (see eqn (12.18)).

12.3.4 Examples

Simple two-state systems

Let us consider a system with the Hamiltonian

$$H = \mathbf{R} \cdot \boldsymbol{\sigma}. \quad (12.37)$$

The vectors $\mathbf{R} = (X, Y, Z)$ are the set of external parameters. We know that the two eigenstates of the system are

$$|1\rangle = \begin{pmatrix} \cos \frac{\theta}{2} e^{-i\varphi/2} \\ \sin \frac{\theta}{2} e^{i\varphi/2} \end{pmatrix}; \quad |2\rangle = \begin{pmatrix} -\sin \frac{\theta}{2} e^{-i\varphi/2} \\ \cos \frac{\theta}{2} e^{i\varphi/2} \end{pmatrix};$$

where θ, φ are the usual spherical variables of \mathbf{R} . One has, for instance for $|1\rangle$

$$\begin{aligned}A_R &= \frac{1}{i} \left\langle 1 \left| \frac{\partial}{\partial R} \right| 1 \right\rangle = 0; \quad A_\theta = \frac{1}{i} \left\langle 1 \left| \frac{\partial}{\partial \theta} \right| 1 \right\rangle = 0; \\ A_\varphi &= \frac{1}{i} \left\langle 1 \left| \frac{\partial}{\partial \varphi} \right| 1 \right\rangle = -\frac{1}{2} \cos \theta.\end{aligned}$$

That is, in Cartesian coordinates

$$\begin{aligned} A_X &= \frac{\partial \varphi}{\partial X} A_\varphi = \frac{1}{2} \frac{Y}{X^2 + Y^2} \frac{Z}{R}; & A_Z &= 0; \\ A_Y &= \frac{\partial \varphi}{\partial Y} A_\varphi = -\frac{1}{2} \frac{X}{X^2 + Y^2} \frac{Z}{R}. \end{aligned}$$

The “magnetic field” can be found to be

$$\mathbf{H} = \nabla_{\mathbf{R}} \times \mathbf{A} = \frac{1}{2} \frac{\mathbf{R}}{R^3}.$$

It is the field of a magnetic monopole, a radial field corresponding to a pointlike source at $\mathbf{R} = 0$, the point of the degeneracy of the Hamiltonian. For any closed path Stokes' theorem gives

$$\Gamma = \oint \mathbf{A} \cdot d\mathbf{R} = \int_S \mathbf{B} \cdot d\mathbf{S} = \frac{1}{2} \Omega,$$

where S is a surface enclosed by the path and Ω is the solid angle spun by S .

Spin in a rotating magnetic field

The result obtained in Chapter 12.2 is a special case of the example discussed above. In the static case ($\omega = 0$) H has two eigenvalues, $\pm \hbar\Omega/2$, with $\Omega = \sqrt{\omega_0^2 + \omega_1^2}$. The classical description is that of the precession of spin around the direction $\mathbf{n} = (\omega_0, \omega_1, 0)/\Omega$ (see also Problem 4.4).

Suppose now that the magnetic field is slowly rotating, with $\omega \rightarrow 0$, but for a sufficiently long time for it to make a full rotation, for $T = 2\pi/\omega$. In this limit the first factor in eqn (12.12) becomes

$$U \rightarrow e^{-i\pi\sigma_3} = -\mathbb{I}.$$

The second factor can be written in general as

$$\begin{aligned} e^{-i\frac{T}{2}((\omega_0 - \omega)\sigma_3 + \omega_1\sigma_1)} &= \cos\left(\frac{1}{2}\Omega'T\right) - i \sin\left(\frac{1}{2}\Omega'T\right) \mathbf{n}'\sigma; \\ \Omega' &= \sqrt{(\omega_0 - \omega)^2 + \omega_1^2} \sim \Omega - \frac{\omega_0\omega}{\Omega} + \mathcal{O}(\omega^2) \\ \mathbf{n}' &\simeq \mathbf{n} + \mathcal{O}(\omega). \end{aligned}$$

Therefore by inserting the factor -1 as a shift of phase by π and by utilizing $\omega T = 2\pi$ we have

$$\begin{aligned} U &= \cos\left(\frac{\Omega}{2}T + \delta\varphi\right) - i\mathbf{n}\sigma \sin\left(\frac{\Omega}{2}T + \delta\varphi\right) = e^{-i(\frac{\Omega}{2}T + \delta\varphi)\mathbf{n}\sigma}; \\ \delta\varphi &= \pi\left(1 - \frac{\omega_0}{\Omega}\right). \end{aligned}$$

Now let $|+\rangle, |-\rangle$ be the eigenstates of the static Hamiltonian, H_0 . Evidently

$$\mathbf{n}\sigma|\pm\rangle = \pm|\pm\rangle.$$

Therefore during a full circle of the magnetic field the two vectors acquire a phase

$$\delta\varphi_{\pm} = \pm\pi \left(1 - \frac{\omega_0}{\Omega}\right).$$

The ratio $\omega_0/\Omega = \cos\theta$ is the angle between the direction of the magnetic field and the z axis, the axis of rotation of \mathbf{B} , and hence

$$\delta\varphi_{\pm} = \pm\pi(1 - \cos\theta).$$

But this factor is precisely the solid angle of the area encircled by the magnetic field during its rotation:

$$S(\theta) = \int_0^\theta 2\pi \sin\theta d\theta = 2\pi(1 - \cos\theta).$$

The phase acquired is thus

$$\delta\varphi_{\pm} = \pm\frac{1}{2}S(\theta).$$

This is the Berry phase in this process: as is evident the result is purely geometrical; it does not depend on the way the magnetic field is varied as a function of time.

12.4 Some nontrivial systems

12.4.1 A particle within moving walls

Let us now consider a particle bound in an infinitely high one-dimensional potential well $[0, L]$. We know (Subsection 3.3.1) that the energy levels and the associated eigenfunctions are given by

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}; \quad (12.38)$$

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2m L^2}; \quad u_n(x, L) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi n x}{L}\right).$$

What happens if the walls (the boundaries of the potential) are moved?

- If the boundaries move very slowly we expect the adiabatic theorem to be valid. Both for expanding and contracting walls, if the system is initially in the ground state, we are tempted to conclude that it will remain so during the evolution. This is almost right. We have noted already that, in the case of a slow *expansion*, the energy level spacing—we talk about the instantaneous eigenvalues—decreases as $1/L^2$, so eventually there will be a time when the adiabatic approximation fails, unless the rate of expansion is simultaneously decreased, so as to maintain inequality (12.22).
- In the case of a very rapid expansion of the walls, we may appeal to the “impulse approximation”: the wave function has no time to

adjust itself to the change of the wall width. And this can be verified numerically (see below). But what if the walls were abruptly contracted? The wave function cannot possibly remain invariant, however rapidly such a contraction may be made: if it did, the portion outside the new walls would be cut out, the unitarity (the conservation of the total probability) would be violated.

- What happens if the walls are moved with a moderate velocity, neither adiabatically nor instantaneously? Can we make any interesting general statements? Can we evaluate the evolution of the states—for instance by a numerical method—easily?
- Does a resonance-like phenomenon occur if the time variation $L(t)$ is appropriately tuned?
- How does the energy of the system vary in general? For instance suppose that the system is in the ground state (with energy E_0) initially and contract the walls. As all the energy levels increase with time and *all* of them will be larger than E_0 , the energy of the system will be certainly increased. For small velocities we expect that $dE/dt \propto -\dot{L}$ so the energy will decrease in the case of expansion instead.

To study these questions, taking into account that the domain of the Hamiltonian changes as L is varied, one can make use of an expansion in terms of the “instantaneous” eigenstates, and write for generic t

$$\psi(x, t) = \sum_k b_k(t) u_k(x, L),$$

where the functions $u_k(x, L)$ are the instantaneous eigenfunctions of H , (12.38), without the factor $e^{-iE_n t/\hbar}$, but dependent on time through $L(t)$. Schrödinger’s equation is

$$i\hbar \sum_k \left(b_k u_k + b_k \frac{\partial u_k}{\partial t} \right) = \sum_k b_k E_k u_k,$$

and multiplying it by u_n^* and integrating over $[0, L]$, one finds that

$$i\hbar \dot{b}_n + i\hbar \sum_k b_k \langle u_n | \partial_t u_k \rangle = E_n b_n.$$

From the orthogonality of $\{u_k\}$ it follows that

$$0 = \partial_t \langle u_n | u_k \rangle = \langle \partial_t u_n | u_k \rangle + \langle u_n | \partial_t u_k \rangle = \langle u_k | \partial_t u_n \rangle^* + \langle u_n | \partial_t u_k \rangle.$$

We define an anti-Hermitian matrix,

$$F_{nk} \equiv \langle u_n | \partial_t u_k \rangle, \quad F_{nk}^* = -F_{kn}.$$

In the case we are dealing with the matrix elements of F_{nk} are real, so F is antisymmetric. The equation of motion can be rewritten as

$$\dot{b}_n + \sum_k F_{nk} b_k = -\frac{i}{\hbar} E_n b_n; \quad \dot{b}_n^* - \sum_k F_{kn} b_k^* = +\frac{i}{\hbar} E_n b_n^*. \quad (12.39)$$

Due to the antisymmetric nature of the matrix F it follows that

$$\frac{d}{dt} \sum_n |b_n|^2 = \sum_{nk} F_{nk} (b_n^* b_k + b_k^* b_n) = 0 :$$

the total probability is conserved, as it should be.

Consider now the energy. The energy expectation value at time t is given by

$$E(t) = \sum_n |b_n|^2 E_n(L).$$

By using the explicit form of $E_n(L)$ we have $\partial_t E_n = -2E_n \dot{L}/L$, and

$$\frac{dE}{dt} = -2 \frac{\dot{L}}{L} E - \sum_{nk} F_{nk} (b_n^* b_k + b_k^* b_n) E_n.$$

We manipulate this expression making use of the antisymmetric property of F_{nk} , to arrive at

$$\frac{dE}{dt} = -2 \frac{\dot{L}}{L} E - \sum_{nk} F_{nk} b_n^* b_k (E_n - E_k) \equiv -2 \frac{\dot{L}}{L} E - \sum_{n \neq k} F_{nk} b_n^* b_k (E_n - E_k).$$

We now use the explicit form of F_{nk}

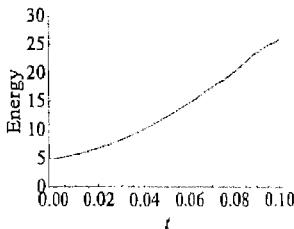


Fig. 12.5 Fast compression of the state which is initially in the ground state. In the lower figure the energy expectation value is plotted against t .

We leave it as an exercise to the reader to show that

$$F_{nn} = 0, \quad F_{nk} = \dot{L} \int_0^L dx u_n(x, L) \frac{\partial}{\partial L} u_k(x, L) = \frac{\dot{L}}{L} \left[(-1)^{n-k} \frac{2nk}{n^2 - k^2} \right]. \quad (12.40)$$

This result confirms our intuitive idea about the sign of the energy: as the particle in the well exerts a positive (outward) pressure on the wall, the environment does work on the microscopic system during the contraction, increasing its energy; vice versa the microsystem does work during the expansion, losing its energy.

Equation (12.41) has another interesting interpretation. We have

$$\frac{d\psi}{dx} = \sum_k b_k \sqrt{\frac{2}{L}} \frac{k\pi}{L} \cos\left(\frac{k\pi x}{L}\right) \Rightarrow \psi'(L) = \sqrt{\frac{2}{L}} \sum_k (-1)^k b_k \frac{k\pi}{L},$$

so that eqn (12.41) can be written as

$$\frac{dE}{dt} = -\frac{\dot{L}}{2m} \left| \hbar \partial_x \psi(L) \right|^2. \quad (12.42)$$

This means that for a rapid compression the wave function, having to remain inside the well, has a large derivative at the boundary, and the

energy required for the compression becomes very large. Furthermore, the term $\hbar \partial_x \psi(L)$ represents the momentum at the boundary,

$$|\hbar \partial_x \psi(L)|^2 \sim p^2 |\psi|^2 \sim p^2 / L$$

so that eqn (12.42) can be written as

$$\frac{dE}{dt} = -\frac{V}{L} \frac{p^2}{2m} = -E \frac{V}{L}, \quad (12.43)$$

where V is the velocity of the wall. This can be easily understood. A particle of velocity v which hits a wall which recedes with velocity V on impact loses energy $2mvV$, so after $N = v/2L$ collisions per unit time,

$$dE/dt = -2mvV N = -4E \frac{V}{v} N = -2VE/L,$$

in qualitative agreement with eqn (12.43). An extra factor of two may be interpreted as being due to the fact that the stationary state represents only half of the time a particle traveling towards the right, and only such particle gives away energy on collision with the wall.

What has been said can be numerically verified. Let us begin with the case of a rapid compression: the change of the wave function is shown in Figure 12.5. The energy increases, as expected.

In the case of fast expansion (Figure 12.6) the wave function must remain more or less invariant, which is indeed verified.

During a slow expansion, the wave function instead “follows” the change of the potential, remaining in the instantaneous eigenstate. Figure 12.7 nicely illustrates such a behavior of the wave function. Also the time dependence of E agrees with what is expected from the adiabatic theorem, $E \sim E_1(L(t))$ (dashed line).

Note that at large times, though, adiabaticity is expected, and indeed seen to fail, for the reasons mentioned already.

Note on the change of variables

A useful observation which allows analysis of the problem at hand, and other problems, is that the width of the well is the only length scale of the problem, so a scale change allows one to convert to a problem with a static wall, with $L = 1$. Concretely, let us make the change

$$x = L \cdot y \quad t = t_1.$$

Then

$$\frac{\partial}{\partial x} = \frac{1}{L} \frac{\partial}{\partial y}, \quad \frac{\partial}{\partial t} = \frac{\partial}{\partial t_1} - \frac{\dot{L}}{L} y \frac{\partial}{\partial y}.$$

By calling the new time variable t_1 t again, Schrödinger's equation and the boundary condition become

$$i \frac{\partial}{\partial t} \Psi = -\frac{1}{2mL^2} \left[\partial_y^2 \Psi - i 2m \dot{L} Ly \partial_y \Psi \right]; \\ \Psi(0, t) = \Psi(1, t) = 0. \quad (12.44)$$

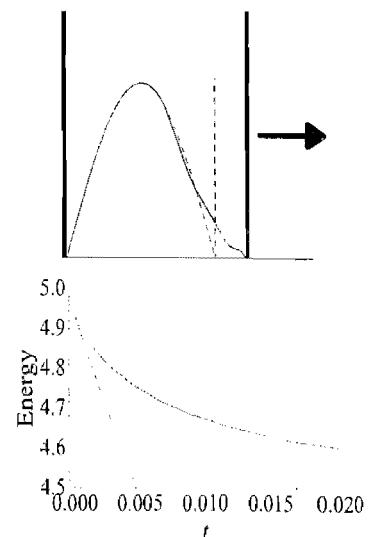


Fig. 12.6 Rapid expansion. The dashed curve is the initial (ground state) wave function. The full curve is $|\psi(x, t)|$. For the energy, the dashed curve represents $E_1(L(t))$.

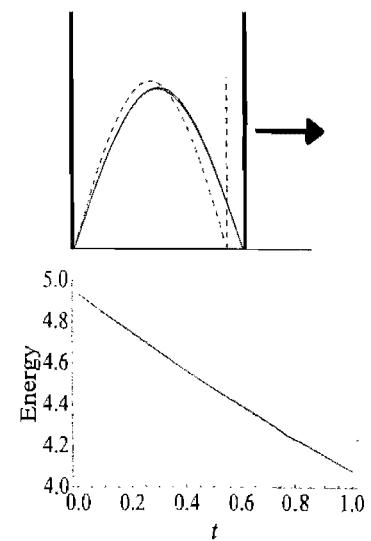


Fig. 12.7 Adiabatic expansion starting with the ground state. The dashed curve is the initial wave function $\psi_0(x, L_0)$, one of the full curves is $|\psi(x, t)|$ (numerical), the other, almost overlapping, is the adiabatic wave function $\psi_0(x, L(t))$. The dashed line in the energy plot represents $E_1(L(t))$, as compared to $E(t)$.

Once a solution $f(y, t)$ of eqn (12.44) is found, the solution of the original Schrödinger equation is simply

$$\psi(x, t) = f\left(\frac{x}{L(t)}, t\right).$$

We have a more complicated differential equation but with a fixed boundary condition. Standard techniques can be applied to eqn (12.44). For example we can choose a grid in the plane (t, y) and follow the time evolution starting from the initial configuration. These are part of the standard numerical methods. The figures above were obtained by using **Mathematica** (see the Problems for numerical analysis at the end of the chapter).

12.4.2 Resonant oscillations

A very instructive case is that of an oscillating wall, e.g., with

$$L(t) = L(1 + A \sin(\Omega t)) \quad (12.45)$$

A and Ω are the amplitude and frequency of the oscillation. To analyze this situation it is convenient to use the adiabatic expansion coefficients (see Section 12.3):

$$b_k(t) = c_k(t) e^{-i/\hbar \int_0^t dt' E_k(t')}$$

From eqn (12.39) it immediately follows that

$$\dot{c}_n = - \sum_k e^{i/\hbar \int_0^t dt' (E_n(t') - E_k(t'))} F_{nk} c_k \quad (12.46)$$

i.e., eqn (12.17).

Suppose that the perturbation to the system induced by the movement of the wall is sufficiently small, so that the levels remain practically invariant, and that the system is initially in a stationary state, i.e., $c_n = \delta_{na}$. In our case the small parameters are the amplitude A , or \dot{A} . Note that the matrix elements F_{nk} would vanish if there were no perturbation, so $F_{nk} \sim \mathcal{O}(A)$. In fact, expand c_k ,

$$c_k = c_k^{(0)} + c_k^{(1)} + \dots,$$

in the sense of perturbation expansion in A . To the lowest order $c_k^{(0)} = \delta_{ka}$. At the first order in A c_k can be substituted on the right-hand side of eqn (12.46) by $c_k^{(0)}$, as $F_{nk} \sim \mathcal{O}(A)$. Thus only the term $k = a$ survives in the sum, and for $n \neq a$ we have

$$\frac{d}{dt} c_n^{(1)} = -e^{\frac{i}{\hbar} \int_0^t dt' (E_n(t') - E_a(t'))} F_{na} c_a \sim -e^{i t (E_n - E_a)/\hbar} F_{na} c_a$$

The term on the right-hand side normally oscillates so rapidly that on the average it vanishes, which means that the system remains in the original state. The situation changes dramatically if the matrix element

F_{na} has a Fourier component that cancels exactly or approximately the frequency $(E_n - E_a)/\hbar$: in this case the variation of the coefficient does not average out to zero, and that particular coefficient grows with time. This is the typical signal of *resonance*.

We are in fact verifying the intuition by Bohr, in the context of a simple model, of how quantum mechanics works, which helped him to formulate his model of atoms. The resonance frequency, here Ω , is related to the *difference* of the energy between the states, and not to the classical oscillation frequency itself of the state in question.

Let us suppose for simplicity that F is a harmonic function with frequency Ω , for instance,

$$F_{ab} = F_+ e^{i\Omega t} + F_- e^{-i\Omega t}. \quad (12.47)$$

If Ω is such that there exists a state with $E_n = E_a \pm \Omega$ the amplitude for this state cannot be considered a small quantity. A reasonable procedure would then be to treat the equation for this state in an exact way, neglecting, however, all other non-resonant states. Let b be a state such that $E_b = E_a + \Omega$ and consider the equation

$$\dot{c}_a = -e^{i(E_a-E_b)t/\hbar} F_{ab} c_b \equiv -e^{-i\omega t} F_{ab} c_b, \quad (12.48a)$$

$$\dot{c}_b = +e^{i(E_b-E_a)t/\hbar} F_{ba} c_a \equiv +e^{i\omega t} F_{ab}^* c_a. \quad (12.48b)$$

In rewriting eqn (12.48) we have assumed that $E_b > E_a$; ω is the “transition frequency”.

There is one more simplification (used also in harmonic perturbation theory): only one of the terms in eqn (12.47) contributes to the resonance effect, the term having the right exponential to cancel the phase oscillation in eqn (12.48). Concretely,

$$F_{ab} = F_+ e^{i\Omega t} + F_- e^{-i\Omega t} \rightarrow F_+ e^{i\Omega t}, \quad F_{ab}^* = F_+^* e^{-i\Omega t} + F_-^* e^{i\Omega t} \rightarrow F_+^* e^{i\Omega t}.$$

It can be checked immediately that the phase of the coefficient F_+ can be reabsorbed in the global, arbitrary phase of c_b . Therefore if we set $F = |F_+|$,

$$\begin{aligned} \dot{c}_a &= -e^{-i\omega t} F e^{i\Omega t} c_b, \\ \dot{c}_b &= +e^{i\omega t} F e^{-i\Omega t} c_a. \end{aligned}$$

Thus we are led to a simple coupled equation, valid for $\Omega \sim \omega$. The reader will recognize in the above the same equations appearing in the problem of a spin in a rotating magnetic field (Subsection 12.2). As in that case the equations are exactly solvable: we leave the exercise to the reader and content ourselves with the particular case of $\Omega = \omega$, i.e., at the exact resonance frequency.

$$\dot{c}_a = -F c_b \quad \dot{c}_b = F c_a \quad c_a(0) = 1; c_b(0) = 0.$$

The solution in this case is

$$c_a(t) = \cos(Ft) \quad c_b(t) = \sin(Ft),$$

i.e. there is a continuous oscillation between the two levels with a frequency depending on the coupling. The probability of observing the system in the states a, b varies with time as

$$P_a(t) = \cos^2(Ft), \quad P_b(t) = \sin^2(Ft).$$

The reader will have noticed that the situation is identical to the oscillation between the two levels according to the Hamiltonian

$$H = \begin{pmatrix} E_0 & F \\ F & E_0 \end{pmatrix}.$$

What has been said is quite general; in our particular problem the calculation can be brought to an end and F can be determined explicitly. From eqns (12.40) and (12.45) we get for a not-too-large amplitude

$$\begin{aligned} F_{nk} &= \frac{\dot{L}}{L} \left[(-1)^{n-k} \frac{2nk}{n^2 - k^2} \right] = \frac{A\Omega \cos(\Omega t)}{1 + A \sin(\Omega t)} \left[(-1)^{n-k} \frac{2nk}{n^2 - k^2} \right] \\ &\sim \frac{A\Omega}{2} (e^{i\Omega t} + e^{-i\Omega t}) \left[(-1)^{n-k} \frac{2nk}{n^2 - k^2} \right], \end{aligned} \quad (12.49)$$

and hence

$$F = A\Omega \frac{nk}{|n^2 - k^2|} = A \frac{\hbar\pi^2}{2mL^2} nk, \quad (12.50)$$

remembering eqn (12.38). To verify what has been said, there are two possibilities: (a) Use eqn (12.39) directly with a finite number of modes kept; (b) numerically solve Schrödinger's equation, finding $\psi(x, t)$ and then calculating the coefficients with respect to the base (12.38).

For example let us consider the oscillation between the lowest two levels: between the ground state and the first excited state. In this case, with $n = 1, k = 2$ in eqn (12.50)

$$F = \frac{\hbar\pi^2}{mL^2} A, \quad T_0 = \frac{\pi}{2F} = \frac{mL^2}{2\hbar\pi A}.$$

T_0 is the time required to invert the probabilities between the two states. In Figure 12.8 are shown the numerical results for $A = 0.05$. We note that the system behaves as expected, showing that the approximation of considering only the finite number of modes is indeed a good approximation. The calculation has been done with the parameters $\hbar = m = L = 1$ and the inversion time expected is $T_0 = 3.18$, in excellent agreement with the numerical result in the figure.

For larger amplitudes we can expand eqn (12.49) in powers of A , so we expect to find harmonics of Ω which can induce resonance with other levels. As an illustration we report in Figure 12.9 the case with $A = 0.05, \Omega = (E_3 - E_1)/2$. The second harmonic should induce a resonance between the ground state and the second excited state. As the coupling goes as A^2 in this case we expect the transition time to be much longer, as indeed it is.

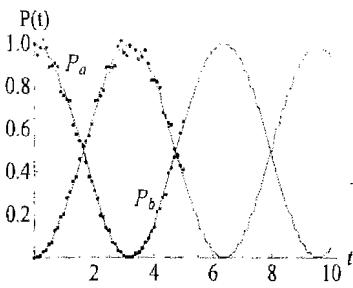


Fig. 12.8 The probabilities P_a, P_b for resonance between the first two levels, with an amplitude $A = 0.05$. The approximation with finite modes is shown by the full curve and from Schrödinger's equation by points.

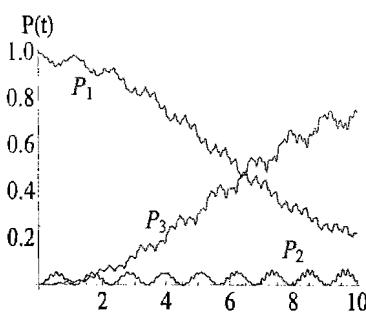


Fig. 12.9 The probabilities P_1, P_2, P_3 for the frequencies $\Omega = (E_3 - E_1)/2$. $A = 0.05$.

12.4.3 A particle encircling a solenoid

Let us now consider a particle moving on a circle of radius R . The Hamiltonian is

$$H = \frac{\hbar^2}{2m} \left(\frac{1}{i} \frac{1}{R} \frac{\partial}{\partial \varphi} \right)^2.$$

We are actually interested in the problem of a charged particle encircling a solenoid as shown in Figure 12.10. The Hamiltonian in this case is obtained by the minimal substitution $\mathbf{p} \rightarrow \mathbf{p} - e\mathbf{A}/c$, where \mathbf{A} is the vector potential, with \mathbf{A} having only the component A_φ :

$$H = \frac{\hbar^2}{2m} \left(\frac{1}{i} \frac{1}{R} \frac{\partial}{\partial \varphi} - \frac{e}{\hbar c} A_\varphi \right)^2, \quad (12.51)$$

$$i \frac{\partial \psi}{\partial t} = H\psi = \frac{\hbar^2}{2m} \left(\frac{1}{i} \frac{1}{R} \frac{\partial}{\partial \varphi} - \frac{e}{\hbar c} A_\varphi \right)^2 \psi.$$

$$\oint A_\varphi R d\varphi = F \quad A_\varphi = \frac{F}{2\pi R}, \quad (12.52)$$

where F is the magnetic flux of the solenoid.

By denoting $\theta = eF/(2\pi\hbar c)$, we have

$$H = \frac{\hbar^2}{2mR^2} \left(\frac{1}{i} \frac{\partial}{\partial \varphi} - \frac{eF}{2\pi\hbar c} \right)^2 \equiv \frac{\hbar^2}{2mR^2} \left(\frac{1}{i} \frac{\partial}{\partial \varphi} - \theta \right)^2.$$

The eigenvalues and eigenstates of H are (cf. Section 3.2.2):

$$\psi_n(\varphi) = \frac{1}{\sqrt{2\pi R}} e^{in\varphi}; \quad E_n = \frac{\hbar^2}{2mR^2} (n - \theta)^2. \quad (12.53)$$

Before continuing, let us briefly review the fundamental observables in the presence of electromagnetic interactions. The charge density and current density are modified to

$$\rho = e|\psi|^2; \quad \mathbf{j} = i \frac{e\hbar}{2m} \left[(\nabla\psi)^* \psi - \psi^* (\nabla\psi) \right] - \frac{e^2}{mc} \mathbf{A} |\psi|^2,$$

and in our case, with only the azimuthal current component present,

$$\rho = e|\psi|^2; \quad j = i \frac{e\hbar}{2mR} \left[\frac{\partial\psi^*}{\partial\varphi} \psi - \psi^* \frac{\partial\psi}{\partial\varphi} \right] - \frac{e^2}{mc} A_\varphi |\psi|^2.$$

For states (12.53) we have

$$j^{(n)} = \left(\frac{e\hbar}{mR} n - \frac{e^2}{mc} A_\varphi \right) |\psi_n|^2 = \frac{1}{2\pi} \frac{e\hbar}{mR^2} (n - \theta).$$

We wish to find out what happens if the magnetic field inside the solenoid varies with time, i.e., $F = F(t)$, or $\theta = \theta(t)$. The adiabatic states corresponding to eqn (12.53) are

$$\psi_n(\varphi, t) = \frac{1}{\sqrt{2\pi R}} e^{in\varphi} e^{-i/\hbar \int_0^t E_n(t') dt'}. \quad (12.54)$$

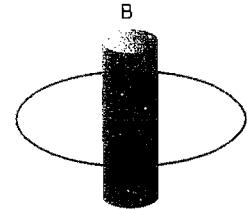


Fig. 12.10 Motion around a solenoid.

But

$$i\hbar \frac{\partial}{\partial t} \psi_n(\varphi, t) = E_n(t) \psi_n(\varphi, t) = \frac{\hbar^2}{2mR^2} (n - \theta(t))^2 \psi_n(\varphi, t),$$

$$H \psi_n(\varphi, t) = \frac{\hbar^2}{2mR^2} \left(\frac{1}{i} \frac{\partial}{\partial \varphi} - \theta \right)^2 \psi_n(\varphi, t) = \frac{\hbar^2}{2mR^2} (n - \theta(t))^2 \psi_n(\varphi, t),$$

and so the adiabatic states are exact solutions of Schrödinger's equation; in other words the process is always adiabatic whatever the variation of the flux $\theta(t)$ may be. The form of solution (12.54) also shows that in this case there is no Berry phase. This is understandable as the parameter space is one-dimensional here.

The change of the mean energy can be calculated as follows, assuming that initially the system was in a stationary state:

$$\frac{dE_n(t)}{dt} = -\frac{\hbar^2}{mR^2} (n - \theta(t)) \dot{\theta} = -\frac{2\pi\hbar}{e} j^{(n)} \dot{\theta} = -\frac{1}{c} j^{(n)} F. \quad (12.55)$$

By Faraday's law, $\text{rot}\mathbf{E} = -\frac{1}{c} \partial_t \mathbf{B}$, and eqn (12.55) can be rewritten, considering that the flux F can be re-expressed as a line-integral along the ring by Green's theorem, as follows

$$\frac{dE_n(t)}{dt} = -\frac{1}{c} \int_S \dot{\mathbf{E}} \cdot \mathbf{j}^{(n)} dS = \oint \mathcal{E} j^{(n)} R d\varphi, \quad (12.56)$$

where \mathcal{E} is the electric field induced, and eqn (12.56) expresses the change of the energy of the system by the work done by the electric field on the particle, in accordance with classical electromagnetism.

The numerical analysis and a more detailed discussion are given as the solution to Problems for numerical analysis, at the end of this chapter.

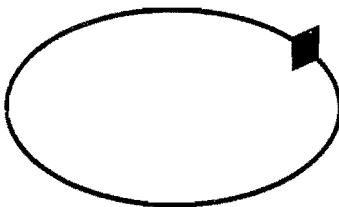


Fig. 12.11 Schematic view of a one-dimensional motion with a nontrivial boundary condition.

⁵For any parameter θ , the Hamiltonian and momentum operators are self-adjoint, and the system with a generalized periodic condition (12.57) is sometimes called a *self-adjoint extension* of the system with a trivial periodic condition ($\theta = 0$). Systems for different θ are all physically distinct.

12.4.4 A ring with a defect

A system closely related to that discussed in the preceding section is that of a particle moving on a ring, with a nontrivial boundary condition,

$$H = -\frac{\hbar^2}{2mR^2} \frac{d^2}{d\varphi^2}; \quad \psi(2\pi) = e^{i\theta} \psi(0). \quad (12.57)$$

For a fixed value of θ the problem has been considered in Subsection 3.2.2: the energy levels and eigenfunctions are given by⁵

$$\psi_n(\varphi) = \frac{1}{\sqrt{2\pi R}} e^{i(n + \frac{\theta}{2\pi})\varphi}; \quad E_n = \frac{\hbar^2}{2mR^2} \left(n + \frac{\theta}{2\pi} \right)^2. \quad (12.58)$$

We note that the probability density $|\psi|^2$ and the current density are continuous everywhere, e.g., for a stationary state, the latter is

$$j = i \frac{\hbar}{2mR} \left(\frac{\partial \psi^*}{\partial \varphi} \psi - \psi^* \frac{\partial \psi}{\partial \varphi} \right) = \frac{\hbar}{2\pi mR^2} (n + \theta)$$

and is constant in φ (and so continuous).

Formally, by a redefinition of the wave function

$$\Phi = e^{-i\frac{\theta}{2\pi}\varphi} \psi \quad (12.59)$$

the system would look exactly like eqn (12.51). This fact should not mislead the attentive reader into the (generally false) conclusion that the two problems are physically equivalent. Only if the parameter θ (or A_φ) is constant, can the two problems be regarded as two different ways of looking at the same problem.

A subtle point is that redefinition (12.59) cannot in general be considered a proper (or acceptable) gauge transformation, as the gauge transformation function is not single-valued everywhere. When the external parameter θ (or A_φ) is taken to be a generic function of time, the problem considered here and the one in the preceding subsection are physically entirely different.⁶

An interesting phenomenon occurs in the adiabatic variation of the parameter θ . Suppose that $\theta = \theta(t)$ varies slowly. The adiabatic (instantaneous) states are

$$\Phi_n(\varphi, t) = e^{-i \int_0^t E_n(t') \, dt'} \psi_n(\varphi);$$

they are not exact solutions of Schrödinger's equation, as can be checked explicitly. We know, however, that they do correctly describe the evolution of the states in the adiabatic limit. Let us now consider an adiabatic variation of θ , $\theta \rightarrow \theta + 2\pi$. As the parameter θ enters as a phase, it is an angular variable. The system, after a 2π rotation of θ , must go back to the original system. The state may not, however. In fact, the adiabatic theorem tells us that if the system starts with a state $|n, \theta\rangle$, as θ is slowly increased by 2π , it will "move up" by one level,

$$|n, \theta\rangle \xrightarrow{\theta \rightarrow \theta + 2\pi} |n+1, \theta\rangle.$$

If θ varies as $\theta \rightarrow \theta - 2\pi$, the state will end up in the state one level lower, if $\theta \rightarrow \theta + 4\pi$, two levels higher, and so on. The situation is illustrated in Figure 12.12.

This phenomenon is characteristic of any system with a periodic parameter, and is known as *spectral flow*. Such a phenomenon can, of course, be verified by a numerical integration of the equation of motion,

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi, \quad \Psi(\varphi, 0) = \psi_n(\varphi).$$

An example is shown in Figure 12.12 with time evolution for the state $n = 1$ (calculated numerically) with an adiabatic evolution, for two velocities, slow and fast.

Of course, the spectral flow itself is characteristic of the ensemble of systems parametrized by different values of θ , quite independent of whether or not the adiabatic approximation is valid. The spectrum for $\theta = 2n\pi$ for any integer n is characterized by a double degeneracy of nonzero eigenvalues, with the sole ground state being non-degenerate.

⁶ A class of systems where the consideration of this paragraph may be relevant is particles moving in periodic potentials, which frequently occur in condensed matter physics. In this correspondence, the role of the parameter θ is played by the lattice momentum, which is indeed an angular variable.

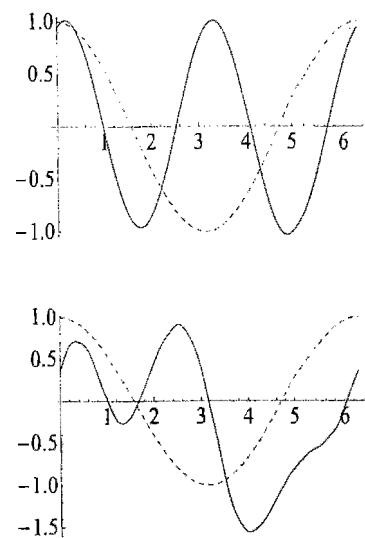
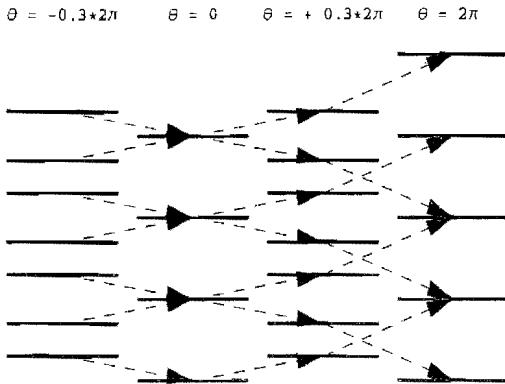


Fig. 12.12 The evolution of the wave function with time (the real part is shown). $\theta_i = 0$, $\theta_f = 2\pi$ for a slow ($\dot{\theta} = 0.01 \cdot 2\pi$) and rapid ($\dot{\theta} = 0.5 \cdot 2\pi$) variations.

Fig. 12.13 Variation of the levels as θ is varied.

For any generic value of θ , there is no degeneracy at all. An exception occurs for the values $\theta = (2n + 1)\pi$, where *all* levels become doubly degenerate. The situation is illustrated in Figure 12.13.

Another interesting feature of the adiabatic evolution of these systems is the change of the phase of the wave function. From the general expression (12.17)

$$\frac{d}{dt} c_k(t) = - \sum_s c_s(t) e^{\frac{i}{\hbar} \int_0^t (E_k(t') - E_s(t')) dt'} \left\langle k(\theta) \left| \frac{\partial}{\partial t} \right| s(\theta) \right\rangle.$$

By using eqn (12.58) we easily find that ($\hbar = m = R = 1$)

$$\left\langle k(\theta) \left| \frac{\partial}{\partial t} \right| s(\theta) \right\rangle \equiv F_{ks} = \begin{cases} \frac{i\dot{\theta}}{2} & s = k, \\ \frac{\dot{\theta}}{2\pi} \frac{1}{s-k} & s \neq k. \end{cases}$$

Therefore the n -th state acquires a phase during the variation $\theta \rightarrow \theta + 2\pi$:

$$|n, \theta\rangle \xrightarrow{\theta \rightarrow \theta + 2\pi} \left[e^{-i \int dt E_n(t)} e^{-i \int dt \frac{\dot{\theta}}{2}} \right] |n+1, \theta\rangle = e^{-i\delta_n(T)} e^{-i\pi} |n+1, \theta\rangle$$

that is, a phase $-\pi$ (a minus sign) in addition to the dynamical phase $\delta_n(T)$. Such a phase cannot be reabsorbed in the definition of the wave function and is analogous to the Berry phase.

Finally during a non-adiabatic variation of θ the state jumps from one level to another (this is quite evident from the second graph of Figure 12.12).

More details of the numerical and analytical study of these systems are to be found in the Mathematica notebook as the solution to Problems for numerical analysis at the end of the chapter.

12.5 The cyclic harmonic oscillator: a theorem

A very interesting class of physics problems is associated with a harmonic oscillator with a time-dependent frequency (we set $m = 1$),

$$H(t) = \frac{p^2}{2} + \frac{1}{2} \omega(t)^2 q^2 . \quad (12.60)$$

The Hamiltonian (12.60) in fact appears in many different physics contexts, optics, wave mechanics, cosmology (structure formation), etc., and indeed has been studied in various contexts [Lewis and Riesenfeld (1969), Dodonov and Man'ko (1978), Sebawe Abdulla and Colgrave (1985), Wolf and Korsch (1988)].

In this section, our special interest however will be in a particular class of variations, *periodic (cyclic)* variations of the frequency ω , i.e., a time variation such that

$$\omega(T) = \omega(0) .$$

We shall not further specify the time variation of $\omega(t)$. We are interested in what happens to the state during a generic, *non-adiabatic* periodic variation of the system. A theorem [Konishi and Paffuti (2006)] holds very generally for such systems:

Theorem 12.2. (The cyclic oscillator) *Let system (12.60) be in a stationary state at the time $t = 0$. Then for any cyclic variation of the frequency, i.e., $\omega(T) = \omega(0)$, the final energy expectation value is not smaller than the initial energy:*

$$\langle \psi(t) | H | \psi(t) \rangle \geq \langle \psi(0) | H | \psi(0) \rangle = E_{in} .$$

Proof The proof is easiest in the Heisenberg picture. The Heisenberg equations of motion tell us that $q(t)$, $p(t)$ are linear combinations of q , p ; they furthermore preserve the commutation relation (we set $\hbar = 1$)

$$[q(t), p(t)] = i .$$

In other words the time evolution is described by a transformation of the type

$$y(t)_\alpha = S_{\alpha\beta}(t) y(0)_\beta, \quad S_{\alpha\beta} S_{\gamma\delta} \epsilon_{\beta\delta} = \epsilon_{\alpha\gamma}, \quad S \epsilon S^T = \epsilon, \quad (12.61)$$

where we have written $y_\alpha = (q, p)$. Or writing

$$S = \begin{pmatrix} a & b \\ c & d \end{pmatrix}, \quad a, b, c, d \text{ real}$$

the condition (12.61) reduces to

$$ad - bc = \det(S) = 1.$$

The energy expectation value at time t is given by

$$\bar{E}(t) = \langle \psi | H(t) | \psi \rangle = \frac{1}{2} \langle \psi | p(t)^2 + \omega(t)^2 q(t)^2 | \psi \rangle. \quad (12.62)$$

At the end of a cycle (we set $\omega(0) = 1$),

$$E_{fin} = \frac{1}{2} \langle \psi | p_H(t_0)^2 + q_H(t_0)^2 | \psi \rangle.$$

By using eqn (12.61) and by defining

$$D = \frac{1}{2} (q p + p q),$$

we see that the quadratic form becomes

$$\begin{aligned} & (S_{11} q + S_{12} p)^2 + (S_{21} q + S_{22} p)^2 \\ &= (S_{11}^2 + S_{21}^2) q^2 + (S_{12}^2 + S_{22}^2) p^2 + 2(S_{11} S_{12} + S_{21} S_{22}) D. \end{aligned}$$

By using the virial theorem

$$\frac{1}{2} \langle \psi | p^2 | \psi \rangle = \frac{1}{2} \langle \psi | q^2 | \psi \rangle = \frac{1}{2} E_{in}$$

and the fact (valid for real wave functions) that

$$\langle \psi | D | \psi \rangle = 0,$$

we find that the final energy is given by

$$E_{fin} = \frac{1}{2} E_{in} [S_{11}^2 + S_{21}^2 + S_{12}^2 + S_{22}^2].$$

The problem is then to find the minimum of a quadratic form

$$Q = a^2 + b^2 + c^2 + d^2$$

under the constraint $ad - bc = 1$. By introducing a Lagrange multiplier, the extremum of

$$a^2 + b^2 + c^2 + d^2 + 2\lambda(ad - bc - 1)$$

is given by⁷

$$\lambda = -1, \quad a = d, \quad b = -c, \quad S = \begin{pmatrix} a & b \\ -b & a \end{pmatrix}, \quad a^2 + b^2 = 1,$$

that is, when S is orthogonal. In that case the quadratic form takes the value 2 and therefore in general

$$E_{fin} = \frac{1}{2} E_{in} Q \geq E_{in}.$$

□

⁷As the set of evolution matrices is unbounded, this extremum can only be a minimum. In an alternative proof given in (12.72) this fact is obvious.

The meaning of the theorem is clear: on the average the microscopic system can never give excess energy to the external environment. The energy transfer occurs one way: from the macroscopic environment to the microscopic system. The same result obviously holds for the ensemble of such harmonic oscillators. The microscopic system cannot generate net energy for the environment.⁸

The theorem might appear surprising at first sight, since during a generic (non-cyclic) time variation of external parameters, the microscopic system can either give energy away to, or absorb it from, the environment. Also, such a theorem certainly does not hold in general in a system in a finite-dimensional Hilbert space, such as a spin- $\frac{1}{2}$ system in a varying magnetic field.

⁸A spaceship cannot continue her journey forever, getting her energy supply from the inexhaustible zero-point energy of the vacuum [Nagata (1998)].

Remarks

- (i) In the adiabatic limit, the system follows the variation of the spectrum "riding" the initial eigenstate while it varies, and comes back to the original state, so we expect that $E_f \rightarrow E_{in}$. In the instantaneous variation limit, the wave function does not "make it" change as the external parameter goes through a rapid cyclic variation, so that $E_f \rightarrow E_{in}$ again.

- (ii) The above result is also valid in the case of a forced oscillator.

Consider

$$H = \frac{1}{2}(p^2 + \omega(t)^2 q^2) - \kappa(t)q,$$

where $\kappa(t)$ is an arbitrary function with $\kappa(0) = \kappa(T) = 0$. Heisenberg's equations are

$$\begin{aligned}\dot{p} &= i[H, p] = -\omega^2 q + \kappa, \\ \dot{q} &= i[H, q] = p,\end{aligned}$$

and so

$$\ddot{q} = -\omega^2 q + \dot{\kappa}. \quad (12.63)$$

Let us now consider a solution $Q_c(t)$ of (12.63) with the boundary condition

$$Q_c(0) = \dot{Q}_c(0) = 0;$$

it follows immediately that q is a sum of the homogeneous solution plus the particular one Q_c

$$\begin{aligned}q_H(t) &= Q_c(t) + q_H^{(\kappa=0)}(t), \\ p_H(t) &= \dot{Q}_c(t) + p_H^{(\kappa=0)}(t).\end{aligned}$$

One then has

$$E_f = E_f^{(\kappa=0)} + \frac{1}{2} \left(Q^2 + \dot{Q}^2 \right) + \left(Q_c \left\langle q_H^{(\kappa=0)}(t) \right\rangle + \dot{Q}_c \left\langle p_H^{(\kappa=0)}(t) \right\rangle \right).$$

As the expectation values of q_H and p_H vanish in the initial stationary state it follows that

$$E_f = E_f^{(\kappa=0)} + \frac{1}{2} \left(Q^2 + \dot{Q}^2 \right) \geq E_i,$$

where the result of the preceding paragraphs has been used.

- (iii) In perturbation theory the theorem can be easily seen to be valid. By writing $\omega(t)^2 x^2 = \omega_0^2 x^2 + \delta\omega(t) x^2$, $\delta\omega(t_0) = \delta\omega(0) = 0$, one sees that the first-order transition probability

$$P_{fi} = \frac{1}{\hbar^2} \left| \int_0^{t_0} dt \frac{\delta\omega(t)}{2} e^{i\omega_{fi} t} (x^2)_{fi} \right|^2$$

is larger for the process $n \rightarrow n+2$ than for $n \rightarrow n-2$, and hence $\langle H \rangle \geq E_{in}$.

- (iv) In perturbation theory, the theorem is valid for a more general class of perturbing potentials. Indeed, it can be easily seen that for any perturbation of the form

$$\Delta V(t, x) = \delta\omega(t) x^N, \quad \delta\omega(t_0) = \delta\omega(0) = 0$$

the theorem is valid, as $|(\langle x^N \rangle)_{n+m,n}| \geq |(\langle x^N \rangle)_{n-m,n}|$ ($m > 0$). This might suggest that the theorem actually holds for a wider class of periodic potentials, $V(t_0, x) = V(0, x)$.

- (v) The theorem obviously applies for a system of N independent oscillators

$$H = \sum_{i=1}^N \left[\frac{p_i^2}{2} + \frac{1}{2} \omega_i(t)^2 q_i^2 \right], \quad (12.64)$$

with arbitrary, periodic variations of ω , $\omega_i(t_0) = \omega_i(0)$, if the initial state is a stationary state $|n_1, n_2, \dots, n_N\rangle$.

- (vi) The theorem cannot hold for a generic initial pure state⁹. Since in some cases the final energy expectation value (i.e., in the pure state $U(t_0)|\psi(0)\rangle$) is strictly higher than the initial value, it suffices to consider the time-reversed process of such an evolution, time-reversing also the variation of $\omega(t)$, to find a counter-example¹⁰. On the other hand, for an initial state which is not an eigenstate of energy, the operational meaning of the theorem itself would become somewhat unclear.

- (vii) There is an important case in which the theorem applies for a initial mixed state. Consider the N -oscillator system of eqn (12.64) and suppose that the system is originally in thermal equilibrium with a heat bath at temperature T . The theorem then clearly holds in a statistical and quantum average sense.

- (viii) The energy gain factor, $R \equiv \langle \psi | H | \psi \rangle / E_{in}$, is universal, in the sense that it does not depend on the particular initial stationary state chosen.

- (ix) Note that the (classical) canonical equations of motion and Heisenberg's equations have the same form, and the evolution matrix S is the same in both cases. As a result, a similar theorem holds in classical mechanics, if one takes an average over random initial values (p, q) over a given (fixed-energy) trajectory.

⁹The condition that the initial state be a stationary state is sufficient but not necessary. In fact, for initial states of the form $\psi = \sum_n a_n \psi_n$, $n = n_0 + 4m$, $m \in \mathbb{Z}$, with a fixed n_0 , which are pure but non-stationary, the theorem can be shown to hold by a slight generalization of the proof given here.

¹⁰We thank Tomas Tyc for a useful communication on this point.

12.5.1 Inverse linear variation of the frequency

For illustration and as a check of some of the general remarks above, let us consider the following explicit form for $\omega(t)$:

$$\omega(t) = \frac{\omega_0}{\lambda(t)}, \quad \lambda(t) = 1 + vt,$$

where ω_0 and v are constants. For a periodic variation we shall consider an increase of ω followed by a decrease, or vice versa, below. From Heisenberg's equations one gets

$$\frac{d^2q}{d\lambda^2} + \Omega^2 \frac{q}{\lambda^2} = 0, \quad \Omega = \frac{\omega_0}{v}.$$

By setting $q(t) = \lambda(t)^\beta$, one gets the characteristic equation

$$\beta(\beta - 1) + \Omega^2 = 0,$$

with solutions

$$\beta_{1,2} = \frac{1}{2} \pm \delta, \quad \delta \equiv \sqrt{\frac{1}{4} - \Omega^2},$$

so that the general solution of Heisenberg's equations reads

$$q_H = c_1 \lambda^{\beta_1} + c_2 \lambda^{\beta_2}, \quad p_H = v(c_1 \beta_1 \lambda^{\beta_1} + c_2 \beta_2 \lambda^{\beta_2}).$$

By imposing the initial condition one finds that

$$\begin{aligned} q_H(t) &= \frac{1}{2\delta} \left\{ (\beta_2 \lambda^{\beta_1} - \beta_1 \lambda^{\beta_2}) q + \frac{1}{v} (\lambda^{\beta_2} - \lambda^{\beta_1}) p \right\}, \\ p_H(t) &= \frac{v}{2\delta\lambda} \left\{ \beta_1 \beta_2 (\lambda^{\beta_2} - \lambda^{\beta_1}) q + \frac{1}{v} (\beta_2 \lambda^{\beta_2} - \beta_1 \lambda^{\beta_1}) p \right\}. \end{aligned} \quad (12.65)$$

As a check, consider the adiabatic limit, $v \rightarrow 0$, $\Omega \rightarrow \infty$. One has $\beta_{1,2} \simeq \pm i\omega_0/v$, so that

$$\lambda^{\beta_{1,2}} \rightarrow (1 + vt)^{\mp i\omega_0/v} \rightarrow e^{\mp i\omega_0 t},$$

and

$$\begin{aligned} q_H(t) &\rightarrow \frac{q}{2} (e^{-i\omega_0 t} + e^{i\omega_0 t}) + \frac{p}{2i\omega_0} (-e^{-i\omega_0 t} + e^{i\omega_0 t}) \\ &= q \cos \omega_0 t + \frac{p}{\omega_0} \sin \omega_0 t, \end{aligned}$$

which is the correct result.

Writing eqn (12.65) in the form of eqn (12.61) with $S = S(\omega_0, v, \lambda)$, one gets, by inserting this into eqn (12.62) and by using the virial theorem,

$$\begin{aligned} \langle \psi | H | \psi \rangle &= \frac{1}{2} E_0 \left[\frac{1}{\lambda^2} (S_{11}^2 + S_{12}^2) + S_{21}^2 + S_{22}^2 \right] = \\ &= \frac{E_0}{2} \frac{\lambda^{2\delta} + \lambda^{-2\delta} + 2(4\delta^2 - 1)}{4\lambda\delta^2}. \end{aligned} \quad (12.66)$$

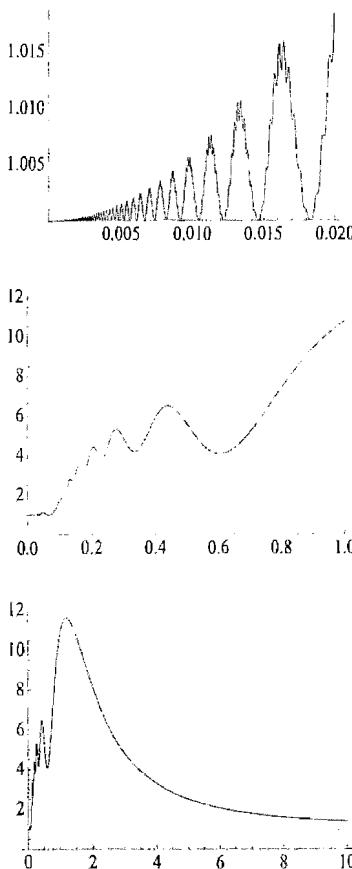


Fig. 12.14 The energy gain factor as a function of v for fixed $\lambda (= 10)$, at small, medium, and large v .

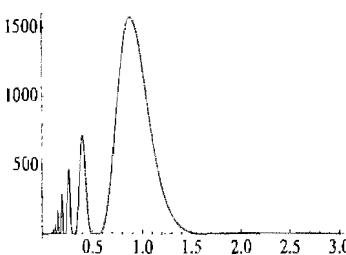


Fig. 12.15 The energy gain factor as a function of v after the box repeats an expansion (up to $\lambda = 10$) followed by contraction three times.

At time t , $\lambda = 1 + vt$, the mean energy value (12.66) can be larger or smaller than the original energy depending on the sign of the velocity v (and hence the scale factor λ is smaller or larger than unity). The results for more general frequency variations are given in Sections 12.5.3 and 12.5.4.

However, as our main concern is with *cyclic variations* of ω , let us consider the evolution from the original frequency ω_0 to a final frequency $\frac{\omega_0}{\lambda}$, and then back to ω_0 . The second half of the evolution is simply described by the transformation $S = S(\frac{\omega_0}{\lambda}, -v, \frac{1}{\lambda})$ so that the total evolution is described by the Heisenberg evolution,

$$\begin{pmatrix} q_H(t_0) \\ p_H(t_0) \end{pmatrix} = S^{\text{cyc}} \begin{pmatrix} q_H(0) \\ p_H(0) \end{pmatrix}, \quad S^{\text{cyc}} \equiv S\left(\frac{\omega_0}{\lambda}, -v, \frac{1}{\lambda}\right) \cdot S(\omega_0, v, \lambda), \quad (12.67)$$

where S is defined by eqn (12.65).

In the case of linear variation (12.66), (12.67), the energy gain factor $R(\omega_0, v, \lambda) = \langle \psi | H | \psi \rangle / E_0 = \frac{1}{2} \text{Tr}[S^{\text{cyc}}(S^{\text{cyc}})^T]$ can be studied numerically for various values of ω_0 , v and λ , λ being the scale factor ($\omega = \omega_0/\lambda$) at the moment of maximal contraction ($\lambda < 1$) or expansion ($\lambda > 1$). See Figure 12.14. Such a numerical analysis confirms that $R(\omega_0, v, \lambda) \geq 1$ always, in agreement with the Theorem 12.2, but there is more:

Remarks

- (i) At fixed λ , $R(\omega_0, v, \lambda) \rightarrow 1$ both in the adiabatic ($v \rightarrow 0$) and impulse approximation ($v \rightarrow \infty$) limits, as expected.
- (ii) There are various resonance effects at small v (see Figure 12.14): the adiabatic limit is non-analytic. As a function of the velocity v at a fixed λ , R reaches a maximum of the order of $O(1/\lambda)$ (for $\lambda < 1$) or $O(\lambda)$ (for $\lambda > 1$) at some critical value of v , and then rather smoothly approaches the impulse-approximation value 1 asymptotically.
- (iii) When the system goes through N cycles, numerical results suggest that the maximal energy gain factor (which occurs at a certain critical velocity) grows as $R \sim (1/\lambda)^N$ or $R \sim \lambda^N$, a huge factor if λ is small (or large). Such a *cumulative effect* (see Figure 12.15) might be useful in some physical application of our theorem.
- (iv) There are values of (v, λ) at which R attains values either exactly equal to or very close to unity (Figure 12.14).
- (v) As a function of λ , the maximum of R grows indefinitely as $\lambda \rightarrow 0$ or as $\lambda \rightarrow \infty$.

12.5.2 The Planck distribution inside an oscillating cavity

As a possible physical application of these ideas, let us consider the black body spectrum confined into a perfectly reflecting three-dimensional box

of linear dimension L . The electromagnetic fields are described by the Lagrangian

$$L = \frac{1}{8\pi} \left(\frac{L}{2} \right)^3 \left\{ \sum_{\mathbf{n}} \frac{1}{c^2} (\dot{Q}_{1n}^2 + \dot{Q}_{2n}^2) - \sum_{\mathbf{n}} k_n^2 (Q_{1n}^2 + Q_{2n}^2) \right\},$$

where $k_n \equiv \pi n/L$. A redefinition of Q_{in} and a Legendre transformation leads to the Hamiltonian per unit volume

$$H = \sum_{\mathbf{k}} \left(\frac{c^2}{4} p_{(1)}^2 + k^2 q_{(1)}^2 \right) + \sum_{\mathbf{k}} \left(\frac{c^2}{4} p_{(2)}^2 + k^2 q_{(2)}^2 \right).$$

At temperature T the energy distribution is

$$u(\nu) d\nu = \frac{8\pi}{c^3} \frac{\hbar\nu}{e^{\hbar\nu/kT} - 1} \nu^2 d\nu. \quad (12.68)$$

Suppose that at a certain moment the box starts to contract or expand with a constant linear velocity. How does the energy distribution change with the linear size of the box?

At time $t = 0$ various modes are distributed according to the Planck distribution, eqn (12.68). Each mode simply transforms as in eqn (12.65): ($|\delta| \gg 1$, $\delta = i|\delta|$),

$$E_n \rightarrow \langle H \rangle = \frac{E_n}{2} \frac{\lambda^{2\delta} + \lambda^{-2\delta} + 2(4\delta^2 - 1)}{4\lambda\delta^2} \simeq \frac{E_n}{\lambda}.$$

Since

$$\omega = \frac{\pi |\mathbf{n}| c}{L_0}, \quad L(t) = L_0(1 + v t), \quad |V| = L_0 |v| \ll c,$$

$$\Omega = \frac{\omega}{v} = \frac{\pi |\mathbf{n}| c}{|V|} \gg 1, \quad \delta = \sqrt{\frac{1}{4} - \Omega^2} \simeq i \frac{\pi |\mathbf{n}| c}{|V|},$$

the process is entirely adiabatic, for all modes. The distribution remains Planckian; each mode is either red-shifted (in an expanding box) or shifted towards the ultraviolet (a contracting box), simply by the scale factor λ .¹¹

Thus this process is not a very interesting example of an application of our theorem, unless the walls of the box can move with a relativistic velocity. Nevertheless, this process could possibly have some relevance in the phenomenon of *sonoluminescence*. In so-called single-bubble sonoluminescence [Gaitan (1990), Brenner, et. al. (2002)], a gas bubble trapped in a liquid is made to oscillate radially by acoustic waves, and at the moment its radius attains the minimum the bubble emits a pulse of light in the visible to ultraviolet wavelength range. In a typical experiment, the linear dimension of the bubble contracts up to a factor of $\lambda = 10^{-4}$: this is compatible with the observed increase of an effective temperature of a factor of 10^4 or more.¹² The energy density increases according to Stefan's law,

$$U = \sigma T^4; \quad \sigma = 7.64 \times 10^{-15} \text{ erg cm}^{-3} \text{ K}^{-4} \quad (12.69)$$

¹¹The cosmic microwave background radiation remains Planckian as the universe expands and cools down.

¹²In an experiment at the Lawrence Livermore National Laboratory [Gaitan (1990)] 10^5 – 10^6 photons are observed within a pulse, with energy of the order of 10^{-7} erg, which seems to be compatible with such a rough estimate. Note also that the visible light corresponds to the effective temperature of $T = 10^4$ – 10^5 or to the energy for a single photon of order of $\hbar\nu \sim kT \sim 10^{-12}$ erg.

but since the volume itself decreases by a factor λ^3 the total energy of black body radiation increases only by a factor of $\frac{1}{\lambda}$. It is possible that this excess energy is released in the form of a visible light pulse at each cycle.

12.5.3 General power-dependent frequencies

Consider the case of a generic power law frequency,

$$H(t) = \frac{1}{2m} p^2 + \frac{1}{2} m \omega_0^2 z^{k-2} x^2, \quad z = 1 + vt.$$

For $k = 0$ we recover the case discussed in the text. In the following, we shall set $m = 1, \omega_0 = 1$. Note that v has the dimension of a frequency, so that to recover the dependence on ω_0 it suffices to replace it by v/ω_0 . Heisenberg's equation of motion gives

$$\ddot{q}_H + z^{k-2} q_H = 0.$$

Multiplying this by $1/v^2$ one gets

$$\frac{d^2}{dz^2} q_H + \frac{1}{v^2} z^{k-2} q_H = 0.$$

Its general solution is of the form

$$q_H(t) = A \sqrt{z} J_{1/k} \left(\frac{2}{kv} z^{\frac{k}{2}} \right) + B \sqrt{z} Y_{1/k} \left(\frac{2}{kv} z^{\frac{k}{2}} \right),$$

where J, Y are Bessel functions of the first and second kind, respectively. Differentiation with respect to time yields

$$p_H(t) = v \frac{d}{dz} q_H(t).$$

The coefficients A and B are determined by imposing the initial conditions

$$q_H|_{z=1} = q \quad p_H|_{z=1} = p;$$

$$\begin{aligned} A &= -\frac{\pi}{kv} \left[q \cdot Y_{1+\frac{1}{k}} \left(\frac{2}{kv} \right) + (p - vq) \cdot Y_{\frac{1}{k}} \left(\frac{2}{kv} \right) \right]; \\ B &= \frac{\pi}{kv} \left[q \cdot J_{1+\frac{1}{k}} \left(\frac{2}{kv} \right) + (p - vq) \cdot J_{\frac{1}{k}} \left(\frac{2}{kv} \right) \right]. \end{aligned}$$

The expression for

$$E(t) = \langle 0 | \frac{1}{2} p_H(t)^2 + \frac{1}{2} z^{k-2} q_H(t)^2 | 0 \rangle.$$

is quite complicated but can be analyzed numerically. We note that:

- (1) The case $k = -2$ reduces to the known result.

- (2) The behavior is qualitatively similar for all k , with a phase of monotonic increase following the initial, oscillating phase, as a function of v (see Figure 12.16).
- (3) At a fixed final “physical scale”, $z_{fin} = \lambda^{-\frac{2}{k-2}}$, $z_{fin}^{k-2} = \lambda^{-2}$, the asymptotic behavior in v turns out always to be the same as in the case $k = -2$, i.e.,

$$E_f \simeq \frac{\omega}{4} \left(1 + \frac{1}{\lambda^2} \right). \quad (12.70)$$

This assertion is based on graphical evidence (see Figure 12.16), for the moment. For generic order, the functions J, Y have essential singularities at $v = \infty$, which prevent us from analyzing either the adiabatic or large- v limit analytically.

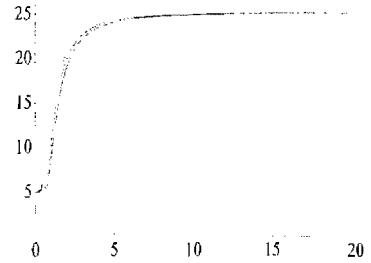


Fig. 12.16 Energy as a function of v for a fixed $\lambda = 1/10$, with $k = -2, -3, -4$. The expected asymptotic value is $1/4(1+100) = 25.25$.

12.5.4 Exponential dependence

As a second example, let us consider the Hamiltonian

$$H = \frac{1}{2} p^2 + \frac{1}{2} e^{2vt} q^2.$$

Heisenberg's equation is

$$\ddot{q}_H + e^{2vt} q_H = 0.$$

Changing the variable to $\tau = vt$ one has

$$\frac{d}{d\tau^2} q_H + \frac{1}{v^2} e^{2vt} q_H = 0,$$

which has

$$q_H(t) = A J_0\left(\frac{1}{v} e^{vt}\right) + B Y_0\left(\frac{1}{v} e^{vt}\right)$$

$$p_H(t) = \frac{dq_H}{dt} = -A e^{vt} J_1\left(\frac{1}{v} e^{vt}\right) - B e^{vt} Y_1\left(\frac{1}{v} e^{vt}\right)$$

as general solutions. As before the coefficients are determined by the initial condition:

$$A = -\frac{\pi}{2v} \left[p Y_0\left(\frac{1}{v}\right) + q Y_1\left(\frac{1}{v}\right) \right], \quad B = \frac{\pi}{2v} \left[p J_0\left(\frac{1}{v}\right) + q J_1\left(\frac{1}{v}\right) \right].$$

The mean energy can be computed as in the preceding cases.

$$E(t) = \frac{\pi^2 z^2}{16\pi^2} \left\{ -2J_0\left(\frac{z}{v}\right) Y_0\left(\frac{z}{v}\right) \left[J_0\left(\frac{1}{v}\right) Y_0\left(\frac{1}{v}\right) + J_1\left(\frac{1}{v}\right) Y_1\left(\frac{1}{v}\right) \right] \right. \\ + J_0^2\left(\frac{z}{v}\right) \left[Y_0^2\left(\frac{1}{v}\right) + Y_1^2\left(\frac{1}{v}\right) \right] + J_1^2\left(\frac{z}{v}\right) \left[Y_0^2\left(\frac{1}{v}\right) + Y_1^2\left(\frac{1}{v}\right) \right] \\ + 2J_1\left(\frac{z}{v}\right) Y_1\left(\frac{z}{v}\right) \left[J_0\left(\frac{1}{v}\right) Y_0\left(\frac{1}{v}\right) + J_1\left(\frac{1}{v}\right) Y_1\left(\frac{1}{v}\right) \right] + \\ \left. + \left[J_0^2\left(\frac{1}{v}\right) + J_1^2\left(\frac{1}{v}\right) \right] \left[Y_0^2\left(\frac{z}{v}\right) + Y_1^2\left(\frac{z}{v}\right) \right] \right\}$$

where $z = e^{vt}$. It is also possible to get the asymptotic behavior in v at fixed z :

$$E_{as} = \frac{1}{4} (1 + z^2) - \frac{1}{16v^2} (z^2 - 1)^2,$$

which is compatible with eqn (12.70) as $z = 1/\lambda$.

12.5.5 Creation and annihilation operators; coupled oscillators

The whole problem can be analyzed by the use of creation and annihilation operators. We introduce at each instance the variables $q_i(t)$, $p_i(t)$ in which the frequency is diagonal, $\omega_{ij}(t) = \delta_{ij}\omega_i(t)$; then define $a_i(t)$, $a_i^\dagger(t)$ in the standard manner in terms of $q_i(t)$, $p_i(t)$. The time evolution introduces a linear transformation among $a_i(t)$, $a_i^\dagger(t)$, which has a general form,

$$a_i^\dagger \rightarrow A_{ik}a_k^\dagger + B_{ik}a_k, \quad a_i \rightarrow A_{ik}^*a_k + B_{ik}^*a_k^\dagger.$$

The coefficients must be such that the canonical commutation relations are preserved (in a matrix form):

$$AA^\dagger - BB^\dagger = 1, AB^T - BA^T = 0. \quad (12.71)$$

For a single oscillator, the theorem of Section 12.5 can be immediately proven:

$$\begin{aligned} E_f &= \frac{\omega}{2} + \omega \langle n | (a')^\dagger a' | n \rangle = \frac{\omega}{2} + \omega \langle n | (|A|^2 + |B|^2) a^\dagger a | n \rangle \\ &= \frac{\omega}{2} + n (1 + 2|B|^2) \omega \geq \omega \left(n + \frac{1}{2} \right) = E_{in}. \end{aligned} \quad (12.72)$$

For N oscillators which are originally in a stationary state (ignoring the zero point energy),

$$\begin{aligned} E_i &= \langle \Psi | \sum_i \omega_i a_i^\dagger a_i | \Psi \rangle = \sum_i \omega_i n_i \\ E_f &= \langle \Psi | \sum_i \omega_i a_i^\dagger a_i | \Psi \rangle = \langle \Psi | \sum_i \omega_i (A_{ik}a_k^\dagger + B_{ik}a_k)(A_{ik}^*a_k + B_{ik}^*a_k^\dagger) | \Psi \rangle \\ &= \sum_{i,k} \omega_i (A_{ik}A_{ik}^*n_k + B_{ik}B_{ik}^*(n_k + 1)). \end{aligned}$$

For the diagonal matrices A and B (uncoupled oscillators), eqn (12.72) generalizes trivially. For coupled oscillators, the generalization of the theorem 12.2 is not obvious.

We shall content ourselves here with a somewhat weaker result: it asserts that the occupation number (number of phonons) does not diminish under cyclic variations of frequency. Indeed,

$$\begin{aligned} N_i &= \langle \Psi | \sum_i a_i^\dagger a_i | \Psi \rangle = \sum_i n_i \\ N_f &= \langle \Psi | \sum_i a_i^\dagger a_i | \Psi \rangle = \langle \Psi | \sum_i (A_{ik}a_k^\dagger + B_{ik}a_k)(A_{ik}^*a_k + B_{ik}^*a_k^\dagger) | \Psi \rangle \\ &= \sum_{i,k} (A_{ik}A_{ik}^*n_k + B_{ik}B_{ik}^*(n_k + 1)), \end{aligned}$$

eqn (12.71) implies that

$$\sum_i A_{ik} A_{ik}^* = \sum_i B_{ik} B_{ik}^* + 1,$$

and therefore

$$N_f = \sum_k n_k + \sum_{i,k} B_{ik} B_{ik}^* (2n_k + 1) \geq N_i.$$

Guide to the Supplements

The examples discussed in the text of a particle on a ring or between moving walls are examined more extensively in the problems of this chapter, where some more exotic questions are answered, such as the connection with Galilei invariance, Problem 12.4, and the equivalence

between accelerated systems and gravitational problems, Problem 12.3. An intriguing possibility is explored briefly in Problem 12.5: the equation of motion induced on the (macroscopic) walls by the microscopic evolution. All these questions are studied numerically also.

Problems

- (12.1) A charged particle is constrained to move on a circle of radius R , in the xy plane. The circle encloses a perfectly isolated cylindrical solenoid with the axis along z , radius $a < R$, and carrying a magnetic flux F .

- (a) Find the energy eigenstates.
- (b) Describe the time evolution for the flux varying with time.

For the solution to this and the following problems, see the Mathematica notebook, `ProbChap12.nb` and the pdf file, `ProbChap12.pdf`, on the accompanying CD.

- (12.2) A particle moves on a circle of radius R . A device on the circle adds a phase $2\pi\alpha$ when it is crossed. Study the stationary state solutions and let $\alpha = \alpha(t)$.
- (12.3) A free particle moves in a box, $[x_L, x_R]$. The boundary conditions are $\psi(x_L) = \psi(x_R) = 0$. The boundaries can move.

- (a) Make a change of variables which brings the problem to a fixed boundary value problem.
- (b) Study as a particular case a rigid motion and explore the connection with Galilei transformations.
- (c) Show that for an accelerating rigid motion the solution is unitarily equivalent to a motion in a gravitational field (equivalence principle).
- (d) For $x_L = 0$ fixed, reformulate the change of variables as a unitary scale transformation.

- (12.4) A free particle moves in a box, $[x_L, x_R]$. The boundary conditions are $\psi(x_L) = \psi(x_R) = 0$. The boundaries can move.
- (a) Give a formal solution as an expansion in adiabatic modes.
 - (b) Recover the case of rigid uniform translations as a Galilei transformation.
 - (c) Study the time dependence of the mean energy and mean momentum on a generic state.

- (d) Consider the case of oscillating walls and explore the possibility of resonances.
- (12.5) A particle moves in a box, $[0, L]$. Study the evolution of the states for a moving wall at $x = L$.

Generalize the problem to the case of both walls moving. Try to construct a self-consistent equation for the walls, defining a mass for them. Study the case of wall oscillations and associated selection rules.

Numerical analyses

- (12.1) Study the motion of a particle on a ring with non-periodic boundary conditions varying with time.
- (12.2) Study the motion of a particle in a box $[0, L]$, with L a function of time.
- (12.3) Integrate numerically Schrödinger's equation for a

Hamiltonian (the Landau-Zener effect):

$$H = \begin{pmatrix} E_1(t) & F \\ F^* & E_2(t) \end{pmatrix} :$$

with $E_1(t) = -vt/2$, $E_2(t) = +vt/2$.

13

Metastable states

In Nature various *metastable* states appear, i.e., states which, even though they behave like stationary states for a time duration longer than their characteristic periods of quantum motion, after much longer times make transitions to states in the continuum, i.e., decay. It suffices to think of all the excited states of atoms and molecules, or unstable nuclei, to realize the ubiquitous nature of the problem. Many examples of these processes have already been treated in the context of perturbation theory in Section 9.4; an analysis of a particle in external potentials has been made in the semi-classical approximation in Chapter 11.

In this chapter problems related to metastable systems are discussed in a more general way, and the methods for determining the decay width are given. To pave the way for our analysis we shall first discuss the Green function, already briefly treated in Section 8.1, more systematically, as an analytic function of the energy.

13.1 Green functions

The time evolution of the state is described by

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H|\psi(t)\rangle ; \quad |\psi(t)\rangle = U(t,t')|\psi(t')\rangle . \quad (13.1)$$

From eqn (13.1) it follows that $U(t,t')$ satisfies

$$i\hbar \frac{\partial}{\partial t} U(t,t') = H(t)U(t,t') , \quad U(t,t) = 1 , \quad (13.2)$$

and the convolution law

$$U(t,t_1)U(t_1,t_0) = U(t,t_0) ,$$

already noted in Section 8.1. We shall deal in the following with the time-independent Hamiltonian H . $U(t,t')$ has the well-known form

$$U(t,t') = e^{-iH(t-t')/\hbar} . \quad (13.3)$$

Only in very special cases is it possible to write down the explicit form of the Green function (13.3); it is thus of interest to study the general properties of $U(t)$. Let us first distinguish between the cases $t > t'$ and those in which $t < t'$, by introducing the operators

$$\mathcal{G}_+(t-t') = \theta(t-t')e^{-iH(t-t')/\hbar} ; \quad (13.4a)$$

$$\mathcal{G}_-(t-t') = -\theta(t'-t)e^{-iH(t-t')/\hbar} . \quad (13.4b)$$

13.1 Green functions	343
13.2 Metastable states	356
13.3 Examples	368
13.4 Complex scale transformations	370
13.5 Applications and examples	374
Further reading	379
Problems	379
Numerical analyses	379

The first is called the retarded Green function, and describes the evolution in the future direction, while the second is the advanced Green function. By using $\theta(x) + \theta(-x) = 1$ it follows that

$$U(t - t') = \mathcal{G}_+(t - t') - \mathcal{G}_-(t - t').$$

From $\frac{\partial}{\partial t} \theta(t - t') = \delta(t - t')$ and eqn (13.2) it follows that

$$\left(i\hbar \frac{\partial}{\partial t} - H \right) \mathcal{G}_{\pm}(t - t') = i\hbar \delta(t - t'). \quad (13.5)$$

These equations can be converted to integral equations. Let $H = H_0 + H_I$ be the decomposition of the Hamiltonian into the free Hamiltonian and the interaction Hamiltonian. By indicating with $\mathcal{G}_{0\pm}$ the free Green function H_0 ,

$$\mathcal{G}_{0\pm}(t - t') = \pm \theta(\pm(t - t')) e^{-iH_0(t-t')/\hbar},$$

one finds that

$$\mathcal{G}_{\pm}(t - t') = \mathcal{G}_{0\pm}(t - t') + \frac{1}{i\hbar} \int_{-\infty}^{\infty} dt_1 \mathcal{G}_{0\pm}(t - t_1) H_I \mathcal{G}_{\pm}(t_1 - t'). \quad (13.6)$$

Differentiating eqn (13.6) with respect to time one recovers constraint (13.5), as the reader can easily verify. Equations (13.5) and (13.6) can be solved by Fourier transform. Let us write

$$\mathcal{G}_{\pm}(t) = \frac{i}{2\pi} \int dE e^{-iEt/\hbar} G_{\pm}(E). \quad (13.7)$$

Using the integral representation of the delta function

$$\hbar \delta(t - t') = \delta((t - t')/\hbar) = \int_{-\infty}^{\infty} e^{-iE(t-t')/\hbar} \frac{dE}{2\pi},$$

we see that eqn (13.5) is transformed into an algebraic equation

$$(E - H) G_{\pm}(E) = 1. \quad (13.8)$$

Similarly, remembering that a convolution becomes a simple product under Fourier transform, the integral equation (13.6) becomes

$$G_{\pm}(E) = \mathcal{G}_{0\pm}(E) + \mathcal{G}_{0\pm}(E) H_I G_{\pm}(E). \quad (13.9)$$

In order to write the solution to this equation, we must decide how to treat the singularities, corresponding to the spectrum of E , i.e., the values for which $E - H$ has no inverse. To see how this can be fixed, let us write the inverse of eqn (13.7),

$$G_+(E) = \frac{1}{i\hbar} \int_{-\infty}^{+\infty} dt e^{iEt/\hbar} \mathcal{G}_+(t) = \frac{1}{i} \int_0^{\infty} \frac{dt}{\hbar} e^{iEt/\hbar} \mathcal{G}_+(t). \quad (13.10)$$

The possible divergences come from the region of $t \rightarrow \infty$ and can be regularized by adding a small positive imaginary part $i\varepsilon$ to E . Thus

$$\begin{aligned} G_+(E) &= \lim_{\varepsilon \rightarrow 0} \frac{1}{i\hbar} \int_0^\infty dt e^{i(E+i\varepsilon)t/\hbar} G_+(t) \\ &= \lim_{\varepsilon \rightarrow 0} \frac{1}{i\hbar} \int_0^\infty dt e^{i(E+i\varepsilon)t/\hbar} e^{-iHt/\hbar} = \lim_{\varepsilon \rightarrow 0} \frac{1}{E + i\varepsilon - H}. \end{aligned} \quad (13.11)$$

H is self-adjoint, and its spectrum is a subset of \mathbb{R} . This means that all the singularities of eqn (13.11) are of the type $E = \lambda_R - i\varepsilon$, i.e., they lie in the lower half-plane, $\text{Im}(E) < 0$. This fact ensures that $G_+(t) = 0$ for $t < 0$. Indeed, from eqn (13.7) it follows that

$$G_+(t) = \frac{i}{2\pi} \int dE e^{-iEt/\hbar} \frac{1}{E + i\varepsilon - H}.$$

For $t < 0$ the integral can be evaluated by closing the contour with a semi-circle in the upper half-plane E . In this region the real part of the exponent is $\text{Im}(E) \cdot t < 0$ for $t < 0$, so the contribution from the semi-circle is zero, and the integral vanishes by Cauchy's theorem.

One can analogously construct the advanced Green function. Together,

$$G_\pm(E) = \lim_{\varepsilon \rightarrow 0} \frac{1}{E \pm i\varepsilon - H}. \quad (13.12)$$

This result (13.12) is of fundamental importance and tells us that the two Green functions are the values at the boundary (on the real axis) of the *same* analytic expression, the resolvent

$$G(z) = \frac{1}{z - H}. \quad (13.13)$$

Integral equation (13.9) in this language can be rephrased as

$$\frac{1}{z - H} = \frac{1}{z - H_0} + \frac{1}{z - H_0} H_I \frac{1}{z - H},$$

and is a consequence of the identity

$$\frac{1}{A} = \frac{1}{B} + \frac{1}{B} (B - A) \frac{1}{A},$$

for $A = z - H$, $B = z - H_0$.

13.1.1 Analytic properties of the resolvent

The spectrum of H in general will have discrete and continuous portions. The discrete, isolated eigenvalues of H are the poles in z : the continuous spectrum corresponds to a cut in the complex plane z .

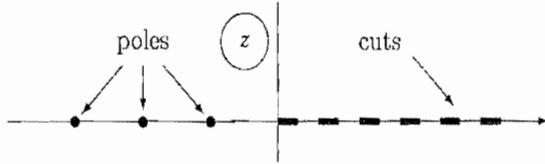


Fig.13.1

Figure 13.1 illustrates a case in which both isolated poles for $z < 0$ and a cut at $z > 0$ are present. The resolvent is analytic in the complex plane, outside the regions of the spectrum. In fact, let us consider a point in z which is distant from any point in the spectrum, at least for the distance d . Let us call $|\alpha\rangle$ an orthonormal basis of eigenvectors of H (which is in general improper basis), where α is a set of quantum numbers including the energy. Consider a state vector in the Hilbert space

$$|\psi\rangle = \sum_{\alpha} c_{\alpha} |\alpha\rangle.$$

We find, by using the orthonormality of the functions, that

$$|\langle\psi|G(z)|\psi\rangle| = \left| \sum_{\alpha} \frac{|c_{\alpha}|^2}{z - E_{\alpha}} \right| \leq \frac{1}{d} \sum_{\alpha} |c_{\alpha}|^2 = \frac{1}{d}.$$

The series is absolutely convergent so all the matrix elements of $G(z)$ are analytic functions. An analogous discussion is valid for non-diagonal elements as well. That is, $G(z)$ is analytic. To fix the idea, let us consider a generic state $|a\rangle$ and consider $\langle a|G(z)|a\rangle \equiv G_a(z)$: this is an ordinary function of the variable z . Suppose that H is limited from below (i.e., has a ground state); then certainly there will exist a half-line on the real axis on which $G_a(z)$ is real and analytic. By the known properties of the analytic functions (Schwarz's principle of analytic continuation), the function $G_a(z)$ is defined in the lower half-plane by

$$G_a(z^*) = [G_a(z)]^* ; \quad \text{Im}(z) > 0. \quad (13.14)$$

Let us now consider the behavior of $G_a(z)$ when z approaches one of the values in the spectrum of H . We let $z \rightarrow \mathbb{R}^+$, for instance, from the upper or lower parts of the complex plane. Equation (13.14) implies that in general, corresponding to the cut, the imaginary part of G suffers from a discontinuity:

$$2i \text{Im } G_a(E) \equiv \lim_{\varepsilon \rightarrow 0^+} [G_a(E + i\varepsilon) - G_a(E - i\varepsilon)] \neq 0; \quad E \in \mathbb{R}.$$

The analyticity of G_a allows us to write a *dispersion relation*. In fact, let us apply Cauchy's theorem with the closed contour shown in Figure 13.2

$$G_a(z) = \frac{1}{2\pi i} \oint_C dz' \frac{G_a(z')}{z' - z} = - \sum_n \frac{R_n}{E_n - z} + \frac{1}{\pi} \int_0^{\infty} dx \frac{\text{Im } G_a(x)}{x - z}. \quad (13.15)$$

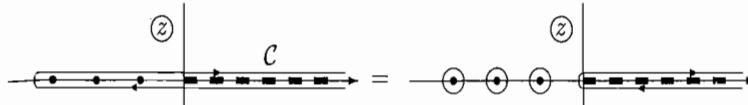


Fig.13.2

In the second equality we have deformed the integration path as in Figure 13.2, the sum is over the isolated discrete levels; R_n are the residues at the poles. The sign $(-)$ comes from the clockwise direction taken in the circle.

We could simplify the derivation of eqn (13.15) by using the distribution inside the integral. By using

$$\frac{1}{x + i\varepsilon} = \mathcal{P}\frac{1}{x} - i\pi\delta(x), \quad (13.16)$$

near the pole, as $\text{Im}(z') > 0$

$$G_a(z') \rightarrow \frac{R_n}{z' + i\varepsilon - E_n} \Rightarrow \text{Im } G_a(z')|_{\text{pole}} = -\pi R_n \delta(z' - E_n).$$

We can then write

$$-\sum_n \frac{R_n}{E_n - z} = \frac{1}{\pi} \int_{E_0}^0 dz' \frac{\text{Im } G_a(z')}{z' - z}.$$

E_0 is the minimum eigenvalue of H ; we thus have the general dispersion relation

$$G_a(z) = \frac{1}{\pi} \int_{E_0}^{\infty} dz' \frac{\text{Im } G_a(z')}{z' - z} = -\frac{1}{\pi} \int_{E_0}^{\infty} dz' \frac{\text{Im } G_a(z')}{z - z'} . \quad (13.17)$$

Equation (13.17) holds for any state $|a\rangle$, so is valid for the operator $G(z)$.

What are the meanings of the residue of the poles and of $\text{Im } G_a$? By using the spectral decomposition of H we can write

$$G(z) = \sum_i \frac{P_i}{z - E_i} + \int \frac{dE' P(E')}{z - E'} . \quad (13.18)$$

$P_n, P(E')dE'$ indicate symbolically the projectors on the subspace of energy E_n and E' , respectively. By comparing eqn (13.18) with eqn (13.15) and eqn (13.17) we find that

$$R_n = \langle a | P_n | a \rangle \geq 0; \quad -\frac{1}{\pi} \text{Im } G_a(E) = \langle a | P_E | a \rangle \geq 0 .$$

The inequality follows from the fact that it is the norm of the vectors projected onto the subspace corresponding to a fixed eigenvalue of H .

It is perhaps appropriate to make the notation more explicit. Let us choose a basis made of the eigenvectors of an operator which commutes with H . Let the discrete states be $|E_n, \alpha\rangle$, where α distinguishes possible degenerate states (for instance, states with different eigenvalues of L_z in the case of a particle

moving in a spherically symmetric potential). The states in the continuum are indicated by $|\lambda\rangle$. Because the basis is compatible with H (e.g., $|\lambda\rangle \rightarrow |\mathbf{p}\rangle$ for a free particle), $H|\lambda\rangle = E(\lambda)|\lambda\rangle$. The decomposition of the identity is given by

$$1 = \sum_n \sum_{\alpha} |E_n, \alpha\rangle \langle E_n, \alpha| + \int d\lambda |\lambda\rangle \rho(\lambda) \langle \lambda| .$$

The function $\rho(\lambda)$ depends on the normalization chosen for the states in the continuum and is defined such that

$$\left(\int d\lambda |\lambda\rangle \rho(\lambda) \langle \lambda| \right) |\lambda'\rangle = |\lambda'\rangle . \quad (13.19)$$

If $\langle \lambda | \lambda' \rangle = N(\lambda)\delta(\lambda - \lambda')$ then $\rho(\lambda) = 1/N(\lambda)$. The spectral decomposition of H is then:

$$H = \sum_n \sum_{\alpha} |E_n, \alpha\rangle E_n \langle E_n, \alpha| + \int d\lambda |\lambda\rangle \rho(\lambda) E(\lambda) \langle \lambda| ,$$

with the projectors

$$P_n = \sum_{\alpha} |E_n, \alpha\rangle \langle E_n, \alpha| ; \quad (13.20a)$$

$$P_E = \int d\lambda |\lambda\rangle \rho(\lambda) \delta(E - E(\lambda)) \langle \lambda| \equiv \int d\lambda |\lambda\rangle \rho_E(\lambda) \langle \lambda| . \quad (13.20b)$$

From eqn (13.20) it follows that

$$R_n = \sum_{\alpha} |\langle E_n, \alpha | a \rangle|^2 ; \quad -\frac{1}{\pi} \text{Im } G_a(E) = \int d\lambda \rho_E(\lambda) |\langle \lambda | a \rangle|^2 .$$

It is instructive to re-obtain the same result by proceeding inversely, i.e., from the definition of $\mathcal{G}_+(t)$. By using the same complete set of states we can write

$$\langle a | \mathcal{G}_+(t) | a \rangle = \sum_{n,\alpha} |\langle E_n, \alpha | a \rangle|^2 e^{-iE_n t/\hbar} + \int d\lambda \rho(\lambda) |\langle \lambda | a \rangle|^2 e^{-iE(\lambda)t/\hbar} ; \quad t \geq 0 .$$

By taking the Fourier transform, generalized to complex z with $\text{Im}(z) > 0$, one again obtains eqn (13.18):

$$G_a(z) = \frac{1}{i\hbar} \int_0^\infty dt e^{izt/\hbar} \langle a | \mathcal{G}_+(t) | a \rangle = \sum_{n,\alpha} \frac{|\langle E_n, \alpha | a \rangle|^2}{z - E_n} + \int d\lambda \rho(\lambda) \frac{|\langle \lambda | a \rangle|^2}{z - E(\lambda)} .$$

This analytic representation allows one to assert not only that $G_a(z)$ has no poles except for the spectrum of H , in the cut complex plane, but that in this region it has no zeros either. In fact, for $\text{Im } z > 0$, $z = u + iv$; $v > 0$ one has

$$\text{Im } G(z) = -\frac{|\langle E_n, \alpha | a \rangle|^2}{(u - E_n)^2 + v^2} v - \int d\lambda \rho(\lambda) \frac{|\langle \lambda | a \rangle|^2}{(u - E(\lambda))^2 + v^2} v < 0 . \quad (13.21)$$

Similarly, for $\text{Im } z < 0$ the imaginary part of $G(z)$ is strictly positive, and therefore $G(z)$ does not vanish. For $z \in \mathbb{R}$ and $z < E_0$, below the smallest eigenvalue of H , $\text{Re}(G)$ is negative definite, and G cannot vanish on that half-line either.

Let us stress an important point: as $\text{Im } G$ is a continuous function, eqn (13.21) implies that near the cut for $\text{Im } z > 0$ we have $\text{Im } G < 0$, so passing to the complex conjugate, one has $\text{Im } G > 0$ below the cut. That is, in the region $0 < \arg(z) < 2\pi$.

Lastly let us note that the very form of the spectral decomposition (13.18) allows us to express the projectors on the states of the discrete spectrum, isolated, in terms of $G(z)$. The discrete eigenvalues can be surrounded by small circles C_i , such that inside each circle there are no other singularities of $G(z)$. By applying Cauchy's theorem to each of these contours and using eqn (13.18) one gets:

$$P_i = \oint_{C_i} dz G(z) \quad (13.22)$$

13.1.2 Free particles

As an example consider the case of a free particle. In Section 8.1 we have calculated \mathcal{G} for a free particle in one dimension. In three dimension the result is

$$\mathcal{G}_+(t; \mathbf{x}, \mathbf{y}) = \left(\sqrt{\frac{m}{2i\hbar\pi t}} \right)^3 e^{im(\mathbf{x}-\mathbf{y})^2/2\hbar t}. \quad (13.23)$$

Let us obtain the same result by using the resolvent operator.

In the coordinate representation the resolvent $G(E)$ takes the form,

$$G(E; \mathbf{x}, \mathbf{y}) = \langle \mathbf{x} | \frac{1}{E + i\varepsilon - H_0} | \mathbf{y} \rangle.$$

By inserting a complete set of states $|\mathbf{p}\rangle$, which diagonalizes H_0 , we get

$$G(E; \mathbf{x}, \mathbf{y}) = \int \frac{d^3 \mathbf{p}}{(2\pi\hbar)^3} e^{i\mathbf{p}(\mathbf{x}-\mathbf{y})/\hbar} \frac{1}{E + i\varepsilon - \frac{\mathbf{p}^2}{2m}}.$$

The states are normalized as

$$\langle \mathbf{p} | \mathbf{p}' \rangle = (2\pi\hbar)^3 \delta^3(\mathbf{p} - \mathbf{p}'),$$

and this explains the factor $1/(2\pi\hbar)^3$ in the integral, see eqn (13.19). By setting $r = |\mathbf{x} - \mathbf{y}|$, the angular integration gives

$$\begin{aligned} G(E; \mathbf{x}, \mathbf{y}) &= \frac{1}{(2\pi\hbar)^3} 2\pi \int_0^\infty dp p^2 \int_0^\pi d\theta \sin\theta e^{ipr \cos\theta/\hbar} \frac{1}{E + i\varepsilon - \frac{p^2}{2m}} = \\ &= -\frac{1}{4\pi^2\hbar^2} \frac{1}{ir} \int_0^\infty dp p \left(e^{-ipr/\hbar} - e^{ipr/\hbar} \right) \frac{1}{E + i\varepsilon - \frac{p^2}{2m}} = \\ &= -\frac{1}{4\pi^2\hbar^2} \frac{1}{ir} \int_{-\infty}^{+\infty} dp p \frac{e^{ipr/\hbar}}{\frac{p^2}{2m} - (E + i\varepsilon)} \equiv G(E; r). \quad (13.24) \end{aligned}$$

A cut in the region $E \geq 0$ is evident. Let us calculate eqn (13.24) in two ways. Let us first consider the calculation in the region $E < 0$ and set $E = -\hbar^2\chi^2/2m$, $p = k'\hbar$:

$$G(E; r) = -\frac{2m}{4\pi^2\hbar^2} \frac{1}{ir} \int_{-\infty}^{+\infty} dk' k' \frac{e^{ik'r}}{k'^2 + \chi^2}.$$

The integral can be evaluated by using the method of residues, by encircling the integration contour with a large semi-circle in the upper

half-plane, $\text{Im } k' > 0$, where the integrand decreases exponentially. In this region the denominator develops a pole at $k' = +i\chi$; $\chi > 0$ and one has

$$G(E; r) = -\frac{m}{2\pi\hbar^2} \frac{e^{-\chi r}}{r} = -\frac{m}{2\pi\hbar^2} \frac{1}{r} \exp\left(-\frac{\sqrt{-2mE}}{\hbar} r\right). \quad (13.25)$$

The sign of the root in eqn (13.25) is fixed, the pole in $i\chi$ was the one in the upper half-plane, so $\chi > 0$. Normally one uses the variable

$$k = i \frac{1}{\hbar} \sqrt{-2mE}; \quad \frac{\hbar^2 k^2}{2m} = E; \quad G(E; \mathbf{x}, \mathbf{y}) = -\frac{m}{2\pi\hbar^2} \frac{e^{ikr}}{r}; \quad (13.26)$$

namely it represents an expanding spherical wave. The sign of the root in eqn (13.25) is again chosen in such a way that in the analytic continuation from $E > 0$ to $E < 0$ through the upper half-plane, that is $E \rightarrow E e^{i\pi}$, $ik \rightarrow i e^{i\pi/2} |k| = -|k|$, giving rise to an exponential decrease.

The convention of the phase is such that for $\arg(E) = 0$, i.e., along the real positive axis, $\arg(k) = 0$. In general,

$$\arg(E) = 2 \arg(k).$$

Therefore as the phase of k varies from 0 to π the first Riemann sheet $0 < E < 2\pi$ is covered, while when k is in the lower half-plane, the energy E is in the second Riemann sheet. On the lower tip of the cut, at $E \rightarrow e^{2\pi i} E$, that is, $k \rightarrow -k$, the propagator has the form of a contracting wave. Thus

$$\lim_{E \rightarrow |E| \pm i\epsilon} G(E; r) = -\frac{m}{2\pi\hbar^2} \frac{e^{\pm i|k|r}}{r}, \quad (13.27)$$

confirming eqn (13.14).

The second method directly uses the definition (13.24) for $E > 0$; in this way the significance of the “ ϵ -prescription” is better appreciated. Writing $E = \hbar k^2 / 2m$ and $p = \hbar k'$, we get

$$G(E; r) = -\frac{2m}{4\pi^2\hbar^2} \frac{1}{ir} \int_{-\infty}^{+\infty} dk' k' \frac{e^{ik'r}}{k'^2 - k^2 - i\epsilon}$$

By closing the integration contour in the upper half-plane, one encircles the pole,

$$+\sqrt{k^2 + i\epsilon} \rightarrow +k + i\epsilon; \quad k > 0,$$

and the residue theorem gives

$$G(E; r) = -\frac{m}{2\pi\hbar^2} \frac{e^{ikr}}{r}, \quad k = \frac{\sqrt{2mE}}{\hbar}.$$

This second method clarifies the meaning of the ϵ prescription and of the particular solution of eqn (13.8). In the coordinate representation this equation becomes

$$(k^2 + \nabla^2) G(\mathbf{x}, \mathbf{y}) = \frac{2m}{\hbar^2} \delta^3(\mathbf{x} - \mathbf{y}).$$

From eqn (13.27) the discontinuity across the cut is given by

$$2i \operatorname{Im} G(E; r) = -\frac{m}{2\pi\hbar^2} \frac{1}{r} (e^{ikr} - e^{-ikr}) \Rightarrow \operatorname{Im} G(E; r) = -\frac{m}{2\pi\hbar^2} \frac{\sin kr}{r}.$$

By changing the variable to $E' = p^2/2m$ in the second of eqns (13.24) one obtains

$$G(E; r) = -\frac{m}{2\pi^2\hbar^2} \frac{1}{r} \int_0^\infty dE' \frac{\sin k'r}{E' - E} = \frac{1}{\pi} \int_0^\infty dE' \frac{\operatorname{Im} G(E'; r)}{E' - E},$$

confirming eqn (13.17).

13.1.3 The free Green function in general dimensions

In any dimension the invariance under translations and under space rotations imposes on the Green function the condition that the dependence on the position be of the form

$$\langle \mathbf{x}|G|\mathbf{y}\rangle = G(\mathbf{x}; \mathbf{y}) = G(|\mathbf{x} - \mathbf{y}|) \equiv G(r).$$

In one dimension

$$\left(\frac{d^2}{dx^2} + k^2 \right) G = \frac{2m}{\hbar^2} \delta(x); \quad E = \frac{\hbar^2 k^2}{2m}. \quad (13.28)$$

By using the identity

$$\frac{d}{dx}|x| = \epsilon(x); \quad \frac{d}{dx}\epsilon(x) = 2\delta(x),$$

($\epsilon(x) = \pm 1$ according to the sign of x), one verifies immediately that

$$G(E, x) = \frac{m}{i\hbar^2 k} e^{ik|x|}, \quad k = \frac{\sqrt{2mE}}{\hbar}; \quad d = 1 \quad (13.29)$$

satisfies eqn (13.28) and represents the “expanding wave”.

In two dimensions the equation for G is, in radial coordinates,

$$\frac{1}{r} \frac{d}{dr} r \frac{d}{dr} G + k^2 G = \frac{2m}{\hbar^2} \delta^{(2)}(\mathbf{x}). \quad (13.30)$$

By changing the variable to $kr = z$, we see that eqn (13.30) for $\mathbf{x} \neq 0$ becomes

$$G'' + \frac{1}{z} G + G = 0,$$

which is Bessel's equation of zeroth order. The combination, which behaves as an expanding wave, is the Hankel function of the first kind,

$$H_0^{(1)}(z) = J_0(z) + iY_0(z); \quad H_0^{(1)}(z) \simeq \begin{cases} \frac{2i}{\pi} \log(z) & z \rightarrow 0 \\ \sqrt{\frac{2}{i\pi z}} e^{iz} & z \rightarrow \infty \end{cases} \quad (13.31)$$

By applying Gauss' theorem,

$$\int_D d^2x \nabla^2 f = \oint_{\partial D} \mathbf{n} \cdot \nabla f ,$$

to the small circle around the origin to the function $\log(r)$, one has

$$\int d^2x \nabla^2 \log(r) = \int d\varphi r \frac{\partial}{\partial r} \log(r) = 2\pi .$$

To have the correct singularity (13.30) the short-distance behavior must be such that

$$\frac{2m}{\hbar^2} \frac{1}{2\pi} \log(r) .$$

From eqn (13.31) it then follows that

$$G(r) = \frac{2m}{\hbar^2} \frac{1}{4i} H_0^{(1)}(kr) ; \quad d = 2 . \quad (13.32)$$

In general dimensions (d), one has

$$G(E, r) = \frac{1}{i} \frac{2m}{\hbar^2} \frac{k^{d-2}}{\pi^{\frac{d}{2}-1} 2^{\frac{d}{2}+1}} (kr)^{1-\frac{d}{2}} H_{\frac{d}{2}-1}^{(1)}(kr) .$$

See Problem 13.2.

13.1.4 Expansion in powers of H_I

The form of the eqn (13.9) allows one to find a formal perturbative expansion in H_I . We can in fact write a sequence $G^{(n)}$ of approximants, with $G^{(0)} = G_0$ and solving eqn (13.9) iteratively,

$$G^{(n+1)} = G_0 + G_0 H_I G^{(n)} , \quad (13.33)$$

obtaining

$$G^{(1)} = G_0 + G_0 H_I G_0 ; \quad G^{(2)} = G_0 + G_0 H_I G_0 + G_0 H_I G_0 H_I G_0 ; \quad \dots \quad (13.34)$$

It is instructive to think of eqn (13.34) in terms of graphs. If the propagator G_0 is represented by a line and H_I by a circle, the series has the form

$$G = \text{---} + \text{---} \bigcirc \text{---} + \text{---} \bigcirc \text{---} \bigcirc \text{---} + \dots$$

The product of Fourier transforms corresponds to a convolution in the time variables, so the figure can be interpreted in terms of physical processes. Let us recall in fact that we are using the retarded Green function so that a term such as

$$\int \mathcal{G}_0(t - t_1) H_I \mathcal{G}_0(t_1 - t_2) H_I \mathcal{G}_0(t_2 - t_3)$$

implies that $t \geq t_1 \geq t_2 \dots$ and it can be interpreted as the particle freely propagating to a point, interacting, and again freely propagating, and so on.

Let us study the evolution of an eigenstate $|a\rangle$ of H_0 . To second order, by inserting the complete set of states, we have for $G(E)|a\rangle$ a term of the type

$$\frac{1}{E - E_n} |n\rangle \langle n| H_I |m\rangle \frac{1}{E - E_m} \langle m| H_I |a\rangle \frac{1}{E - E_a} . \quad (13.35)$$

To each graph there corresponds an amplitude in which the state passes to (virtual) intermediate states of H_0 . Clearly the amplitude from an initial state to a final state is given by the sum of all possible amplitudes.

Let us now consider a concrete problem, e.g. bound states of a system. They correspond to the poles of the resolvent. On the other hand, we have a procedure to calculate the discrete eigenvalues of H perturbatively (Chapter 9): do they give a consistent answer? In other words, can one recover the perturbation series from eqn (13.33)? Equation (13.35) shows a possible problem, and at the same time, its resolution. If one seeks for a value of E near E_0 , one sees that in the sum (13.35) there appear "large" terms, when the intermediate states have energy E_a , i.e., when $|n\rangle = |a\rangle$ for a non-degenerate system, and the terms of the order of $H_I/\Delta E$, in other cases. This is due to the fact that G_0 lets all the states propagate. In order to identify the (small) perturbative correction in the background of these large corrections due to the propagation of the initial state, one has to re-sum these large terms exactly first, and then treat the rest as perturbation. One knows how to isolate the specific terms: we use projection operators. We do not know the projectors which commute with H : otherwise we would be able to solve the problem exactly; but we do know the projectors commuting with H_0 , because by assumption this system can be treated exactly.

Anticipating an important application in the next section we may formulate the question as follows. Suppose we know a linear subspace \mathcal{V} of the eigenstates of H_0 , which is not necessarily one dimensional (so we allow for possible degeneracies). Let P be the projection operator on this subspace, and Q its complement,

$$P + Q = 1 ; \quad PQ = 0 ; \quad QP = 0 .$$

P, Q commute with H_0 and therefore with G_0 ; that is,

$$G_0 = (Q + P)G_0(Q + P) = QG_0Q + PG_0P ,$$

namely we can separate the propagation of the states belonging to \mathcal{V} from the rest. Graphically this means that each line (propagator) splits into two, one describing the states in \mathcal{V} , the other the remaining states:

$$PG_0P = \text{———} \quad QG_0Q = \text{---} \quad H_I = \text{○}$$

Similarly one can consider the amplitude for remaining in the same manifold or for going out of it, starting from a state of \mathcal{V} ,

$$GP = PGP + QGP .$$

It is clearly possible to reorganize the perturbative series as:

$$PGP = \text{---} + \text{---} \bullet \text{---} + \text{---} \bullet \text{---} \bullet \text{---} + \dots$$

where a black circle, indicated by $R(z)$ contains an arbitrary number of the dashed propagators,

$$R = \bullet = \circlearrowleft + \circlearrowleft \circlearrowright - \circlearrowleft \circlearrowright + \circlearrowleft \circlearrowright - \circlearrowleft \circlearrowright - \circlearrowleft \circlearrowright + \dots$$

R is called the *mass matrix*, or *self-energy* in field theory.

Such a rearrangement of terms is a standard procedure in quantum field theory (quantum theory of elementary particles). Formally,

$$R(z) = H_I + H_I Q G_0 Q H_I + H_I Q G_0 Q H_I Q G_0 Q H_I + \dots \quad (13.36)$$

The power series in R is a simple geometric one,

$$PG_0P + PG_0P(PRP)PG_0P + PG_0P(PRP)PG_0P(PRP)PG_0P + \dots$$

so can be readily re-summed. The same can be done for the term QGP , and the final result is

$$G(z)P = \left\{ P + \frac{Q}{z - H_0} R(z) \right\} \frac{P}{z - PH_0P - PR(z)P} . \quad (13.37)$$

The definition holds in the upper half-plane $\text{Im } z > 0$ and can be analytically continued to the lower half-plane, avoiding the cut, according to eqn (13.14). In particular,

$$[R(z)]^\dagger = R(z^*) ,$$

as can be verified from eqn (13.36) also, taking into account the fact that H_0, H_I, Q are Hermitian operators.

The operator R satisfies an important relation, which is a consequence of unitarity. By writing $G_0^Q = QG_0Q$, one sees that it follows from eqn (13.36) that

$$R(z) = H_I + H_I G_0^Q(z) R(z) , \quad (13.38)$$

that is, since H_I is self-adjoint

$$H_I = R(z) - H_I G_0^Q(z) R(z) ; \quad H_I = R^\dagger(z) - R^\dagger(z) (G_0^Q)^\dagger(z) H_I .$$

Let us now write $R - R^\dagger$ using eqn (13.38) and substituting for H_I by the second and the first relation respectively:

$$\begin{aligned} R(z) - R^\dagger(z) &= (R^\dagger - R^\dagger(G_0^Q)^\dagger H_I) G_0^Q R - R^\dagger(G_0^Q)^\dagger (R - H_I G_0^Q R) = \\ &= R^\dagger \left(G_0^Q - (G_0^Q)^\dagger \right) R . \end{aligned}$$

Letting z approach the real axis from above, i.e., $z = E + i\varepsilon$, one has:

$$2i \operatorname{Im} R(E) = R(E+i\varepsilon) - R(E-i\varepsilon) = -2\pi i R^\dagger Q \delta(E-H_0) QR ; \quad E \in \mathbb{R}. \quad (13.39)$$

Equation (13.37) allows us to recover the result of perturbation theory for the discrete spectrum. Let P be the projection operator for the subspace of the eigenstates of H_0 with eigenvalue E_0 , our subspace \mathcal{V} in this case. In the spirit of perturbation theory, one can assume that for sufficiently small perturbation the exact eigenvalue is close to E_0 . Thus for a discrete spectrum the second term in the bracket of eqn (13.37) has no poles for $E \sim E_0$, in fact, the presence of the projector Q ensures that in the intermediate states only the states not belonging to \mathcal{V} appear. The eigenvalues of H are the poles of $G(z)$ and we can isolate a pole near E_a by making a contour integration around it. The only term which can have a pole in this region is the last one in eqn (13.37), so the exact eigenvalues are the roots of the equation

$$E - PH_0P - PR(E)P = 0. \quad (13.40)$$

Equation (13.40) is an algebraic equation in the subspace of dimension $\dim(\mathcal{V})$ selected out by P , the singular points correspond to the zero eigenvalues of the matrix

$$\det [E \delta_{\alpha\beta} - \langle \alpha | (PH_0P + PR(E)P) | \beta \rangle] = 0, \quad (13.41)$$

α, β indicating an orthonormal basis of \mathcal{V} .

In the case where there is no degeneracy in the unperturbed system, one finds that

First order: $E - E_a - \langle a | H_I | a \rangle = 0$;

$$\begin{aligned} \text{Second order: } 0 &= E - E_a - \langle a | H_I | a \rangle - \sum_{n \neq 0} \langle 0 | H_I | n \rangle \frac{1}{E - E_n} \langle n | H_I | a \rangle \\ &\simeq E - E_a - \langle a | H_I | a \rangle - \sum_{n \neq a} \langle a | H_I | n \rangle \frac{1}{E_a - E_n} \langle n | H_I | a \rangle. \end{aligned}$$

Thus one recovers the well-known perturbative expansion for the eigenvalues. In the degenerate case, condition (13.41) corresponds to the diagonalization, order by order, of the perturbation in the subspace \mathcal{V} .

As for the eigenvectors, we recall that by the spectral decomposition (13.18) the residue of the pole of the resolvent is the projector on the kernel of $(H - E_i)$, so if \bar{E} is a solution of eqn (13.41),

$$\left\{ P + \frac{Q}{E - H_0 + i\varepsilon} R(E) \right\}_{E=\bar{E}} |a\rangle \quad (13.42)$$

is proportional to the eigenvector. The normalization of eqn (13.42) is just the one used in our treatment of perturbation theory (Section 9.1): the projector on the eigenvector $|a\rangle$ is 1 and the expansion is of the form

$$|\psi\rangle = |a\rangle + \frac{Q}{\bar{E} - H_0 + i\varepsilon} R(\bar{E})|a\rangle.$$

We leave the reader to verify that order by order this reproduces our earlier results.

13.2 Metastable states

Strictly speaking, few physical systems are truly stable. It suffices to think of all excited states of atoms, all of the radioactive nuclei, unstable molecules: none of them are truly stationary and their proper definition would require some physical process in which these states are “produced” or “prepared”. In laboratories and in Nature this happens usually through some scattering processes; for instance under the bombardment of an electron beam or under the effect of external radiation the hydrogen atom gets excited to the states $2p$, to $2s$ and so on. Furthermore, only if the system remains for a sufficiently long time (say, τ) in the same state can one talk about the properties of such a state, its quantum numbers, etc. As the typical time scale of the system involved is of the order of \hbar/E , where E is the energy or the energy difference between the levels. We shall therefore require the condition $\tau \gg \hbar/E$ for such a metastable state can be defined unambiguously. The quantity $1/\tau$ characterizes the probability per unit time for the decay, and if we write $1/\tau = \Gamma/\hbar$, Γ has the dimension of the energy. For reasons which will become clear in the following, Γ is called the *width* of the level. The above-mentioned condition is then

$$\Gamma \ll E. \quad (13.43)$$

13.2.1 Formulation of the problem

Let us consider the following situation: the system is composed of two parts, described by the Hamiltonians H_A, H_B , respectively. Suppose that in the absence of interactions, the Hamiltonian is simply $H_0 = H_A + H_B$: let us suppose that this Hamiltonian has a discrete spectrum, with eigenvalues $E_A + E_B$. Let H_I be the interaction between the two systems. This interactions in general cause some distortion of the spectrum. The question is: do the stationary states of H_0 still make part of the discrete spectrum of H ? Or more generally, if the state in the absence of interactions H_I consists of a discrete eigenstate of H_A and an eigenstate (not necessarily discrete) of H_B , what are the characteristics of the system once the interactions are turned on?

The emphasis on the discrete spectrum reflects the fact that the corresponding states are normalizable, i.e., they are bound states. The question is therefore whether such a state survives the interactions. If the unperturbed level $E_A + E_B$ is an isolated eigenstate of H_0 we expect for continuity that the eigenvalue and the eigenfunction will have a small corrections. It is a typical situation, for instance, for an excited level of an atom. In the zeroth-order approximation we can neglect interactions among the electrons and have the atomic levels in the Coulomb potential of the nucleus. The perturbations lift the degeneracy, and shift the energy levels.

The second case is the one in which the unperturbed eigenstate is normalized but the eigenvalue of H_0 in question is not isolated but immersed in the continuum. In this case it is easy to imagine that even

a tiny perturbation will cause the mixing with the continuum. Suppose that the system has a characteristic dimension $r \sim a$, and that the normalized eigenstates have space extension in this region, essentially. The states in the continuum on the other hand are not confined in such a region; in a first approximation they can be thought to be free waves. Once mixed, the state will have the form

$$|0\rangle + \alpha|c\rangle, \quad |c\rangle \in \text{continuum spectrum} \quad \Rightarrow \quad |c(t)\rangle \sim e^{i(\mathbf{k}x-Et)}.$$

A free particle has a time evolution similar to that of a plane wave, and describes an unconstrained motion: this means that the perturbation has caused a decay of the bound state, and in particular introduces an *irreversibility* in the process.¹.

The interactions H_I cause the system to decay with a mean lifetime $\frac{\hbar}{\Gamma}$. Such an effect is in addition to the usual effect of perturbation: a shift in energy ΔE . A “metastable state” thus has an energy $E_0 + \Delta E$ and a mean lifetime $\frac{\hbar}{\Gamma}$. These concepts are well defined so long as the perturbation H_I only changes the unperturbed state a little: it is then natural to require that

$$\Delta E \ll E, \quad (13.44)$$

besides eqn (13.43).

Examples

Let us discuss a few concrete examples.

- (1) System *A* is an atom, say, a hydrogen atom, to be concrete, with the Hamiltonian H_A . System *B* is the electromagnetic radiation, with the Hamiltonian, H_B . The unperturbed level is specified by assigning the atomic level and the wave number and the multiplicity of the photons (for simplicity we neglect the polarization). $|A; (n_1, \mathbf{k}_1; n_2, \mathbf{k}_2 \dots)\rangle$ represents a state in which the atom is in the state *A* and there are n_1 photons with frequency ω_1 , n_2 photons with frequency, ω_2 etc.

Let us consider the atom in an excited state, $2p$, in the absence of external photons. The energy level is $E_0 = E_{2p}$. Immersed in the continuum of states with the photons (with the direction of \mathbf{k} arbitrary) this level is infinitely degenerate with all the states of the form $|1s, (\mathbf{k}), \mathbf{k}\rangle$, \mathbf{k} is the wave vector with $\hbar c |\mathbf{k}| = \hbar \omega = E_{2p} - E_{1s}$. The interactions will cause the decay of the level, and produce a state in which the atom is in the ground state $1s$ and the photon travels away: this is the spontaneous decay.

In the case under consideration the spectrum of $H_0 = H_A + H_B$ has the lower tip $E = E_g < 0$ which is the ground state energy of the atom, and extends to infinity. There are no isolated levels. For instance, the system composed of the atom in the ground states $1s$ together with a photon of the energy $\hbar \omega$ has the energy arbitrarily close to E_{1s} for $\omega \rightarrow 0$. The usual “bound state atomic states” refer to the atoms without the photons. These states are normalizable and appear as the poles in the Green function, overlapping with the continuous spectrum.

¹This situation must be compared to the well-known case of the discrete spectrum, such as the Rabi oscillation considered in Chapter 9.

- (2) Consider a nucleus of charge $Z = 2$ and two electrons, neglecting the interactions between the latter. This is a zeroth-order approximation of a helium atom. The corresponding levels have the energy

$$E_{n,m} = -\frac{Z^2}{2} \left(\frac{1}{n^2} + \frac{1}{m^2} \right).$$

The continuous spectrum of this system has a minimum energy corresponding to the ionized electron and an electron in the state $1s$, that is

$$E_c = -\frac{Z^2}{2}.$$

Let us consider a state of the type $|2s, 2s\rangle$: it has energy

$$E_{2s,2s} = -\frac{Z^2}{2} \left(\frac{1}{4} + \frac{1}{4} \right) > -\frac{Z^2}{2} \cdot \frac{1}{2} > E_c.$$

This state is therefore immersed in the continuum. The presence of H_I will cause this state to decay, with the final state consisting of the atom with one electron in the $1s$ or $2s$ level and a free electron. This is the process of *self-ionization*.

In the following paragraph we shall see how the processes of this type can be described by using the resolvent $G(E)$. Let us anticipate the result.

Result: In the presence of H_I the pole on the real axis migrates into the second Riemann sheet, to the position $E_R - i\Gamma/2$. Such a state is called a metastable state or resonance. Γ represents the probability of decay per unit interval of time (in the unit $\hbar = 1$). The distribution in the energy of the decay product is a Lorentzian distribution with width Γ .

13.2.2 The width of a metastable state; the mean half-lifetime

To introduce the problem consider a non-degenerate eigenstate $|a\rangle$ of H_0 . According to eqns (13.7) and (13.37) the amplitude for finding the state $|a\rangle$ at time t (the *survival amplitude*) is given by

$$A(t) = \lim_{\varepsilon \rightarrow 0} \frac{i}{2\pi} \int_{-\infty}^{+\infty} dE e^{-iEt/\hbar} \frac{1}{E + i\varepsilon - E_a - R_a(E + i\varepsilon)}, \quad (13.45)$$

with $R_a(E) \equiv \langle a | R(E) | a \rangle$. Let us decompose the function $R_a(E)$ into the real and imaginary parts,

$$\lim_{\varepsilon \rightarrow 0} R_a(E + i\varepsilon) = F_R(E) - i \frac{1}{2} F_I(E).$$

From eqn (13.39) one knows that

$$\begin{aligned} F_I(E) &= -2\text{Im } R(E) = 2\pi \langle a | R^\dagger Q \delta(E - H_0) QR | a \rangle \\ &= \sum_{s \neq a} \delta(E - E_s) |\langle s | R | a \rangle|^2 \geq 0 . \end{aligned}$$

The sum, by virtue of the projector Q , is over all eigenstates of H_0 different from $|a\rangle$.

Integration in eqn (13.45) is dominated by the region of E in which the denominator is small, and would have a pole at $E = E_a$ in the absence of the perturbation. Let us suppose that the interactions are weak, with H_I proportional to λ , with $\lambda \ll 1$. In this situation, if $|R_a|$ is a bounded function and for sufficiently small λ the terms F_R, F_I gives a small contribution in the region $E \sim E_a$, while outside this region the whole integral is small, and therefore one can write

$$E - E_a - \left(F_R(E) - i\frac{1}{2}F_I(E) \right) \simeq E - E_a - F_R(E_a) + \frac{i}{2}F_I(E_a) ,$$

approximately. By writing

$$\Delta E = F_R(E_a); \quad \Gamma = F_I(E_a) ,$$

we see that the effect of the interactions has been that of shifting the pole of the integrand to $E_a + \Delta E - i\Gamma/2$. In this approximation integral (13.45) can be evaluated immediately by closing the integration contour in the half-plane $\text{Im}(E) < 0$, for $t > 0$, giving

$$A(t) = e^{-i(E_a + \Delta E)t/\hbar} e^{-\Gamma t/2\hbar}; \quad P(t) = |A(t)|^2 = e^{-\Gamma t/\hbar} .$$

Thus the state $|a\rangle$ becomes *metastable*, with half-lifetime \hbar/Γ and with energy $E_a + \Delta E$.

As for the propagator, one has, in this approximation,

$$\langle a | G(E) | a \rangle = G_a(E) = \frac{1}{E - E_R + i\frac{\Gamma}{2}}; \quad E_R = E_a + \Delta E .$$

Note that

$$\text{Im } G_a(E) = -\frac{\Gamma/2}{(E - E_R)^2 + \Gamma^2/4} ,$$

and from eqn (13.15) that

$$G_a(E) = \frac{1}{\pi} \int_{E_c} dE' \frac{1}{E - E'} \frac{\Gamma/2}{(E' - E_R)^2 + \Gamma^2/4} . \quad (13.46)$$

In the approximation in which we are working the integration limits have not much importance, the integral being dominated by the region of the width Γ around E_R .

Let us now consider the problem from the point of view of the exact Hamiltonian. Suppose for simplicity that the eigenstates of H are of the

form, $|E, \alpha\rangle$ with α labeling the degenerate states, and normalized as $\langle E', \alpha'|E, \alpha\rangle = \delta(E - E')\delta_{\alpha\alpha'}$. Then from (E_g being the ground state energy)

$$|a\rangle = \int_{E_g} dE \sum_{\alpha} c_{\alpha}(E) |E, \alpha\rangle; \quad (13.47a)$$

$$|a(t)\rangle = \int dE \sum_{\alpha} c_{\alpha}(E) |E, \alpha\rangle e^{-iEt/\hbar}; \quad (13.47b)$$

it follows that

$$\mathcal{U}(t) = \langle a|a(t)\rangle = \int_{E_g} dE \sum_{\alpha} |c_{\alpha}(E)|^2 e^{-iEt/\hbar}. \quad (13.48)$$

The function $\mathcal{U}(t)$ is defined for each t and coincides with $\mathcal{A}(t)$ for $t > 0$. We cannot compare this equation directly with eqn (13.45): in the latter E is an integration variable in $-\infty$ a $+\infty$ and the pole approximation refers to this variable. In fact the exponential behavior has been obtained by considering a closed contour. The same cannot be done if the integral is to be done over an interval as in eqn (13.48). In order to calculate $\langle a|G(E)|a\rangle$, one can start from eqn (13.48), making the Fourier transform

$$G_a(E) = \lim_{\epsilon \rightarrow 0} \frac{1}{i\hbar} \int_0^{\infty} e^{i(E+i\epsilon)t/\hbar} A(t) = \int_{E_g} dE' \frac{1}{E - E'} \sum_{\alpha} |c_{\alpha}(E')|^2. \quad (13.49)$$

Now the exact expression (13.49) and the approximate one (13.46) have the same form (the lower limit of (13.46) can be modified without changing the approximation), so one obtains

$$\sum_{\alpha} |c_{\alpha}(E)|^2 = \frac{1}{\pi} \frac{\Gamma/2}{(E - E_R)^2 + \Gamma^2/4}. \quad (13.50)$$

This result illustrates well the physical mechanism underlying the description of metastable states. In the absence of interactions $|a\rangle$ is a discrete eigenstate of H_0 . Suppose that the spectrum of H is continuous: eqn (13.47) indicates how the discrete state has disintegrated into a superposition of eigenstates if H , and eqn (13.50) shows that the distribution of these states is a Lorentzian, centered around E_R and with width Γ . Only these states interfere positively to form the time evolution of $|a\rangle$. A crucial aspect is that the probability distribution (13.50) is correctly normalized, i.e.,

$$\int_{E_g} dE \sum_{\alpha} |c_{\alpha}(E)|^2 \simeq \int_{-\infty}^{+\infty} dE \frac{1}{\pi} \frac{\Gamma/2}{(E - E_R)^2 + \Gamma^2/4} = 1.$$

We have not “lost” states: the superposition found is, in the pole approximation, a complete set of states describing the evolution.

Let us note for future reference that using $E \rightarrow E + i\varepsilon$ in eqn (13.49) and

$$\frac{1}{x + i\varepsilon} = \mathcal{P} \frac{1}{x} - i\pi\delta(x)$$

we have

$$\text{Im}[G_a(E)] = -\pi \sum_{\alpha} |c_{\alpha}(E)|^2,$$

and the projection of the evolution operator $\mathcal{U}(t)$ in eqn (13.48) can be written as

$$\mathcal{U}(t) = -\frac{1}{\pi} \int_{E_g} dE \text{Im}[G_a(E)] e^{-iEt/\hbar}. \quad (13.51)$$

The slightly more general treatment of the next section will generalize the result more or less obviously to the case of initial degenerate states, but above all, will clarify the analytic structure ruling the position of the poles in the propagator.

13.2.3 Formal treatment

Let \mathcal{V} be the space spanned by the normalizable states of H_0 whose time evolution is our interest. \mathcal{V} can represent a degenerate state, as in the case of the $2p$ level of the hydrogen atom. Let us indicate by P the projector on this space and with $|\chi_{\alpha}\rangle$ the states in this space. Let us study how the state $|\chi_{\alpha}\rangle$ evolves, by asking what the amplitude for finding the same state at time t is.

According to the general rule of quantum mechanics, the amplitude for finding a state in the same manifold of states, $\chi_{\alpha'}$, is

$$\langle \chi_{\alpha'} | \mathcal{G}(t) | \chi_{\alpha} \rangle \equiv A_{\alpha'\alpha}(t).$$

Going to the Fourier transform and recalling that $\chi_{\alpha} \in \mathcal{V}$ we can write

$$A_{\alpha'\alpha}(t) = \frac{i}{2\pi} \int_{-\infty}^{\infty} dE e^{-iEt/\hbar} \langle \chi_{\alpha'} | PG(E) P | \chi_{\alpha} \rangle.$$

This integral is done by the prescription $E \rightarrow E + i\varepsilon$ and taking the limit $\varepsilon \rightarrow 0$. By using eqn (13.37) we can write

$$A_{\alpha'\alpha}(t) = \frac{1}{2\pi i} \int_{+\infty}^{-\infty} dz e^{-izt/\hbar} \langle \alpha' | \frac{1}{z - PH_0 P - PR(z)P} | \alpha \rangle. \quad (13.52)$$

To evaluate eqn (13.52) one can transform the integral by closing the contour at infinity and by using Cauchy's theorem. For $t > 0$ the contour must be closed in the region $\text{Im } z < 0$. As the original path was running above the cut, the closing of the contour necessarily occurs in the second Riemann sheet.

Let us suppose that the spectrum of H is made of a cut for $E > E_g$ (this is the most important case of radiative decay). We can close the contour as indicated in Figure 13.3.

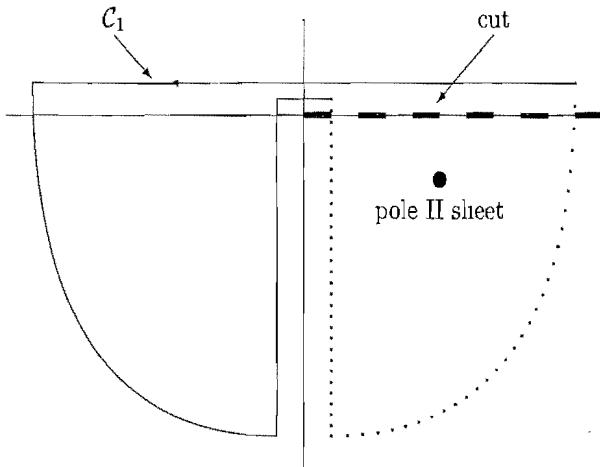


Fig.13.3

The amplitude in eqn (13.52) is defined along the straight path C_1 , the part shown by a dashed line is in the second sheet.

Let us suppose that $G(z)$ has a pole in this sheet, at $\bar{z} = E_R - i\Gamma/2$, and for simplicity let us take the case of an initial non-degenerate state. In this case there is only one state $|\alpha\rangle$ and by applying the residue theorem we get

$$A_{\alpha\alpha}(t) + T_{\alpha\alpha} = e^{-i\bar{z}t/\hbar} = e^{-\frac{\Gamma}{2}t/\hbar - iE_R t/\hbar}. \quad (13.53)$$

$T_{\alpha\alpha}$ is the contribution from the vertical part of the contour in Figure 13.3 (which we shall call the contribution of the continuum).

In the majority of interesting cases the contribution $T_{\alpha'\alpha}$ is negligible, as we shall see, and so the pole is dominant and eqn (13.53) gives the survival probability

$$P_{\alpha\alpha} = e^{-\Gamma t/\hbar}. \quad (13.54)$$

In the general case a singularity of the propagator means that a zero appears in the denominator of eqn (13.52); the singular points in the matrix correspond to the roots of the determinant,

$$\det(z - E_0 - R_{\alpha'\alpha}(\bar{z})) = 0.$$

The matrix of dimension $\dim(\mathcal{V})$, $PR(\bar{z})P$ can be diagonalized. The states thus defined take the name of *decay eigenstates*; they will be indicated by $|\chi\rangle$ (they are linear combinations of the states in \mathcal{V}). In the subspace \mathcal{V} the states evolve according to an effective Hamiltonian

$$H_{\text{eff}} = PH_0P + PR(\bar{z})P = E_0 + \bar{R}_{\alpha'\alpha},$$

and the decay eigenstates are just the eigenstates of H_{eff} :

$$H_{\text{eff}}|\chi\rangle = \left(E_R - i\frac{\Gamma}{2}\right)|\chi\rangle.$$

Let us stress that H_{eff} is not Hermitian. The states $|\chi\rangle$ are those for which the energy and mean lifetime are defined, in the sense of eqn (13.54):

$$A_{\chi\chi}(t) = e^{-iE_R t/\hbar - \frac{\Gamma}{2} t/\hbar}; \quad P_{\chi\chi}(t) = e^{-\Gamma t/\hbar}. \quad (13.55)$$

Γ is known as the *width* of the state, the quantity \hbar/Γ the *half-lifetime*. In general E_R , the real part of the eigenvalue, will be different from E_0 , as the perturbation gives rise to the decay width *and* the shift in energy $\Delta E = E_R - E_0$.

The consistency of the construction requires that $\Gamma > 0$, and this is consistent with the property $P_{\chi\chi}(t) \leq 1$.

Remarks

- For $\Gamma > 0$ eqn (13.52) is not singular. For $\text{Im } z > 0$, in fact, $z - \bar{z} = z - E_R + i\Gamma/2$ has a non-vanishing imaginary part. In the lower half-plane, which can be reached by going round the cut and remaining always in the first sheet, $G(z)$ is defined by eqn (13.14), and therefore there are no poles in this region. The pole at $E_R - i\Gamma/2$ is in the second sheet and is a pole due to the analytic continuation of $G(z)$ in this sheet, reached *through* the cut. Figure 13.4 illustrates the general situation.

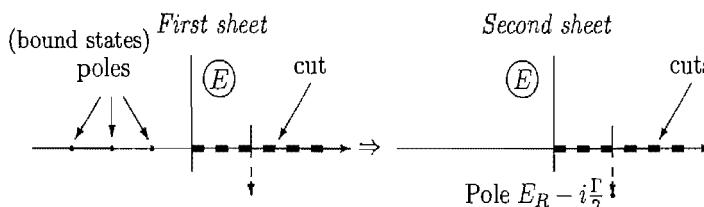


Fig. 13.4

The analytic continuation, by definition, is continuous, and therefore in the second Riemann sheet the propagator behaves as $1/(z - \bar{z})$ and if Γ is sufficiently small, in the first sheet the same behavior will also hold for $\text{Im } z > 0$.

- A priori* there can be more complicated situations in the second sheet, for instance, other poles. In this case, as is clear from eqn (13.55), the dominant pole is the one closest to the real axis.
- $G(z)$ can also have poles in the upper half-plane in the second Riemann sheet; these do not give rise to the residue, in the derivation of eqn (13.53), and give only indirect contributions to the value of the integral of the continuum, $T_{\alpha\alpha}$.

The point to be proven is that for small couplings the situation is precisely the one just described: a pole in the second sheet.

For $z = \bar{z}$ one has

$$\bar{z} - E_0 - R(\bar{z}) = 0 \quad \Rightarrow \quad R(\bar{z}) \equiv \bar{R} = \Delta E - i\frac{\Gamma}{2}. \quad (13.56)$$

From eqn (13.38) it follows that the values of ΔE and Γ approach zero in the limit of small couplings. In this case the pole is near the cut. As $R(z)$ varies continuously passing through the cut we can approximate the value on the upper side of the cut by eqn (13.56), namely, $R(E_R) \simeq \Delta E - i\frac{\Gamma}{2}$. This relation is extended by reflection to the lower part of the cut, in the first sheet, and therefore

$$\langle \chi | (R(E_R + i\varepsilon) - R(E_R - i\varepsilon)) | \chi \rangle = -i\Gamma . \quad (13.57)$$

Let us now write the matrix element of eqn (13.39) for $E = E_R$ in a decay state $|\chi\rangle$. On the right-hand side of eqn (13.39) we insert the completeness relation made up of the eigenstates of H_0 . Due to the projector Q only those states which do not belong to \mathcal{V} contribute, and therefore

$$-i\Gamma = -2\pi i \sum_s |\langle s | R(E_R) | \chi \rangle|^2 \delta(E_R - E_s) ,$$

that is

$$\Gamma = \sum_s |\langle s | R(E_R) | \chi \rangle|^2 2\pi \delta(E_R - E_s) . \quad (13.58)$$

Indeed, $\Gamma > 0$. The reader will recognize in eqn (13.58) a generalization of Fermi's golden rule. A derivation slightly different from this is given at the end of the section.

Equation (13.55) suggests interpreting Γ/\hbar as the probability of the decay per unit time interval: for consistency, we should be able to find the same result by calculating directly the transition probability to the states outside \mathcal{V} . The amplitude for passing to a state $|s\rangle \notin \mathcal{V}$ is

$$\begin{aligned} A_{s\chi}(t) &= \langle s | \mathcal{G}_+(t) | \chi \rangle = \frac{i}{2\pi} \int_{-\infty}^{\infty} dE e^{-iEt/\hbar} \langle s | QG(E)P | \chi \rangle \\ &= \frac{i}{2\pi} \sum_{\chi'} \int dE \langle s | R | \chi' \rangle \frac{e^{-iEt/\hbar}}{E - E_s + i\varepsilon} \left\langle \chi' \middle| \frac{1}{E - PH_0P - PR(E)P} \right| \chi \rangle . \end{aligned} \quad (13.59)$$

We extend the integration contour by considering E as a complex variable and writing

$$A_{s\chi}(t) = \frac{i}{2\pi} \sum_{\chi'} \int dz \langle s | R | \chi' \rangle \frac{e^{-izt/\hbar}}{z - E_s + i\varepsilon} \left\langle \chi' \middle| \frac{1}{z - PH_0P - PR(z)P} \right| \chi \rangle .$$

This expression has two poles, at $z = E_s - i\varepsilon$ and at $z = \bar{z}$. Let χ be an eigenstate of H_{eff} : approximating the second denominator by the sole contribution from the pole, it reduces to a single element, the diagonal one, and eqn (13.59) can be rewritten as:

$$\begin{aligned} A_{s\chi}(t) &= \\ &\frac{i}{2\pi} \int \langle s | R(\bar{z}) | \chi \rangle \frac{e^{-izt/\hbar}}{z - E_s + i\varepsilon} \frac{1}{z - \bar{z}} = \langle s | R(\bar{z}) | \chi \rangle \left(\frac{e^{-iE_s t/\hbar}}{E_s - \bar{z}} + \frac{e^{-i\bar{z}t/\hbar}}{\bar{z} - E_s} \right) \\ &= \langle s | R(\bar{z}) | \chi \rangle \frac{e^{-iE_s t/\hbar}}{E_s - (E_R - i\frac{\Gamma}{2})} \left(1 - e^{(i(E_s - E_R) - \frac{\Gamma}{2})t/\hbar} \right) . \end{aligned}$$

In the evaluation of the integral the residue theorem has been used. The probability for transition to a state $|s\rangle$ is then

$$P_{s\chi}(t) = |\langle s|R|\chi\rangle|^2 \frac{1 + e^{-\Gamma t/\hbar} - 2e^{-\Gamma t/2\hbar} \cos \frac{(E_R - E_s)t}{\hbar}}{(E_s - E_R)^2 + \frac{\Gamma^2}{4}} \quad (13.60)$$

and, for $\Gamma t \gg 1$,

$$P_{s\chi} = \frac{|\langle s|R|\chi\rangle|^2}{(E_s - E_R)^2 + \frac{\Gamma^2}{4}} \simeq \frac{2\pi}{\Gamma} |\langle s|R|\chi\rangle|^2 \delta(E_s - E_R). \quad (13.61)$$

In the last passage the representation for Dirac's delta function,

$$\text{for } \Gamma \rightarrow 0 : \quad \frac{1}{x^2 + \frac{\Gamma^2}{4}} \rightarrow \frac{2\pi}{\Gamma} \delta(x),$$

has been used, which means that a Lorentzian distribution tends to the delta function in the limit of the vanishing width, $\Gamma \rightarrow 0$. Equation (13.61) together with eqn (13.58) ensures the correct relation for $\Gamma t \gg 1$:

$$\sum_s P_{s\chi} \rightarrow 1; \quad P_{\chi\chi} \rightarrow 0;$$

i.e., after a long time² the total decay probability approaches unity.

If we consider eqn (13.60) for small time intervals but large compared to the difference in the energies, $\hbar/(E_s - E_R)$, the oscillating term can be set to zero and one obtains

$$\frac{dP_{s\chi}}{dt} = -\frac{\Gamma}{\hbar} \frac{|\langle s|R|\chi\rangle|^2}{(E_s - E_R)^2 + \frac{\Gamma^2}{4}} \rightarrow -\frac{1}{\hbar} |\langle s|R|\chi\rangle|^2 2\pi \delta(E_s - E_R). \quad (13.62)$$

Equation (13.62) justifies the interpretation of Γ as the decay rate.

Perturbative estimate

For the convenience of the reader we review the procedure in the case of perturbative expansion. The effective Hamiltonian has the form

$$H_{\text{eff}} = M_{\alpha'\alpha} - \frac{i}{2} \Gamma_{\alpha'\alpha}.$$

The matrices M and Γ are called the mass matrix and the decay matrix, respectively; their form is given by the matrix elements of R . Perturbatively

$$R(E) = H_I + H_I Q \frac{1}{E - H_0 + i\varepsilon} Q H_I + \dots$$

²Clearly for all times

$$P_\chi(t) + \sum_s P_{s\chi}(t) = 1.$$

See Problem 13.6.

and therefore

$$\begin{aligned} R_{\alpha' \alpha} = & \langle \alpha' | H_I | \alpha \rangle + \mathcal{P} \sum_s \langle \alpha' | H_I | s \rangle \frac{1}{E - E_s} \langle s | H_I | \alpha \rangle \\ & - i\pi \sum_s \langle \alpha' | H_I | s \rangle \langle s | H_I | \alpha \rangle \delta(E - E_s) + \dots \end{aligned}$$

To second order, then, one has

$$M_{\alpha' \alpha} = E_0 \delta_{\alpha' \alpha} + \langle \alpha' | H_I | \alpha \rangle + \mathcal{P} \sum_s \langle \alpha' | H_I | s \rangle \frac{1}{E_0 - E_s} \langle s | H_I | \alpha \rangle ; \quad (13.63a)$$

$$\Gamma_{\alpha' \alpha} = 2\pi \sum_s \langle \alpha' | H_I | s \rangle \langle s | H_I | \alpha \rangle \delta(E_0 - E_s) . \quad (13.63b)$$

We note that $M = M^\dagger$ and $\Gamma = \Gamma^\dagger$. The sum of s runs over the states orthogonal to the space of the initial states. We note that the correction to the energy has exactly the same form as in the usual perturbation theory, the only difference being in the use of the principal part, \mathcal{P} in the calculation of the integral corresponding to the continuous spectrum.

Remarks

- As should be clear from the derivation above, the law of exponential decay, eqn (13.55), is an approximation, even though experimentally well verified. As is seen from eqn (13.60), for times $t \ll (E_R - E_s)$ the transition probability is quadratic in t , and not exponential. Such a quadratic dependence can be easily understood from the fact that

$$|\langle \psi_0 | e^{-iHt/\hbar} | \psi_0 \rangle|^2 \simeq |1 - it\langle \psi_0 | H | \psi_0 \rangle + \dots|^2 = 1 - ct^2 .$$

These short intervals of time normally do not have much relevance; classically it is as if one were trying to observe the photon before the electron which emitted it finishes a full orbit. It is possible to construct various (apparent) paradoxes by making use of such a t dependence at small t , known as the quantum Zeno effect.³

- Another objection which can be brought forth, by taking eqn (13.55) literally at large t , is the following. Let us consider any state χ and calculate the survival amplitude at time t . We can write

$$\mathcal{A}(t) = \langle \chi | U(t) | \chi \rangle = \int dE \langle \chi | U(t) | E \rangle \langle E | \chi \rangle .$$

$|E\rangle$ indicates the exact eigenstates of H , and by using these to evaluate the matrix elements of U , one can write

$$\mathcal{A}(t) = \int dE e^{-iEt} |\langle E | \chi \rangle|^2 ;$$

namely the survival probability is related to the spectral density of the projection of the initial state on the eigenstates of H . If H is bounded from below it should be that

$$\omega(E) \equiv |\langle E | \chi \rangle|^2 > 0 ; \quad \omega(E) = 0 \text{ per } E \leq E_0 .$$

³Indeed, if one observes N times in the small interval t , the combined probability that the system remains in the original state would be $(1 - ct^2/N^2)^N$. In the limit of continuous observation, $N \rightarrow \infty$, and the survival probability tends to unity: the state never decays! Unlike the famous Zeno paradox on the flying arrow, however, the quantum Zeno effect is a physical effect, confirmed experimentally.

E_0 is the ground state energy of H , and therefore

$$\mathcal{A}(t) = \int_{E_0}^{\infty} dE e^{-iEt/\hbar} \omega(E). \quad (13.64)$$

The Paley–Wiener theorem, which we assume here without proof, asserts that for $E_0 > -\infty$ the “truncated” Fourier transform (13.64) of any positive distribution satisfies the inequality

$$\int_{-\infty}^{\infty} \frac{|\log \mathcal{A}(t)|}{1 + c^2 t^2} dt < \infty; \quad c = \text{const.}$$

Such a constraint is not satisfied by an exponential decay amplitude (the integral diverges), and thus the result (13.55) cannot be exact.

The point again is that law (13.55) is an approximate one: the contribution from other than the pole to the integral considered in the preceding section is small with respect to the terms retained, but as $e^{-\Gamma t}$ decreases exponentially even small terms eventually start dominating over it at sufficiently large t .

Let us estimate the contribution from the cut $T_{\alpha\alpha}$ in eqn (13.52). Assume for simplicity that the cut starts at $E = 0$. By changing the variable to $z = -iy$ and indicating by F^I, F^{II} the expression of the integrand on the first and second sheets,

$$T = \frac{1}{2\pi} \int_0^{\infty} dy e^{-yt/\hbar} [F^I(-iy) - F^{II}(-iy)]. \quad (13.65)$$

The exponential factor implies that the only relevant contribution comes from F for $y \sim 0$. One can take as an order of magnitude the simplest form for the cut, for $E \sim 0$, $R(E) \sim R_0 + \alpha\sqrt{-E}$, with constant R_0 . The imaginary part of R must give the width for $E = E_a$, and therefore we approximately set

$$R(E) \simeq R_0 + \frac{\Gamma}{2\sqrt{E_a}} \sqrt{-E}.$$

All the quantities, R_0, Γ etc, are assumed to be small, according to the general scheme, eqns (13.43) and (13.44). Passing from the first to the second sheet the square root changes sign, so one has approximately for $y \sim 0$

$$F^I - F^{II} \sim \frac{1}{E_a + i\alpha\sqrt{y}} - \frac{1}{E_a - i\alpha\sqrt{y}} \sim \frac{\Gamma}{\sqrt{E_a}} \frac{\sqrt{y}}{E_a^2},$$

and substituting this into eqn (13.65) one gets

$$T \sim \frac{\Gamma}{E_a^{5/2}} \left(\frac{\hbar}{t} \right)^{3/2} \sim \left(\frac{\hbar}{\Gamma t} \right)^{3/2} \left(\frac{\Gamma}{E_a} \right)^{5/2},$$

to be compared with the pole contribution that is of the order of $\exp(-\Gamma t/2\hbar)$. By writing $\Gamma/E_a = 10^{-\beta}$ one can study how

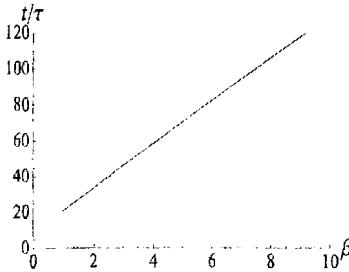


Fig. 13.5

the time t at which the two contributions become comparable, depending on β . Setting $\tau = \hbar/\Gamma$ for the mean lifetime one finds the result shown in Figure 13.5. It can be seen that even for $\Gamma/E \sim 10^{-1}$ the cut contribution becomes relevant only at $t \sim 20\tau$, at which time for all purposes the system has already decayed away. The only exception is for the resonance near the threshold, $E \sim 0$, where the corrections to the exponential behavior can be relevant.

3. In the above the form of the decay probability has been obtained by studying the survival amplitude, but to calculate Γ the *transition amplitudes* have been considered. We have furthermore made use of the continuity of $R(E)$ between the first and second sheets to write eqn (13.57). This procedure though simplifies the derivation makes slightly obscure at which point use was made of the second Riemann sheet. Actually, the same result can be obtained by directly calculating the survival amplitudes throughout.

13.3 Examples

13.3.1 Discrete–continuum coupling

An example which is simple enough that the calculation can be carried through is the following. Consider a system made of just one discrete state with energy $E_a > 0$ and a continuous spectrum $E \geq 0$, with a spectral density $\rho(E)$ (i.e., the number of states per unit energy interval). Suppose that the only non-vanishing matrix element of H_I is

$$\langle E | H_I | a \rangle = \lambda v(E); \quad \langle a | H_I | a \rangle = \langle E' | H_I | E \rangle = 0. \quad (13.66)$$

λ is the coupling constant, which can be varied to study various regimes, from the weak to the strong coupling. P is the projector on the state $|a\rangle$. From the matrix element (13.66) it is obvious that only one term contributes to the series for PRP , eqn (13.36)

$$\langle a | R | a \rangle = \langle a | PRP | a \rangle = \langle a | \bigcirc - - \bigcirc | a \rangle$$

that is:

$$R_a = \langle a | R | a \rangle = \sum_s |\langle a | H_I | E_s \rangle|^2 \frac{1}{E - E_s} = \int dE' \rho(E') \frac{\lambda^2 |v(E')|^2}{E - E'}.$$

By using the usual prescription for real E , $E + i\varepsilon$, and by using the identity (13.16), one has, for $E \in \mathbb{R}$,

$$R(E + i\varepsilon) = \mathcal{P} \int dE' \frac{\rho(E') |v(E')|^2}{E - E'} - i\pi \rho(E) |v(E)|^2 \equiv F_R(E) - i \frac{F_I(E)}{2}.$$

We note that F_R, F_I are proportional to λ^2 and

$$F_R(E) = \frac{1}{\pi} \mathcal{P} \int dE' \frac{F_I(E')}{E - E'}. \quad (13.67)$$

The propagator can be written as

$$G_{a+}(E) = \frac{1}{E - E_a - R_a(E)} = \frac{E - E_a - F_R - iF_I/2}{(E - E_a - F_R(E))^2 + F_I^2/4}.$$

The time evolution can be calculated by using eqn (13.51):

$$\begin{aligned} U_a(t) &= -\frac{1}{\pi} \int_{-\infty}^{+\infty} dE \operatorname{Im} G_a(E) e^{-iEt/\hbar} \\ &= \frac{1}{\pi} \int_{-\infty}^{+\infty} dE \frac{F_I/2}{(E - E_a - F_R(E))^2 + F_I^2/4} e^{-iEt/\hbar} \end{aligned} \quad (13.68)$$

The essential quantity is F_I . From this function one can calculate F_R and finally the time evolution. $F_I(E) \geq 0$ in general, and $F_I(E) = 0$ for $E < 0$. In order for the integrals to make sense, one can assume that $F(E) \rightarrow 0$ sufficiently fast at infinity. The detailed form depends on the state density and on the type of interactions, $v(E)$. A general form of F_I, F_R is the one shown in Figure 13.6. Note that $F_I(E)$ is normally a function without a particular structure, but has a typical extension w_0 , beyond which it decreases quickly. F_R , determined through eqn (13.67), has a typical dispersive structure.

The integrand of (13.68) indicates the distribution of energy of the eigenstates of H which contribute to the time evolution of the initial state vector $|a\rangle$, see eqn (13.48). The only region of E where the state density is significant is where the denominator is small, and as $F_I^2 > 0$ always, the dominant contribution comes from a region near

$$E - E_a - F_R(E) = 0. \quad (13.69)$$

For $\lambda \rightarrow 0$ the perturbative regime discussed in this chapter applies: the solution of eqn (13.69) is approximately

$$E_R \simeq E_a + F_R(E_R) \equiv E_a + \Delta E,$$

and the distribution of the states is a Lorentzian with width

$$\Gamma = F_I(E_R).$$

The situation changes drastically for $\lambda \gg 1$. In this case the root of eqn (13.69) is certainly in the region $|E| \gg |E_a|$. From eqn (13.67) it follows for $|E| \rightarrow \infty$ that

$$F_R \rightarrow \frac{1}{E} \frac{1}{\pi} \int dE' F_I(E') = \frac{\Omega^2}{E};$$

and eqn (13.69) has asymptotically two roots

$$E \simeq \pm \Omega.$$

For large E , one as $F_I \rightarrow 0$ and the integrand of (13.68) (recalling that formally F_I should be understood as $F_I + \varepsilon$) tends to

$$\frac{1}{\pi} \frac{F_I/2}{(E - E_a - F_R(E))^2 + \frac{F_I^2}{4}} \sim \delta(E - \Omega) + \delta(E + \Omega).$$

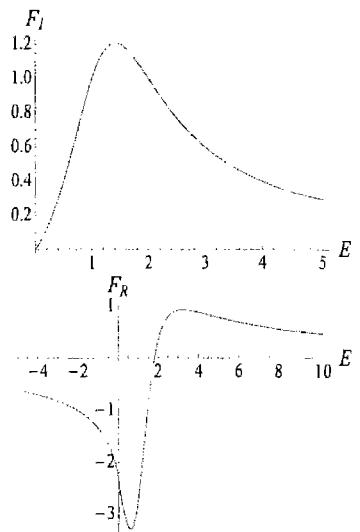


Fig. 13.6 General behavior of F_I and F_R .

Thus one has an oscillation between a pair of levels with frequency Ω/\hbar . Physically the entire continuous spectrum behaves as a single state for $\lambda \rightarrow \infty$, the discrete-continuum coupling reducing to an oscillation between two states.

13.4 Complex scale transformations

In the chapter dedicated to the semi-classical approximation, a method based on the WKB approximation and another, “exact” approach by Gamow and Siegert, were adopted in the determination of the energy and width of a metastable state. Here we shall reconsider the problem from a more modern point of view. The determination of the resonant state requires knowledge of the analytic structure of the resolvent beyond the cut, so the problem is: how does one analytically continue $1/(z - H)$ or its matrix elements?

Before explaining the solution let us briefly summarize the structure of the cut. Let us consider the problem of N particles interacting under a potential V which vanishes at infinity, for instance an atom. The bound states, described by functions in L^2 , give rise to poles in the denominator, on the real negative axis $E < 0$. The improper eigenstates of H instead correspond to the continuum. We can imagine these states as representing a system having its parts very distant from each other, so that asymptotically they behave as free particles. In the case of an atom this picture describes the ionized atom, in which one of the electrons have “freed itself” from the atomic binding. For simplicity we consider just two parts, the electron and the ionized atom. The states of the continuum are the solution of Schrödinger’s equation which in the center of mass looks like

$$-\frac{\hbar^2}{2\mu} \Delta \psi + V \psi = E \psi. \quad (13.70)$$

Asymptotically the electron wave function is a linear combination of the expanding and contracting spherical waves: two solutions of the free radial equation.⁴ The correct combination is determined by the condition of regularity at the origin:

$$\psi \sim c_1 \frac{e^{ikr}}{r} + c_2 \frac{e^{-ikr}}{r}, \quad (13.71)$$

where k is the wave number. If E_0 is the minimum energy needed to free the electron, one has

$$E = E_0 + \frac{\hbar^2 k^2}{2m}; \quad k \propto \sqrt{E - E_0}. \quad (13.72)$$

As differential equation (13.70) and boundary condition (13.71) are both analytic in k , so will be the former’s solution, but in terms of E this implies, by eqn (13.72), the presence of a square branch point for $E = E_0$.

For a particle in an external potential this means that the Riemann sheet for the matrix elements of the resolvent operator is doubly sheeted,

⁴In the Coulomb potential to which V asymptotically tends to, interactions actually persist at infinite distances and the wave function gets distorted, as is well known. We neglect this subtlety in the present intuitive argument.

such as the one induced by the function \sqrt{x} . In the case of the example of the electron and the rest of the (ionized) helium atom, the latter has a hydrogenoid spectrum, with the levels $E_n = -Z^2/2n^2$, while the electron has the (free) energy, $\hbar^2 k^2/2m$. Such a state will appear at energies $E > E_n$, so that there will be a cut starting at $E = E_n$. We say that at this value of energy a new *reaction channel* is open; a new reaction channel corresponds to a new cut. In this example, there will be successive branch cuts, partially overlapping, with the tips at

$$E_1 = -\frac{Z^2}{2} = -2 \text{ a.u.}; \quad E_2 = -\frac{Z^2}{2 \cdot 2^2} = -0.5 \text{ a.u.}; \quad \dots$$

At $E = 0$, furthermore, a new channel is open where the atom is doubly ionized, and so on.

The first Riemann sheet, with $0 < \arg(E) < 2\pi$ is called the *physical sheet*; the rest of the Riemann surface is referred to as unphysical sheets.

This brief discussion should be sufficient to give a general idea as to what stays behind the branch cuts in the resolvent. Let us now consider the poles in unphysical sheets: resonances.

There are at least two ways to describe intuitively these states. The first is related to the geometric form of the potential: it is the case of tunnel effect through a barrier: a particle is bound inside a potential well for a relatively long time, but can decay by tunneling through the barrier. Such an example has been considered earlier in this book in several occasions. In nuclear physics such a state is often referred to as a *shape resonance*. We note that there can be resonances, in the presence of a potential with a barrier, even for energies higher than the barrier height. In this case it is easier to think of such an intermediate state as being formed during a scattering process. Let us think of an *S* wave scattering for a particle in the potential represented in Figure 13.7. Of course, for $E < V_{max}$, there could be the first type of resonance, corresponding to a “capture” of the particle in unstable bound states, which survive a considerable amount of time before decaying.

For energies $E > V_{max}$ one expects the reflection, but again, for certain values of the incident energy, the time spent by the process is larger than the characteristic time, $t \sim a/v$, where a is the size of the well-like part of the potential and v the velocity of the projectile. This leads to an enhancement of the scattering cross section, which for all practical purposes represents a resonance. The excited nucleon resonances N^* , N^{**} , etc., appearing as peaks in the πN (N is a nucleon, i.e., a proton or a neutron) scattering cross sections are states of this sort. Still another case is the following. Suppose that the Hamiltonian of the system is composed of two parts, H_A and H_B , such that in the absence of H_B the system H_A has genuine bound states, i.e., poles on the negative real axis. When H_B is turned on, the bound state might persist, or might get lost in the continuum, with the pole moving to the second sheet. This is the case of self-ionized atoms mentioned above; it is called *Feshbach resonance*.

In the specific case of helium the first threshold is at $-Z^2/2 = -2$ a.u..

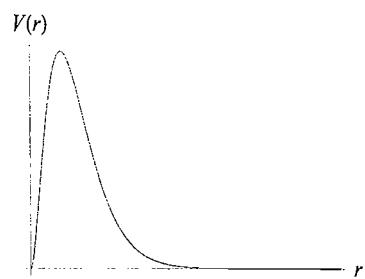


Fig. 13.7

As we have already seen, in the absence of electron-electron interactions the hydrogenoid bound states of the type (n_1, n_2) (n_1, n_2 are the principal quantum numbers of the two electrons) with $(n_1 \geq 2)$ have energy larger than the ionization threshold. Between the first and second ionization thresholds we therefore expect a series of resonances, corresponding to an electron in the state $n_1 = 2$ and another in the state $n_2 \geq n_1$, that is, resonances $(2s, 2s)$, $(2s, 2p)$, $(2p, 2p)$, $(2s, 3s)$, etc. In practice various series of resonances all accumulate around the second threshold, as the bound states $(1s, n)$ pile up around the first threshold. The same holds for higher thresholds; these observations give a glimpse of the analytic structure of the resolvent in general.

13.4.1 Analytic continuation

Consider now a scale transformation of the type

$$\psi(x) \rightarrow \lambda^{1/2} \psi(\lambda x) \equiv U(\lambda) \psi(x) = \psi'(\lambda x). \quad (13.73)$$

where for the purposes of illustration we consider a simple one-dimensional case. Transformation (13.73) is just a change of the coordinates, and as such it transforms an orthonormal basis $f_n(x)$ to another orthonormal basis:

$$\int dx \bar{f}'_n(x) f'_m(x) = \int dx \lambda \bar{f}_n(\lambda x) f_m(\lambda x) = \int d\xi \bar{f}_n(\xi) f_m(\xi) = \delta_{nm};$$

thus the operator U is unitary. In general it does not commute with the Hamiltonian, but as with all unitary transformations it can be thought of as a change of representation. In other words, the new states transform under the transformed operators UAU^{-1} just as the original states do under the operators A . In particular, the new eigenstates of the Hamiltonian H , $U\psi_n(x)$, are eigenstates of $H(\lambda) = U(\lambda)HU^{-1}(\lambda)$. The spectrum of H remains invariant. To each eigenvalue of H corresponds the same eigenvalue of $H(\lambda)$.

The situation changes when the parameter λ is taken to be complex. Let us take for example $\lambda = e^{i\theta}$, to be concrete, and consider the case of discrete levels first. The condition of normalizability still makes sense, only the normalization integral is to be defined along the complex path, instead of the real path. For instance, the normalization integral for a (reduced) radial wave function has the form

$$\int_0^\infty dr \varphi(e^{i\theta} r)^* \varphi(e^{i\theta} r).$$

Bound states typically have exponential behavior at $r \rightarrow \infty$ so the above integral behaves as

$$\exp(-2r \cos \theta), \quad (13.74)$$

which is convergent in the half-plane $-\frac{\pi}{2} < \theta < \frac{\pi}{2}$. As the state is normalizable it is easily verified that, by performing the same change of the variable as in the case $\lambda \in \mathbb{R}$,

$$\frac{\langle n | H | n \rangle}{\langle n | n \rangle} = E_n.$$

This means that the discrete spectrum of the Hamiltonian rotated in the complex plane $H(\theta)$,

$$H(\theta) = \frac{1}{e^{2i\theta}} \frac{p^2}{2m} + V(e^{i\theta}),$$

includes the initial spectrum.

The situation is different for the continuous spectrum. The general solution of Schrödinger's equation for the reduced radial function now has the form

$$\varphi(r) = c_1 \exp(ik e^{i\theta} r) + c_2 \exp(-ik e^{i\theta} r).$$

The two particular solutions for real values of k are obviously not solutions. Acceptable solutions (which do not diverge exponentially) occur only for complex values of k ,

$$k = |k| e^{-i\theta}.$$

(13.75)

We have seen that $k^2/2m$ indicates the energy above the threshold so the spectrum of $H(\theta)$ is complex, $E_s + k^2/2m$ with $\text{Arg}(E - E_s) = -2\theta$.

Let us clarify a point which is potentially confusing. The proper states of the Hilbert space are normalizable vectors. If we adopt a basis which behaves as $f_k \sim r^k \exp(-r)$ for large r , the behavior of eqn (13.74) tells us that there are certainly states which admit continuation to $\theta \neq 0$. This certainly also holds for finite linear combinations of such states, but for infinite sums the situation may vary with θ .

Let us now consider the resolvent. The singularities of the resolvent are the spectrum of H . For states which admit analytic continuation, given by

$$\varphi(r) \rightarrow e^{i\theta/2} \varphi(e^{i\theta} r) = U(\theta)\varphi,$$

one has

$$F(z) = \left\langle \varphi \left| \frac{1}{z - H} \right| \varphi \right\rangle = \left\langle \varphi(\theta) \left| \frac{1}{z - H(\theta)} \right| \varphi(\theta) \right\rangle,$$

in view of the unitary character of these states. The function F is analytic apart from the branch cuts due to the spectrum of the operators. In the region where both operators are defined the expectation value of the resolvent is the same, so that they are just two expressions for the same analytic function $F(z)$. As the spectrum of the two operators H , $H(\theta)$ are in different positions this means that one of the two is the analytic continuation of the other.

Let $\mathcal{R}(z, \theta)$ be the resolvent defined by using the rotated $H(\theta)$. Let us assume for concreteness that $\mathcal{R}(z, 0)$ has points in $E < 0$ corresponding to bound states of H and a cut at $E \geq 0$. As we have seen, the bound states of H are poles for $\mathcal{R}(z, \theta)$ also. The cut instead gets rotated by an angle 2θ in the clockwise direction. The situation is illustrated schematically below, in Figure 13.8.

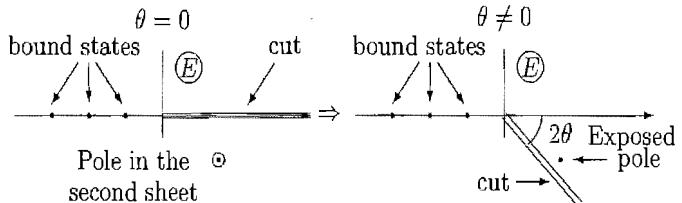


Fig.13.8

Apart from the poles, $\mathcal{R}(z, 0)$ is analytic in the region $0 < \arg(z) < 2\pi$, while $\mathcal{R}(z, \theta)$ is analytic (apart from the poles) in the domain $-2\theta < \arg(z) < 2\pi - 2\theta$. This is an example of the overlapping of the analyticity domain.

We know that the resonances are described by the poles in the second sheet of the Riemann surface of the resolvent, but now we see that as θ is varied this sheet gets gradually revealed, so for

$$2\theta > \arg\left(\frac{\Gamma}{2E_R}\right) \quad (13.76)$$

the resonance at $z = E_R - i\Gamma/2$ becomes a pole of an operator of which we know the form, $\mathcal{R}(z, \theta)$, and so it is a bound state of $H(\theta)$. As it is a bound state pole its position is not changed with θ . We thus have a very efficient way to compute the width and the energy of the resonances: it suffices to study the bound state of $H(\theta)$.

Remarks

- The generalization of the method to systems with arbitrary degrees of freedom is straightforward: it suffices to scale all the variables;
- In a case with more branch points, each cut rotates. It can happen that a cut covers another pole which had emerged: in this case the bound state is obviously no longer visible.
- This method turned out to be very flexible and also adequate for relatively complicated systems such as atomic or molecular resonances.

13.5 Applications and examples

An approach which is known to be very powerful in the study of bound states is the variational one. Once a base is chosen the problem reduces to the diagonalization of the Hamiltonian in a subspace made of a finite number of independent vectors:

$$H_{ij}c_j = Ec_j. \quad (13.77)$$

The same procedure can be used for $H(\theta)$, or in general for $H(\alpha e^{i\theta})$.

In the approach in which the Hilbert space is truncated, the statements made above hold only approximately, but by treating $\lambda = \alpha e^{i\theta}$ as one of the variational parameters one might try to find the solution of

problem (13.77), imposing on it the condition that it is stationary with respect to α and θ .

In the Problems for numerical analysis at the end of the chapter (whose solutions are on the accompanying CD of this book) various cases are dealt with and discussed in some details. Here are some of the results.

13.5.1 Resonances in helium

As the first example consider Feshbach resonances in helium, of which mention was already made in the text. In the Coulomb potential case the situation is particularly simple from the point of view of the variational method. Under the scale change the kinetic energy transforms as $1/\lambda^2$ and the potential energy as $1/\lambda$; therefore, by using the notation used in Hylleraas' treatment of helium atom, problem (13.77) reduces to

$$\frac{1}{\lambda^2} L_{ij} c_j - \frac{1}{\lambda} M_{ij} c_j = N_{ij} c_j ,$$

where the matrices L, M, N are those used in the usual case with $\theta = 0$. For a reasonable and quantitative solution it is necessary to choose the state which one wishes to study and optimize α, θ for it. Here we shall content ourselves with a qualitative treatment. In Figure 13.9 an enlarged picture of the eigenvalue distribution is shown, obtained by using $\theta = \pi/16$ and by keeping a base with 140 elements, already utilized in the study of a helium atom. The calculation is done for two values of the scale factors, $\alpha \sim 4$ in the first case, which is the typical value used for the calculation at $\theta = 0$ of the ground state energy and $\alpha \sim 2$, instead, in the second case.

Recall that one expects an infinite sequences of branch points, situated at

$$E_c = -\frac{Z^2}{2n^2} = -(2, 0.5, \dots)$$

With a finite number of base states there is a distortion, and in particular, with a small base only the first branch cut and another between the second and third can be made evident. Agreement with the theoretical position of the cuts is in any case quite satisfactory. In both plots in Figure 13.9 a state at $E \sim -0.7$ is seen to lie outside the cuts. Experimental data show a resonance state with $(E, \Gamma) = (-0.77, 0.004)$ a.u.: it is the first 1S Feshbach resonance of the system⁵

13.5.2 The potential $V_0 r^2 e^{-r}$

Let us study the S wave resonances for this potential. In the following we shall take $V_0 = 7.5$, and all the quantities will be expressed in atomic units. The potential has the form shown in Figure 13.10, with the maximum height, $V_M = 4$.

This model has been treated in the WKB approximation, yielding

$$E_{WKB} = 3.425 ; \quad \Gamma_{WKB} = 0.0265 .$$

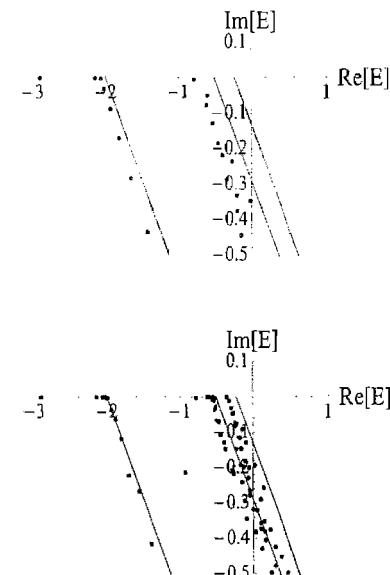
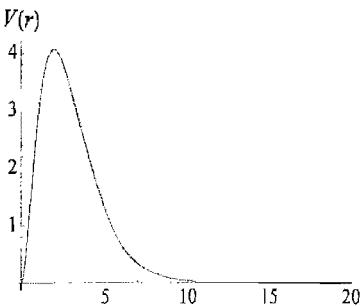
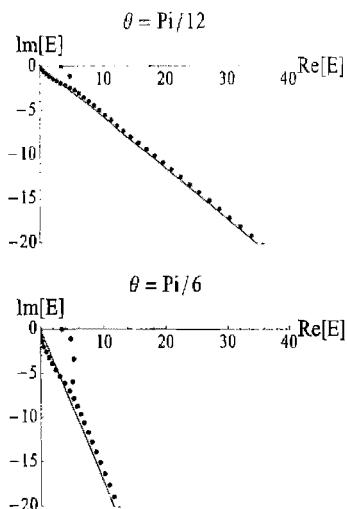
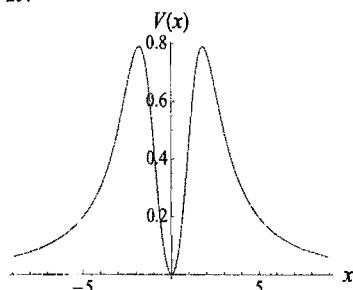


Fig. 13.9 Eigenvalues of the helium atom with a phase rotation $\theta = \pi/16$. The real scale parameter is taken to be 3.9 in the first, 1.9 in the second.

⁵ A detailed variational study is to be found in [Bürgers, et. al. (1995)].

Fig. 13.10 The potential $V_0 r^2 e^{-r}$.Fig. 13.11 Eigenvalues for the potential $V_0 r^2 e^{-r}$, with $\theta = \pi/12$ and $\theta = \pi/6$. The straight line has the slope 2θ .Fig. 13.12 Potential $x^2/(1+gx^4)$ with $g = 0.1$.

It is not possible in this method, based on the tunneling through under the barrier, to obtain the resonance states above the threshold, here with $E > V_M$. Solving Schrödinger's equation with the Gamow-Siegert method one obtains

the first two resonance states

$$E_1 = 3.42639, \Gamma_1 = 0.025549; \quad E_2 = 4.852, \Gamma_2 = 2.12,$$

the second of which is above the threshold.

With the present method of complex scaling, one studies the eigenvalues of the Hamiltonian

$$H = -\frac{1}{2e^{2i\theta}} \left(\frac{d^2}{dr^2} \right) + V(e^{i\theta}r).$$

Again one can solve the problem by a variational method, by using the base of functions $\varphi_i(\alpha r)$. α , the scale parameter, is treated as one of the variational parameters.

A variational study following the lines of Chapter 10 gives the results summarized in Figure 13.11. In the first plot the eigenvalues are given for $\theta = \pi/12$. The rotation of the eigenvalues in the complex plane and the presence of two eigenvalues which emerged in the second sheets are clearly seen.

The same situation is shown in the second plot but with $\theta = \pi/6$. As can be seen, as the angle increases new resonances are revealed, in agreement with eqn (13.76). Numerically we find for the first resonances

$$(E, \Gamma) = (3.42639, 0.025548); (4.83481, 2.23576); (5.27727, 6.77813),$$

in excellent agreement with the preceding results. A similar analysis can be done for any potential. For example, consider

$$V(x) = \frac{x^2}{1+gx^4}.$$

The graph is shown in Figure 13.12. The WKB calculation to first order, for $g = 0.1$, predicts a resonance with parameters

$$E_{WKB} = 0.417; \quad \Gamma_{WKB}/2 = 0.008. \quad (13.78)$$

The spectrum obtained with the complex scaling method is shown in Figure 13.13. Two resonances are seen: numerically, one finds that

$$(E, \Gamma/2) = (0.410, 0.0085); \quad (0.975, 0.295).$$

13.5.3 The unbounded potential; the Lo Surdo-Stark effect

In systems with a spectrum unbounded from below, a very peculiar phenomenon occurs. We shall illustrate it in the case of an unstable oscillator,

$$H = \frac{p^2}{2} + \frac{1}{2}x^2 - \frac{1}{4}gx^4; \quad g > 0. \quad (13.79)$$

This system has no bound state, the spectrum being continuous, $-\infty$ to $+\infty$. We however expect resonances due to metastable states confined in the region near $x = 0$ due to the harmonic part of the potential.

By making a complex rotation $x \rightarrow e^{i\theta} x$ we know that the continuous spectrum must rotate by 2θ around the branch point, but here there are no branch points. What happens here is that, having no branch points, the continuous spectrum disappears, and for $\theta > 0$ only poles in the second sheet are present.⁶

Consider the asymptotic solution of Schrödinger's equation associated with eqn (13.79). For large x the leading term is the quartic term, and so

$$\frac{1}{2}\psi'' \sim -g \frac{x^4}{4} \psi .$$

If we consider a solution with definite parity, we can limit ourselves to the region $x > 0$ where asymptotically

$$\psi(x) \sim C_1(E) \exp\left(i\sqrt{g} \frac{x^3}{6\sqrt{2}}\right) + C_2(E) \exp\left(-i\sqrt{g} \frac{x^3}{6\sqrt{2}}\right) .$$

The exponent does not depend on the energy. The coefficients C_1, C_2 depend on E and are found by imposing continuity near the region of small $|x|$. By making the phase rotation, one has asymptotically

$$e^{-2i\theta} \frac{1}{2}\psi'' \sim -\frac{g}{4} e^{4i\theta} \psi ,$$

with the solution

$$\psi \sim C_1(E) \exp(icx^3 e^{3i\theta}) + C_2(E) \exp(-icx^3 e^{3i\theta}) . \quad (13.80)$$

The real part of this exponent behaves as $\sin(3\theta)x^3$. For $x > 0$, therefore, the second exponent increases as $\exp(x^3)$ and is not acceptable. The solution (13.80) is thus an eigenvector only for the values of E which are the roots of $C_2(E) = 0$. For this (in general, discrete) set of values of E , the part proportional to C_1 describes normalizable functions: they are poles of the resolvent of $H(\theta)$.

In the variational approach with a truncated base of functions, there can appear cuts, which, however, disappear when the dimension of the base is increased. System (13.79) is discussed in Problems for numerical analysis at the end of the chapter. In Figure 13.14 the spectrum for $g = 0.03$ is shown: note the absence of the cuts (cf. the analogous figures (13.11, 13.13)).

An analogous discussion can be had for the case of the Lo Surdo-Stark effect. The Hamiltonian of the hydrogen atom in an external electric field is

$$H = \frac{\mathbf{P}^2}{2} - \frac{1}{r} - Fz . \quad (13.81)$$

H has a continuous spectrum; the values calculated for the energy in perturbation theory really refer to metastable states. Also in this case the spectrum of $H(\theta)$ turns out to be purely discrete, and the poles in

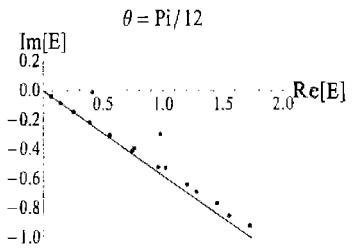


Fig. 13.13 Eigenvalues for the potential $x^2/(1+gx^4)$, $g = 0.1$ and with $\theta = \pi/12$. The straight line has the slope 2θ .

⁶This can be proven rigorously for the case of the Lo Surdo-Stark effect, see [Herbst and Simon (1978)]

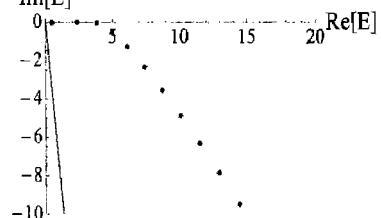
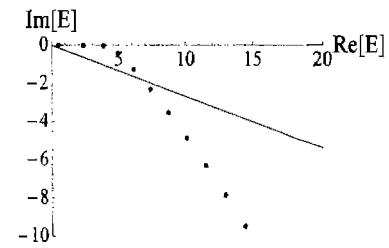


Fig. 13.14 Eigenvalues for potential (13.79) with $g = 0.03$. The figures refer to two phases, $\theta = 2\pi/48$ and $\theta = 11\pi/48$. The dashed line, with slope 2θ , indicates the place where the cut normally appears.

the resolvent in the region $\theta < \pi/3$ correspond to the unstable levels of the system.

We give a qualitative argument here. As in system (13.81), L_z commutes with H , and one can continue to use the eigenvalues m of L_z , to classify the eigenstates. By using parabolic-cylindrical coordinates,

$$x = \sqrt{\xi\eta} \cos \varphi, \quad y = \sqrt{\xi\eta} \sin \varphi, \quad z = \frac{1}{2}(\xi - \eta).$$

φ is the azimuthal angle around the z axis. H is separable in these coordinates, with eigenfunctions of the form $\psi = f_1(\xi) f_2(\eta) \exp(im\varphi)$; the equations for the eigenvalues are

$$\begin{aligned} \frac{d}{d\xi} \left(\xi \frac{df_1}{d\xi} \right) + \left[\frac{E}{2}\xi - \frac{m^2}{4\xi} - \frac{F}{4}\xi^2 \right] f_1 &= -\beta_1 f_1; \\ \frac{d}{d\eta} \left(\eta \frac{df_2}{d\eta} \right) + \left[\frac{E}{2}\eta - \frac{m^2}{4\eta} + \frac{F}{4}\eta^2 \right] f_2 &= -\beta_2 f_2; \end{aligned}$$

with

$$\beta_1 + \beta_2 = 1. \quad (13.82)$$

The parameters β_1, β_2 are functions of E : once they are found eqn (13.82) allows one to determine E . Changing the variables as $f_1 = g_1/\sqrt{\xi}, f_2 = g_2/\sqrt{\eta}$, one has

$$\begin{aligned} \frac{d^2g_1}{d\xi^2} + \left(\frac{E}{2} + \frac{\beta_1}{\xi} - \frac{m^2 - 1}{4\xi^2} - \frac{F}{4}\xi \right) g_1 &= 0; \\ \frac{d^2g_2}{d\eta^2} + \left(\frac{E}{2} + \frac{\beta_2}{\eta} - \frac{m^2 - 1}{4\eta^2} + \frac{F}{4}\eta \right) g_2 &= 0; \end{aligned}$$

Thus we are dealing with two one-dimensional systems with energy $E/4$ and with potential

$$U_1(\xi) = -\frac{\beta_1}{2\xi} + \frac{m^2 - 1}{8\xi^2} + \frac{F}{8}\xi; \quad U_2(\eta) = -\frac{\beta_2}{2\eta} + \frac{m^2 - 1}{8\eta^2} - \frac{F}{8}\eta.$$

The potential $U_2(\eta)$ is the one responsible for the metastability. Asymptotically the solutions for the Hamiltonian rotated by phase θ are of the form

$$\begin{aligned} g_1 &\sim C_1 \exp \left(\alpha e^{i\frac{3}{2}\theta} \xi^{3/2} \right) + C_2 \exp \left(-\alpha e^{i\frac{3}{2}\theta} \xi^{3/2} \right); \\ g_2 &\sim D_1 \exp \left(i\alpha e^{i\frac{3}{2}\theta} \eta^{3/2} \right) + D_2 \exp \left(-i\alpha e^{i\frac{3}{2}\theta} \eta^{3/2} \right), \end{aligned}$$

where α is a numerical, positive coefficient. For $\theta > 0$ the condition for the function being in the spectrum (not an exponentially increasing function) is $C_1 = 0, D_2 = 0$. The resultant functions are normalizable and represent poles of the resolvent. The real parts of the exponents in C_2 and D_1 are $-\alpha \cos(\frac{3}{2}\theta)\xi^{3/2}$ and $-\alpha \sin(\frac{3}{2}\theta)\eta^{3/2}$, respectively. One has an exponential decrease for $\cos(\frac{3}{2}\theta) > 0$ and $\sin(\frac{3}{2}\theta) > 0$, so in the region $0 < \theta < \pi/3$.

Further reading

For the resolvent formalism we refer the reader to the following books [Goldberger and Watson (1964), Cohen-Tannoudji, et. al. (1988), Di Giacomo (1992)], and to these lectures: [Cohen-Tannoudji (1968)]. The complex scaling formalism started in 1971 with [Aguilar and

Combes (1971), Simon (1972)]; more material may be found in [Reed and Simon (1980b)]. An exposition for physicists is in [Reinhardt (1982)]. Some of the problems related to decay are studied in the Mathematica notebook NB-3.7-decay.nb on the accompanying CD.

Problems

- (13.1) Write the Green function for a free particle in one dimension by solving the equation $(E - H)G = 1$ in the x representation. Verify the result by writing G as a sum over eigenstates of H .
- (13.2) Write the Green function for a free particle in any dimension by solving the equation $(E - H)G = 1$ in the x representation.
- (13.3) Compute the Green function for a particle in one dimension in a potential $V(x) = g\delta(x)$ by solving $(E - H)G = 1$ in the x representation and verify the result by considering H eigenstates. Compute the spectral density $g(E)$. Verify the relation between $g(E)$ and scattering phases by computing the transmission and reflection coefficients.
- (13.4) Compute the Green function for a particle in one dimension in a potential $V(x) = g\delta(x-a) + g\delta(x+a)$
- (13.5) Compute the eigenvalues for a free particle in a volume bounded by a parallelepiped with edges (a, b, c) and verify the form of the Weyl expansion.
- (13.6) Show that in the pole approximation for a decay state χ , for all t

$$P_\chi(t) + \sum_s P_{s\chi}(t) = 1$$

Numerical analyses

- (13.1) Use complex scaling methods to study resonances in a radial potential $V_0 r^2 e^{-r}$ and in a one-dimensional potential $x^2/(2(1+gx^4))$.
- (13.2) Use complex scaling methods to study resonances in the potential $x^2/2 - gx^4/2$.
- (13.3) Use complex scaling methods to give a qualitative study of metastable helium states.
- (13.4) Use the stabilization method to study resonances in a radial potential $V_0 r^2 e^{-r}$ and in a one-dimensional potential $x^2/(2(1+gx^4))$.
- (13.5) Compute resonance parameters by scattering phases in a potential $V_0 r^2 e^{-r}$.
- (13.6) Compute resonance parameters by scattering phases in the one-dimensional potentials $x^2/(2(1+gx^6))$ and $x^2/(2(1+gx^4))$. To compute scattering

phases use both the transmission and reflection coefficients and the regular solution of Schrödinger's equation.

- (13.7) Compute the semi-classical approximation for the spectral density in a harmonic oscillator, a purely

quartic oscillator, and an anharmonic oscillator. Compare with the numerical results.

- (13.8) Use the Berry-Tabor formula to obtain the semi-classical approximation for the spectral density for a potential $V(x, y) = x^4/4 + gy^4/4$.

Electromagnetic interactions

14

In quantum mechanics, in contrast to what happens in classical mechanics, the physical meaning of electromagnetism is to be attributed to the phase factor

$$\exp\left(\frac{ie}{\hbar c} \int_Q^P dx^\mu A_\mu\right),$$

where $A_\mu = (\Phi, \mathbf{A})$ are the scalar and vector potential, rather than to the electric and magnetic fields \mathbf{E}, \mathbf{B} themselves. The well-known form of the Hamiltonian of a charged particle in external electromagnetic fields,

$$H = \frac{1}{2m} \left(\frac{\hbar}{i} \nabla - \frac{e}{c} \mathbf{A} \right)^2 + e\Phi - \boldsymbol{\mu} \cdot \mathbf{B}, \quad (14.1)$$

is closely related to this fact. Several general issues concerning the electromagnetic interactions of charged particles will be discussed in this chapter, leaving the study of the atomic structures to the next, separate chapter.

14.1 The charged particle in an electromagnetic field

14.1.1 Classical particles

The classical equation of motion of a particle with mass m and charge e in an external electromagnetic field is

$$m \frac{d\mathbf{v}}{dt} = e \mathbf{E} + \frac{e}{c} \mathbf{v} \times \mathbf{B},$$

where the second term on the right-hand side is the Lorentz force. The corresponding Lagrangian is

$$\mathcal{L} = \frac{1}{2} m \mathbf{v}^2 + \frac{e}{c} \mathbf{v} \cdot \mathbf{A} - e\Phi \quad (14.2)$$

where \mathbf{A}, Φ are the vector and scalar potentials, related to the electromagnetic fields as follows

$$\mathbf{E} = -\nabla\Phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}; \quad \mathbf{B} = \nabla \times \mathbf{A}.$$

14.1 The charged particle in an electromagnetic field	381
14.2 The Aharonov-Bohm effect	392
14.3 The Landau levels	397
14.4 Magnetic monopoles	401
Guide to the Supplements	404
Problems	404
Numerical analyses	404

As is well known, introduction of the vector and scalar potentials automatically solve the homogeneous Maxwell equations

$$\nabla \cdot \mathbf{B} = 0, \quad \nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}.$$

Actually, the information contained in the functions Φ, \mathbf{A} is redundant with respect to \mathbf{E}, \mathbf{B} ; in fact any transformation of the type

$$\mathbf{A} \rightarrow \mathbf{A}' = \mathbf{A} + \nabla \Lambda \quad \Phi \rightarrow \Phi' = \Phi - \frac{1}{c} \frac{\partial \Lambda}{\partial t} \quad (14.3)$$

leaves \mathbf{E}, \mathbf{B} invariant, which are the only physically meaningful quantities classically.¹

Transformations (14.3) are called *gauge transformations*.

Under a gauge transformation the Lagrangian (14.2) transforms as follows

$$\mathcal{L} \rightarrow \mathcal{L}' = \mathcal{L} + \frac{e}{c} \left(\mathbf{v} \cdot \nabla \Lambda + \frac{\partial \Lambda}{\partial t} \right) = \mathcal{L} + \frac{e}{c} \frac{d\Lambda}{dt}.$$

The addition of a total time derivative to the Lagrangian does not modify the Hamilton principle and consequently the Euler-Lagrange equation of motion remains invariant.

In the passage to quantum mechanics it is useful to go to the Hamiltonian formalism, by introducing the conjugate momentum,

$$\mathbf{p} = \frac{\partial \mathcal{L}}{\partial \mathbf{v}} = m \mathbf{v} + \frac{e}{c} \mathbf{A} \quad \Rightarrow \quad m \mathbf{v} = \mathbf{p} - \frac{e}{c} \mathbf{A}. \quad (14.4)$$

The Hamiltonian is

$$H = \mathbf{p} \cdot \mathbf{v} - \mathcal{L} = \frac{1}{2m} \left(\mathbf{p} - \frac{e}{c} \mathbf{A} \right)^2 + e \Phi. \quad (14.5)$$

Formally, this Hamiltonian can be obtained from the one without external fields by a substitution

$$H \rightarrow H + e \Phi \quad \mathbf{p} \rightarrow \mathbf{p} - \frac{e}{c} \mathbf{A}, \quad (14.6)$$

known as *minimal substitution*. Note that the canonical momentum \mathbf{p} is not a mechanical momentum $m \mathbf{v}$; see eqn (14.4). In the Hamiltonian formalism the change of gauge (14.3) yields

$$H = \frac{1}{2m} \left(\mathbf{p} - \frac{e}{c} \mathbf{A} - \frac{e}{c} \nabla \Lambda \right)^2 + e \Phi - \frac{e}{c} \frac{\partial \Lambda}{\partial t}.$$

This change can be reabsorbed by a canonical transformation, which is, in general, dependent on time,

$$\mathbf{p}' = \mathbf{p} - \frac{e}{c} \nabla \Lambda \quad \mathbf{x}' = \mathbf{x} \quad H' = H + \frac{e}{c} \frac{\partial \Lambda}{\partial t}.$$

A way to verify that the above is a canonical transformation is to observe that the Poincaré-Cartan form vary by a total time derivative:

$$\mathbf{p}' d\mathbf{x}' - H' dt = \mathbf{p} d\mathbf{x} - H dt - \frac{e}{c} \nabla \Lambda \cdot d\mathbf{x} - \frac{e}{c} \frac{\partial \Lambda}{\partial t} dt = \mathbf{p} d\mathbf{x} - H dt - \frac{e}{c} d\Lambda.$$

The minimal action principle

$$\delta \int (\mathbf{p} d\mathbf{x} - H dt) = 0$$

then remains invariant, and so do the Poisson parentheses.

¹The other two Maxwell equations can be considered the equations for the scalar and vector potential, in terms of the sources; however, in a fully dynamical situation, the charged particles and the electromagnetic field exert influence upon each other. Here we consider the effects of a prescribed external field on the charged particles.

14.1.2 Quantum particles in electromagnetic fields

In quantum mechanics the interaction is described by the same Hamiltonian, eqn (14.5), obtained by the minimal coupling, eqn (14.6). In the Schrödinger representation

$$\frac{\hbar}{i} \nabla \rightarrow \frac{\hbar}{i} \nabla - \frac{e}{c} \mathbf{A} \quad i\hbar \frac{\partial}{\partial t} \rightarrow i\hbar \frac{\partial}{\partial t} - e\Phi, \quad (14.7)$$

and Schrödinger's equation has the form

$$\begin{aligned} i\hbar \frac{\partial \psi}{\partial t} &= \frac{1}{2m} \left(\frac{\hbar}{i} \nabla - \frac{e}{c} \mathbf{A} \right)^2 \psi + e\Phi \psi \equiv H \psi, \\ H &= \frac{1}{2m} \left(\mathbf{p} - \frac{e}{c} \mathbf{A} \right)^2 + e\Phi. \end{aligned} \quad (14.8)$$

In what follows we shall continue to use the symbol $\mathbf{p} = -i\hbar\nabla$: this is the operator satisfying the canonical commutator

$$[x_i, p_j] = i\hbar \delta_{ij} \quad [p_i, p_j] = 0.$$

The Hamiltonian (14.8) is Hermitian; in particular note that the vector potential enters the Hamiltonian automatically in the symmetrized (Weyl) form, $\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}$.

Let us now discuss physical observables associated with the electromagnetic interactions. In accordance with the fact that $|\psi|^2$ represents the probability density of the particle, $\rho = e|\psi|^2$ represents the charge (probability) density. Sometimes it is useful to introduce an operator $\hat{\rho}(\mathbf{y})$ which describes the charge density at a given point \mathbf{y} : for a system of n particles, we have

$$\hat{\rho}(\mathbf{y}; \mathbf{x}_1 \dots \mathbf{x}_n) = \sum_i e_i \delta(\mathbf{y} - \mathbf{x}_i).$$

For a single particle the expectation value of this operator reproduces the expected result:

$$\langle \psi | \hat{\rho}(\mathbf{y}) | \psi \rangle = e|\psi(\mathbf{y})|^2 \equiv \rho(\mathbf{y}).$$

As for the charge current density, it is given by

$$\mathbf{j} = i \frac{e\hbar}{2m} [(\nabla\psi)^* \psi - \psi^*(\nabla\psi)] - \frac{e^2}{mc} \mathbf{A} |\psi|^2. \quad (14.9)$$

This can be obtained, apart from the factor e , from the standard probability current density of the particle, by the minimal substitution (14.7). It is easily verified that the current density satisfies the continuity equation

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \mathbf{j} = 0;$$

it is, however, instructive to find eqn (14.9) in another way. The current density is defined by the variation of the energy induced by an infinitesimal change of \mathbf{A}

$$\delta H = -\frac{1}{c} \int \mathbf{j} \delta \mathbf{A} d^3x \quad \Rightarrow \quad \frac{\delta H}{\delta \mathbf{A}(\mathbf{x})} = -\frac{1}{c} \mathbf{j}(\mathbf{x}). \quad (14.10)$$

In a generic state then, to first order in $\delta\mathbf{A}$,

$$\begin{aligned}\delta H &= - \int d^3x \frac{e}{2mc} \psi^* (\mathbf{p}\delta\mathbf{A} + \delta\mathbf{A}\mathbf{p}) \psi + \frac{e^2}{mc^2} \int d^3x \delta\mathbf{A}(\mathbf{A}|\psi|^2) \\ &= \int d^3x \frac{i\hbar e}{2mc} \psi^* (\nabla(\delta\mathbf{A}\psi) + \delta\mathbf{A}\nabla\psi) + \frac{e^2}{mc^2} \int d^3x \delta\mathbf{A}(\mathbf{A}|\psi|^2).\end{aligned}$$

Integrating by parts the first term to bring the variation into the form of eqn (14.10), we find that

$$\delta H = - \int d^3x \delta\mathbf{A} \left(\frac{i\hbar e}{2mc} ((\nabla\psi)^*\psi - \psi^*(\nabla\psi)) - \frac{e^2}{mc^2} \mathbf{A}|\psi|^2 \right), \quad (14.11)$$

from which eqn (14.9) follows.

In the case of a particle with spin, the wave function has $2s+1$ components. The spin is an axial vector, as an orbital angular momentum, and such a particle can in general carry a characteristic magnetic moment, μ ,

$$\boldsymbol{\mu} = \mu \frac{\mathbf{s}}{s},$$

besides the mass m and the electric charge, e . The Hamiltonian contains an extra term as a consequence,

$$H = \frac{1}{2m} \left(\frac{\hbar}{i} \nabla - \frac{e}{c} \mathbf{A} \right)^2 \psi + e\Phi - \boldsymbol{\mu} \cdot \mathbf{B}. \quad (14.12)$$

As the spin is quantized in units of $\frac{\hbar}{2}$, and as the classical motion of a charged particle produces a magnetic moment $(e/mc)\ell$, where ℓ is the orbital angular momentum, it is quite natural that all the known elementary particles carry magnetic moments of the order of $e\hbar/mc$. In particular, for the electron and for the nucleon (proton and neutron) the typical magnitudes of their magnetic moments are given by the so-called Bohr and nuclear magnetons, respectively,

$$\mu_B \equiv \frac{|e|\hbar}{2m_e c}, \quad \mu_N \equiv \frac{|e|\hbar}{2m_p c}. \quad (14.13)$$

In these units, the measured electron, proton, and neutron magnetic moments are

$$\mu_e \simeq 1.001 \mu_B; \quad \mu_p \simeq 2.79 \mu_N; \quad \mu_n \simeq -1.91 \mu_N. \quad (14.14)$$

By using the same procedure which led to eqn (14.11) one finds the current density in this case,

$$\mathbf{j} = i \frac{e\hbar}{2m} [(\nabla\psi)^*\psi - \psi^*(\nabla\psi)] - \frac{e^2}{mc} \mathbf{A}|\psi|^2 + c\nabla \times (\psi^* \boldsymbol{\mu} \psi).$$

Gauge invariance

The way the electromagnetic interactions are introduced through minimal coupling, clearly shows the central role played by the vector and

scalar potentials, Φ, \mathbf{A} , in quantum mechanical systems. However, these quantities are defined only up to a gauge transformation: physics must be invariant under such a transformation.

Under a gauge transformation

$$\mathbf{A} \rightarrow \mathbf{A}' = \mathbf{A} + \nabla\Lambda ; \quad \Phi \rightarrow \Phi' = \Phi - \frac{1}{c} \frac{\partial\Lambda}{\partial t} .$$

the Hamiltonian (14.8) is transformed to

$$\begin{aligned} H_\Lambda &= \frac{1}{2m} \left(\frac{\hbar}{i} \nabla - \frac{e}{c} \mathbf{A}' \right)^2 + e\Phi' \\ &= \frac{1}{2m} \left(\frac{\hbar}{i} \nabla - \frac{e}{c} \mathbf{A} - \frac{e}{c} \nabla\Lambda \right)^2 + e\Phi - \frac{e}{c} \frac{\partial\Lambda}{\partial t} . \end{aligned}$$

Schrödinger's equation for the original system, $i\hbar \frac{\partial\psi}{\partial t} = H\psi$, is clearly not invariant under such a change of the Hamiltonian. How can we ascertain that the physical content of the modified equation is the same as the original one?

The crucial step is to "gauge-transform" the wave function also as follows

$$\psi_\Lambda \equiv \exp \left(i \frac{e\Lambda}{\hbar c} \right) \psi .$$

Note that as $\Lambda = \Lambda(t, \mathbf{x})$ in general is a function of space-time, this is not a trivial change of phase typical of quantum mechanics. It is a space-time-dependent unitary transformation. Because

$$\begin{aligned} \frac{1}{2m} \left(\frac{\hbar}{i} \nabla - \frac{e}{c} \mathbf{A} - \frac{e}{c} \nabla\Lambda \right)^2 \psi_\Lambda &= e^{i\frac{e\Lambda}{\hbar c}} \frac{1}{2m} \left(\frac{\hbar}{i} \nabla - \frac{e}{c} \mathbf{A} \right)^2 \psi \equiv e^{i\frac{e\Lambda}{\hbar c}} H\psi , \\ i\hbar \frac{\partial\psi_\Lambda}{\partial t} &= e^{i\frac{e\Lambda}{\hbar c}} i\hbar \frac{\partial\psi}{\partial t} - \frac{e}{c} \frac{\partial\Lambda}{\partial t} e^{i\frac{e\Lambda}{\hbar c}} \psi = e^{i\frac{e\Lambda}{\hbar c}} H\psi - \frac{e}{c} \frac{\partial\Lambda}{\partial t} \psi_\Lambda . \end{aligned}$$

The new wave function satisfies the equation

$$i\hbar \frac{\partial\psi_\Lambda}{\partial t} = H_\Lambda \psi_\Lambda ,$$

as required.

14.1.3 Dipole and quadrupole interactions

Consider the electrostatic interaction energy of an ensemble of charged particles in an external field Φ :

$$U = \sum_i e_i \Phi(\mathbf{x}_i) \equiv \int d^3x \rho(\mathbf{x}) \Phi(\mathbf{x}) ; \quad \rho(\mathbf{x}) = \sum_i e_i \delta^3(\mathbf{x} - \mathbf{x}_i) . \quad (14.15)$$

When the external potential is slowly varying,

$$d|\nabla\Phi| \ll 1 ,$$

where d is the linear dimension of the whole volume, it may be expanded as

$$\Phi(\mathbf{x}) \simeq \Phi(0) + \partial_i \Phi(0) + \frac{1}{2} \xi_i \xi_j \partial_i \partial_j \Phi(0) + \dots,$$

where O is some reference point in the volume.

Substituting into eqn (14.15) and using the definition of the electric field, $E_i = -\partial_i \Phi$, yields

$$U = \int d^3 \xi \rho(\xi) \left[\Phi - \mathbf{\xi} \cdot \mathbf{E} + \frac{1}{2} \xi_i \xi_j \partial_i \partial_j \Phi + \dots \right]. \quad (14.16)$$

Let us discuss various terms separately.

Charge

The first term is

$$\int d^3 \xi \rho(\xi) \Phi = \sum_i e_i \Phi = Q \Phi; \quad (14.17)$$

Q is the total charge of the system. Equation (14.17) is the electrostatic potential energy of the system, treated as a whole.

Dipole

The second term can be written as

$$-\mathbf{E} \cdot \int d^3 \xi \rho(\xi) = -\mathbf{E} \cdot \sum_a e_a \mathbf{\xi}_a.$$

The operator

$$\mathbf{d} = \sum_a e_a \mathbf{\xi}_a \quad (14.18)$$

is called the *dipole moment* of the system, or simply the dipole. Definition (14.18) is invariant under space translation of the whole system, only if the total charge is zero.

The dipole is a polar vector: under parity, it changes sign $P \mathbf{d} P^{-1} = -\mathbf{d}$. This leads to the following selection rules:

- (1) If the Hamiltonian is invariant under parity, each (non-degenerate) state is an eigenstate of it, $P|\psi\rangle = \eta_P |\psi\rangle$, where η_P is a phase. Then

$$\langle \psi | \mathbf{d} | \psi \rangle = \langle \psi | P^\dagger P \mathbf{d} P^{-1} P | \psi \rangle = -|\eta_P|^2 \langle \psi | \mathbf{d} | \psi \rangle = -\langle \psi | \mathbf{d} | \psi \rangle = 0.$$

Thus the expectation value of \mathbf{d} vanishes. The permanent dipole of a non-degenerate atom is always strictly zero. In Chapter 9, we have seen how a system with nearly degenerate levels can effectively acquire a dipole moment.

- (2) The dipole operator has non-vanishing matrix elements only between states of opposite parities.

- (3) As the dipole is a vector, the Wigner–Eckart theorem implies that non-vanishing matrix elements occur only between two states with J differing at most by unity. The transition $0 \rightarrow 0$ is forbidden. The allowed matrix elements are of the forms

$$J' = J, J \pm 1 \quad 0 \not\rightarrow 0$$

$$\begin{array}{lll} d_z & \langle J', J'_z | d_z | J, J_z \rangle & J'_z = J_z \\ d_+ = d_x + id_y & \langle J', J'_z | d_+ | J, J_z \rangle & J'_z = J_z + 1 \\ d_- = d_x - id_y & \langle J', J'_z | d_- | J, J_z \rangle & J'_z = J_z - 1 \end{array}$$

Quadrupole

The sources of the external field are assumed to be positioned outside the region occupied by the charges, so that $\nabla^2\Phi = 0$; the third term of eqn (14.16) can be rewritten as

$$\frac{1}{6} \sum_a e_a \left(3 \xi_i^{(a)} \xi_j^{(a)} - (\xi^{(a)})^2 \delta_{ij} \right) \partial_i \partial_j \Phi .$$

The tensor

$$Q_{ij} = \sum_a e_a \left(3 \xi_i^{(a)} \xi_j^{(a)} - (\xi^{(a)})^2 \delta_{ij} \right) \quad (14.19)$$

is called *quadrupole moment*. Q_{ij} is a symmetric tensor with vanishing trace, and so transform like angular momentum $J = 2$. It is even under parity. Also for quadrupole moments one can easily find the following selection rules:

- (1) Q_{ij} has non-vanishing matrix elements only between two states of the same parity.
- (2) The relation

$$|J - 2| \leq J' \leq J + 2$$

must be satisfied for the initial and final angular momenta J, J' .

- (3) The components of Q_{ij} can be arranged as spherical tensors, which have the same properties as Y_{2m} ; in particular, $J'_z = J_z$ for a transition with Q_{zz} .

The Wigner–Eckart theorem ensures that within a given multiplet of angular momentum ($|J, J_z\rangle$), the matrix elements of Q_{ij} can be rewritten as

$$Q_{ij} \rightarrow \frac{3 Q_J}{2J(2J-1)} \left(J_i J_j + J_j J_i - \frac{2}{3} \mathbf{J}^2 \delta_{ij} \right) . \quad (14.20)$$

The coefficient Q_J , which coincides with the expectation value of Q_{zz} in the state $|J, J_z = J\rangle$, is what is normally called the quadrupole moment.

14.1.4 Magnetic interactions

Let us now consider the effect of a constant magnetic field in eqn (14.1). The gauge can be chosen such that

$$\mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r} ;$$

substitution of this into eqn (14.1) gives (in the gauge $\nabla \cdot \mathbf{A} = 0$)

$$H = \frac{1}{2m} \mathbf{p}^2 - \frac{e}{mc} (\mathbf{B} \times \mathbf{r}) \cdot \mathbf{p} + \frac{e^2}{8mc^2} (\mathbf{B} \times \mathbf{r})^2 + e\Phi - \mu \cdot \mathbf{B} .$$

By making use of the cyclic property of the triple product among vectors, and by introducing the angular momentum $\ell = \mathbf{r} \times \mathbf{p}$, H can be rewritten as

$$H = \frac{1}{2m} \mathbf{p}^2 - \frac{e}{2mc} \ell \cdot \mathbf{B} + \frac{e^2}{8mc^2} (\mathbf{B} \times \mathbf{r})^2 + e\Phi - \mu \cdot \mathbf{B} . \quad (14.21)$$

² One might worry about the fact that not all charged particles of spin- $\frac{1}{2}$ have gyromagnetic ratio 2: for instance the proton has $g \sim 5.6$. There are also neutral spin- $\frac{1}{2}$ particles, such as the neutron, with a magnetic moment ($g \sim -3.8$). Today, these discrepancies are understood as being due to the composite structure of these particles. On the other hand, for more “elementary” particles such as the electron and the muon, the agreement between theory and experiment goes far beyond the success of Dirac’s prediction. The experimental value for g for the electron or muon is very slightly different from 2. In the context of the standard model (the Weinberg–Salam theory for electroweak interactions and quantum chromodynamics for strong interactions), the correction to Dirac’s value of 2 is calculable, and as of today, the theoretical prediction for the muon anomalous gyromagnetic ratio is ($a \equiv \frac{g_\mu - 2}{2}$)

$$a_\mu^{th} = (116\,591\,858 \pm 0.78) \times 10^{-11} ,$$

to be compared with the experimental data

$$a_\mu^{exp} = (116\,592\,080 \pm 1.0) \times 10^{-11} .$$

The agreement is good within $O(10^{-9})$; this is one of the best tests of the standard model at present. (Review of Particle Physics, W.-M. Yao et al., J. Phys. G 33, 1 (2006))

In general the term linear in the magnetic field describes the magnetic moment of the system; therefore eqn (14.21) assigns an “orbital” magnetic moment to the electron, $\frac{e}{2mc}\ell$, in agreement with the classical theory (where this result is known as Larmor’s theorem). As for the last term, the electron has an intrinsic magnetic moment, eqns (14.13), (14.14), i.e.,

$$\mu = g \frac{e}{2mc} \mathbf{s} ,$$

where g is a quantity known as the gyromagnetic ratio. Experimentally,

$$g \sim 2 , \quad (14.22)$$

to a good approximation. The total term proportional to \mathbf{B} is then

$$H_I = -\frac{e}{2mc} (\ell + g\mathbf{s}) \cdot \mathbf{B} . \quad (14.23)$$

One of the great successes of relativistic quantum theory for the electron due to Dirac (Dirac’s equation) has been that of precisely predicting the value $g = 2$ (see eqn (17.19)).²

14.1.5 Relativistic corrections: LS coupling

We study now what further modifications should be made to eqn (14.1) due to the presence of spin. In an atom, classically, the electron encircles the orbit with velocity \mathbf{v} under the influence of the Coulomb electric field \mathbf{E} produced by the nucleus. In the rest frame of the electron, therefore, the electron feels the induced magnetic field $\mathbf{B}' = \mathbf{E} \times \frac{\mathbf{v}}{c}$, assuming that $v/c \ll 1$. We expect therefore an interaction of the type

$$H_I = -g \frac{e}{2mc} \mathbf{s} \cdot \left(\mathbf{E} \times \frac{\mathbf{v}}{c} \right) . \quad (14.24)$$

Actually this kind of argument does not properly take into account the fact that the rest frame of the electron is not an inertial frame. The correct treatment gives eqn (14.24) with g replaced with $g - 1$. This effect is known as *Thomas precession*.

In the particular case in which $g = 2$, Thomas precession halves the coupling. Let us write the interaction as

$$H_I = -(g-1) \frac{e}{2mc} \mathbf{s} \cdot \left(\mathbf{E} \times \frac{\mathbf{v}}{c} \right) = -(g-1) \frac{e}{2m^2 c^2} \mathbf{s} \cdot (\mathbf{E} \times \mathbf{p}) .$$

For a spherically symmetric potential Φ , as in atoms, one has

$$\mathbf{E} = -\nabla\Phi = -\frac{1}{r} \frac{d\Phi}{dr} \mathbf{r} ,$$

and the interactions take the form

$$H_I = (g-1) \frac{e}{2m^2 c^2} \frac{1}{r} \frac{d\Phi}{dr} \mathbf{s} \cdot (\mathbf{r} \times \mathbf{p}) . \quad (14.25)$$

For a Coulomb field, $\Phi = Z|e|/r$. Remembering that the electron charge is $-|e|$, we see that

$$H_I = (g-1) \frac{e^2}{2m^2 c^2} \frac{Z}{r^3} \mathbf{s} \cdot \boldsymbol{\ell} . \quad (14.26)$$

Interactions (14.25), (14.26) are called *fine-structure interactions*, or *spin-orbit coupling*. Equation (14.25) shows that the correction to the Hamiltonian is of the order, $1/c^2$, i.e., the second order in the relativistic corrections. One factor $1/c$ comes from the magnetic interaction itself, and the factor v/c comes from the fact that the effect arises due to the electron in motion, and has arisen from the Lorentz transformation of \mathbf{E} . Interactions (14.25) are particularly interesting as, in the absence of external fields, they are the signal of how the existence of spin changes the dynamics of the system, and in particular the energy levels. For an energy level with well-defined quantum numbers L, S , the addition of interactions (14.25) will split the $(2L+1)(2S+1)$ degeneracy into sublevels with various J , $\mathbf{J} = \mathbf{L} + \mathbf{S}$. For instance, for the hydrogen atom, the level np will split into two levels corresponding to $J = \frac{1}{2}$ and $J = \frac{3}{2}$.

Expressing all the lengths in eqn (14.26) in terms of the Bohr radius $r_B = \hbar^2/me^2$ and writing $\boldsymbol{\ell} = \hbar\mathbf{L}$, $\mathbf{s} = \hbar\mathbf{S}$ one has

$$H_I = \left(\frac{e^2}{\hbar c} \right)^2 \frac{e^2}{r_B} \frac{Z}{2} (g-1) \frac{r_B^3}{r^3} \mathbf{L} \cdot \mathbf{S} .$$

The dimensionless constant

$$\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137}$$

(14.27)

is called the *fine structure constant* and determines the order of magnitude of the effect: the level splitting will be of the order of $\alpha^2 \sim 10^{-4}$

as compared with the ordinary level-spacing. The spectral lines will exhibit detailed (that is, fine) structures on top of the simple, Bohr-like structures.

For a system with many electrons, the interactions take the form

$$H_I = \sum_i \ell_i \cdot s_i , \quad (14.28)$$

where the radial terms for the i -th electron are indicated by f_i . Actually the situation is more complicated as each electron feels not only the Coulomb field of the nucleus but also that due to other electrons; the description such as eqn (14.28) will be appropriate for the effective, spherical potential for each electron, due to the averaging over the wave functions of the other electrons. In this case the total spin \mathbf{S} and orbital angular momentum \mathbf{L} will still commute with the Hamiltonian, as well as \mathbf{J} . By the Wigner-Eckart theorem operator (14.28) will have, in the subspace of the states with definite L, S , the form

$$H_I = A \mathbf{L} \cdot \mathbf{S} , \quad (14.29)$$

where A is a constant depending on the level considered. In general A can a priori have either sign: these questions will be discussed in Chapter 15.

14.1.6 Hyperfine interactions

If the nucleus has a spin, in general it will also possess a magnetic moment, μ_N . The magnetic moment of the nucleus is of the order of the nuclear magneton, $\mu_N = \frac{|e|\hbar}{2m_p c}$, where m_p is the mass of the proton; therefore it is about 2000 times smaller than the Bohr magneton. Let us briefly see how such an effect can be taken into account in the Hamiltonian for the atomic electrons.

We have seen in the preceding subsection that in the presence of an external magnetic field the interactions of an electron can be written, to the first order in the field, as

$$H_I = -\frac{e}{mc} \mathbf{A} \cdot \mathbf{p} - g \frac{e}{2mc} \mathbf{s} \cdot \mathbf{B} = -\frac{e}{mc} (\mathbf{A} \cdot \mathbf{p} + \mathbf{s} \cdot \mathbf{B}) .$$

In the last equality, we have set $g = 2$. The nuclear dipole μ_N generates a field,

$$\mathbf{A} = \frac{\mu_N \times \mathbf{r}}{r^3} \equiv -\mu_N \times \nabla \frac{1}{r} \quad \mathbf{B} = \nabla \times \mathbf{A} . \quad (14.30)$$

Calculation of the magnetic field requires a little care, to treat the singularity at $r = 0$ appropriately. In fact, one finds that

$$\mathbf{B} = -\nabla \times \left(\mu_N \times \nabla \frac{1}{r} \right) = -\mu_N \nabla^2 \frac{1}{r} + (\mu_N \cdot \nabla) \nabla \frac{1}{r} . \quad (14.31)$$

Consider the expression $\partial_i \partial_j (1/r)$: in general this presents singularities at $r = 0$, generically of the form of the delta function. In computing

the matrix elements the only wave functions which do not vanish at the origin are S wave functions, which are spherically symmetric, and thus the singular term takes the form

$$\partial_i \partial_j \frac{1}{r} = \left(\partial_i \partial_j \frac{1}{r} \right)_{\text{reg}} + c \delta_{ij} \delta^{(3)}(\mathbf{r}) = -\frac{1}{r^3} \left(\delta_{ij} - 3 \frac{x_i x_j}{r^2} \right) + c \delta_{ij} \delta^{(3)}(\mathbf{r}) .$$

By performing a trace and remembering that $\nabla^2(1/r) = -4\pi\delta^{(3)}(\mathbf{r})$ one finds thus $c = -4\pi/3$ and hence

$$\partial_i \partial_j \frac{1}{r} = -\frac{1}{r^3} \left(\delta_{ij} - 3 \frac{x_i x_j}{r^2} \right) - \frac{4\pi}{3} \delta^{(3)}(\mathbf{r}) .$$

Also writing the first term in eqn (14.31) explicitly we find that

$$\mathbf{B} = -[\mu_N - 3(\mu_N \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}] \frac{1}{r^3} + \frac{8\pi}{3} \mu_N \delta^{(3)}(\mathbf{r}) .$$

Use of eqn (14.30) finally gives

$$H_I = -\frac{e}{mc} \left(\frac{1}{r^3} \mu_N \cdot \ell \right) + \frac{e}{mc} \left\{ [\mu_N \cdot \mathbf{s} - 3(\mu_N \cdot \hat{\mathbf{r}})(\hat{\mathbf{r}} \cdot \mathbf{s})] \frac{1}{r^3} - \frac{8\pi}{3} \mu_N \cdot \mathbf{s} \delta^{(3)}(\mathbf{r}) \right\} .$$

To avoid confusion about the sign, let us write all the angular momenta in units of \hbar , writing $\mathbf{s} = \hbar \mathbf{S}$ etc., and introducing the gyromagnetic ratio for the nucleus,

$$\mu_N = g_N \frac{|e|\hbar}{2m_p c} \mathbf{S}_N .$$

We obtain, by taking into account the sign of the electron charge,

$$H_I = 2g_N |\mu_B \mu_N| \frac{1}{r^3} \mathbf{L} \cdot \mathbf{S}_N + 2g_N |\mu_B \mu_N| \left\{ \frac{1}{r^3} [3(\hat{\mathbf{r}} \cdot \mathbf{S}_N)(\hat{\mathbf{r}} \cdot \mathbf{S}) - \mathbf{S} \cdot \mathbf{S}_N] + \frac{8\pi}{3} \mathbf{S} \cdot \mathbf{S}_N \delta^{(3)}(\mathbf{r}) \right\} . \quad (14.32)$$

The first term does not contribute for S waves; the last term instead contributes only for S waves. The second term apparently contains a singularity $1/r^3$; actually it is non-singular. The orbital part is proportional to $X_{ij} = r^2 \delta_{ij} - 3x_i x_j$, that is, a symmetric and traceless tensor, which is a quadrupole. Consider a matrix element of $\langle a | X_{ij} | b \rangle$. If both of the states are in an S wave, it vanishes by the selection rule (the Wigner-Eckart theorem); at least one of the states must be in a P wave or higher. But then the product $\psi_a^* \psi_b$ vanishes as r^{1+k} $k \geq 0$. The radial part of the matrix element is then

$$\int r^2 dr \frac{1}{r^3} r^{1+k} ,$$

and is non-singular. If the parity selection rule is also taken into account, the $S - P$ matrix elements vanish, so the exponent k is actually even larger than 1.

14.2 The Aharonov–Bohm effect

One effect which is surprising from the classical point of view but which nicely illustrates the nature of electromagnetism in quantum mechanics as mentioned at the beginning of this chapter is the so-called *Aharonov–Bohm effect*, discovered in 1959 [Aharonov and Bohm (1959)], 30 years after the formulation of quantum mechanics. In spite of the fact that its (theoretical) correctness and experimental verification were soon widely accepted, some subtle doubts lingered. Its definite experimental confirmation came only in the year 1986 (!), thanks to the experiments of Tonomura et al. [Tonomura (1986)], [Tonomura (2000)].

Consider the double-slit experiment à la Young, made with an electron beam, discussed in Chapter 1 (Figure 14.1). Remember that the wave function can be approximated by

$$\psi = \psi_1 + \psi_2, \quad (14.33)$$

where ψ_1 and ψ_2 are the components of the wave function which pass respectively to the upper and lower parts of the figure. The difference in the optical paths between the two components produces a phase difference

$$\Delta\phi = \frac{2\pi}{\lambda} \Delta\ell \quad \Delta\ell = \frac{2xd}{L}, \quad (14.34)$$

causing the typical Young's interference fringes on the screen, due to the interference term in $|\psi|^2 = |\psi_1 + \psi_2|^2$. As was emphasized in Chapter 1 the crucial fact is that the interference fringe pattern is observed in an experimental set up, such that the electrons arrive one by one, with no obvious correlations among them. The wave character is to be attributed to the behavior of individual electrons.

In the Aharonov–Bohm set up, the double-slit experiment is done with the addition of an infinitely long solenoid, stationed just behind the double slit, as in Figure 14.1. The idea is that in an idealized solenoid, the magnetic field is entirely contained inside it, and vanishes everywhere outside. If the electron does not pass through the region with the solenoid, then according to classical mechanics there should be no effect whatsoever from the presence of the solenoid.

Quantum mechanically the situation is very different. Outside the solenoid, the vector potential is nonzero: $\mathbf{A} \neq 0$. The term ψ_1 in eqn (14.33) refers to the propagation of the wave in the upper region of the figure, and in this region the effect of the vector potential is to modify the wave function by a phase

$$\psi_1(\mathbf{r}) \rightarrow \exp\left(i \frac{e}{\hbar c} \int_1^{\mathbf{r}} \mathbf{A} \cdot d\mathbf{x}\right) \psi_1(\mathbf{r}).$$

where \int_1 is along some path from (for instance) the source point to \mathbf{r} . The line integral does not depend on the path chosen as long as we remain on the same side of the solenoid (a simply connected region), for the difference is proportional to

$$\int_1 \mathbf{A} \cdot d\mathbf{x} - \int_{1'} \mathbf{A} \cdot d\mathbf{x} = \int_s d\mathbf{S} \cdot (\nabla \times \mathbf{A}) = \int_s d\mathbf{S} \cdot \mathbf{B} = 0.$$

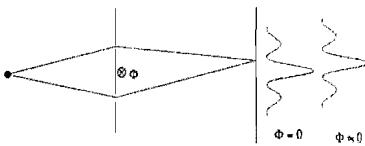


Fig. 14.1 The Aharonov–Bohm experiment.

(see Figure 14.2).

Analogously the component ψ_2 gets modified by

$$\psi_2 \rightarrow \exp\left(i \frac{e}{\hbar c} \int_2^r \mathbf{A} \cdot d\mathbf{x}\right) \psi_2.$$

We then find that the two components of the wave function acquired the phase difference

$$\frac{e}{\hbar c} \int_1^r \mathbf{A} \cdot d\mathbf{x} - \frac{e}{\hbar c} \int_2^r \mathbf{A} \cdot d\mathbf{x} = \frac{e}{\hbar c} \oint \mathbf{A} \cdot d\mathbf{x} = \frac{e}{\hbar c} \Phi,$$

as this time the difference between the two paths encloses the solenoid. Consequently, the phase difference (14.34) gets an additional term,

$$\Delta\phi = \Delta\phi|_{\Phi=0} + \frac{e}{\hbar c} \Phi, \quad (14.35)$$

and as a result the interference fringe pattern will be *shifted* by the amount

$$\delta x = \frac{e \lambda L \Phi}{4\pi c \hbar d},$$

modulated by the flux through the solenoid. For

$$\frac{e}{\hbar c} \Phi = 2n\pi \quad (14.36)$$

the effect should disappear.

The shift of the fringes clearly shows the physical relevance of the vector potential, but it should be noted that \mathbf{A} appears only through the combination

$$\oint \mathbf{A} \cdot d\mathbf{x} = \int d\mathbf{S} \cdot (\nabla \times \mathbf{A}) = \int d\mathbf{S} \cdot \mathbf{B} = \Phi$$

which is gauge invariant, and only in the phase factor.

It is of the utmost importance to appreciate the fact that the effect is indeed gauge invariant yet it cannot be described locally in terms of the magnetic field \mathbf{B} : along the paths taken by the electron \mathbf{B} is everywhere zero. The effectively nontrivial global structure of the space (which was rendered multiply connected by the presence of the solenoid) is essential.

Quite comprehensively, the correctness of the effect, even if the first experiments gave evidence for it, was not accepted immediately by everybody. In spite of the fact that the Aharonov and Bohm's argument was thoroughly compelling, and so was its experimental verification, there remained certain subtle points, both experimental and theoretical, which kept some people wondering whether the observed effect might be explained in some alternative fashion. The final word on the debate was given only quite recently (1986), by a series of beautiful experiments, performed by Tonomura et al.

The debate arose from the following aspects concerning the Aharonov-Bohm experiment. First of all, in quantum mechanics the electron is described by an extended wave function, and it is difficult to completely

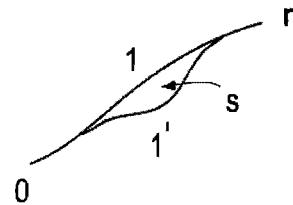


Fig. 14.2

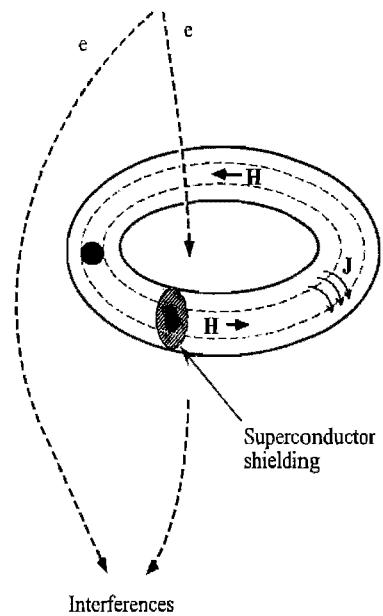


Fig. 14.3 A schematic view of the experiments by Tonomura et.al. (the superconductor "torus" of Figure 14.6 below corresponds to a section (slice) of this double torus).

exclude the possibility that the electron penetrates inside the solenoid. Another experimental subtlety is that a solenoid is never truly infinitely long, and consequently some leakage of the magnetic field outside the solenoid is unavoidable. From a theoretical point of view, it might be possible to choose a gauge so that in the equation only the magnetic field \mathbf{B} and its derivatives appear, instead of \mathbf{A} (the Schwinger gauge). If such a gauge were a “good gauge”, there should not be any effect, assuming that the electron does not pass appreciably into the region where the magnetic field is present. Any observed effect would have to be attributed to some imperfection of the experimental setup.

This last theoretical objection can be argued away, noting that a gauge in which the vector potential is eliminated in favor of \mathbf{B} and its derivatives is necessarily singular, and hence not acceptable.

The first, experimental objections are more insidious. The brilliant idea which allowed the Tonomura's group [Tonomura (1986)], [Tonomura (2000)], following a suggestion by C. N. Yang, to obviate all the objections raised, was that of completely covering small toroidal magnets by a layer of niobium, which becomes superconducting at temperatures below $T_c = 9.2\text{ K}$. See Figure 14.3. Subsection 14.2.1 briefly reviews the most salient features of superconductivity and of the phenomenon of flux quantization.

Letting the beam of electrons pass partially inside the torus and partially outside, and observing the interference fringe, Tonomura and others confirmed the Aharonov–Bohm effect. See Figure 14.4. But the decisive observation is that the phase shift suddenly becomes either zero or π , when the layer of Nb becomes superconducting, as the temperature is brought below the critical value ($T_c = 9.2\text{K}$), while above T_c , $\Delta\phi$ is found to take a random value depending on the sample.

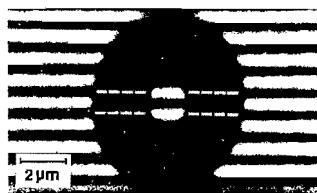


Fig. 14.4 Experimental verification of the Aharonov–Bohm effect (picture provided directly from Dr. A. Tonomura). For more details, see [Tonomura (1986)].

³Here the “torus” refers to a slice of the original torus, which itself has the topology of a torus if only the niobium layer is considered. The quantized magnetic flux thus runs along a circle, in the center of the original torus.

Remarks

- The magnetic field is contained inside the superconducting torus, and cannot leak out, due to the Meissner effect. The toroidal form of the magnet provides an ideal solenoid, without the ends.
- The electron is shielded by the external layer and cannot penetrate inside the ring.
- The magnetic flux inside a toroidal superconductor is quantized as follows³

$$\Phi_n = \frac{2\pi c \hbar}{q} n = \frac{\pi c \hbar}{e} n; \quad q = 2e, \quad n \in \mathbb{Z}.$$

Substituting this into eqn (14.35) we find that the shift of the phase is a multiple of π , as has been observed experimentally. Note the crucial factor 2 between the charge of the Cooper pair ($q = 2e$) and that of the electron.

- The experiment by Tonomura et al. thus kills two birds with one stone: it is a confirmation both of flux quantization and of the Aharonov–Bohm effect.

- As already noted, in the whole discussion the fact that the space is effectively made topologically nontrivial (non-simply connected) is the basic aspect which makes this effect observable.⁴

14.2.1 Superconductors

Let us briefly review here some principal aspects of superconductivity in metals at extremely low temperatures. The electrons in a metal interact through the exchange of phonons (excitation quanta of the crystalline lattices) and form a weakly bound state (a Cooper pair). At extremely low temperatures (below a critical temperature, which depends on the material) the Cooper pairs condense and are described by a sort of macroscopic wave function, Ψ . The discussion below follows that of [Feynman, Leighton, and Sands (2005)].

Maxwell's equation and the macroscopic density are given by the equations⁵

$$\begin{aligned} \nabla \times \mathbf{B} &= \frac{4\pi}{c} \mathbf{j}, \quad \mathbf{B} = \nabla \times \mathbf{A}; \\ \mathbf{j} &= q \frac{1}{4m} \left[\Psi^* \left(\mathbf{p} - \frac{q}{c} \mathbf{A} \right) \Psi - \left\{ \left(\mathbf{p} - \frac{q}{c} \mathbf{A} \right) \Psi \right\}^* \Psi \right], \end{aligned} \quad (14.37)$$

We have called $q = -2|e|$ the charge of the Cooper pair. m is the electron mass, so $2m$ is the mass of the Cooper pair. In general, the wave function Ψ can be written in the form

$$\Psi = \sqrt{\rho} e^{i\theta}, \quad \rho(\mathbf{r}) = \Psi^* \Psi \neq 0.$$

The superconducting state can be characterized by a constant non-vanishing density $\rho = \text{const.} \neq 0$. Such a state is called the condensation of the Cooper pair.

The current (14.37) can then be written as

$$\mathbf{j} = \frac{q\rho}{2m} \left(\hbar \nabla \theta - \frac{q}{c} \mathbf{A} \right).$$

The equation of continuity then implies that $\nabla \cdot \mathbf{j} = 0$, i.e.,

$$\nabla^2 \theta = 0, \quad (14.38)$$

where the gauge $\nabla \cdot \mathbf{A} = 0$ has been used. Inside the volume of the superconductor, eqn (14.38) implies that

$$\theta = \text{const.}$$

The relation

$$\mathbf{j} = -\frac{q^2 \rho}{2mc} \mathbf{A},$$

known as London's equation, follows. Maxwell's equation for the field $\mathbf{B} = \nabla \times \mathbf{A}$ gives

$$\nabla^2 \mathbf{A} = -\frac{4\pi}{c} \mathbf{j} = \frac{2\pi \rho q^2}{mc^2} \mathbf{A} \equiv \lambda^{-2} \mathbf{A}. \quad (14.39)$$

⁴In a more precise mathematical language we say that the reduced space has a nontrivial fundamental group—the first homotopy group— $\pi_1(\mathbb{R}^3/R) \sim \pi_1(S) = \mathbb{Z}$.

⁵Weakly coupled identical bosons tend to occupy the same quantum state. At temperatures below the critical temperature, a macroscopic number of bosons occupy the fundamental and lowest-lying states (Bose-Einstein condensation). The system is described by the distribution of the occupation number $d(\mathbf{p})$ or its Fourier transform, $\Psi(\mathbf{r})$. $|\Psi(\mathbf{r})|^2$ then represents the real density of particles, and no longer the probability density.

We now consider the surface of a superconductor, schematized as a plane $z = 0$ (the metal body occupies the region $z > 0$) the solution of eqn (14.39) has the form

$$\mathbf{A} = A_0 e^{-z/\lambda}, \quad \lambda = \left(\frac{2\pi\rho q^2}{mc^2} \right)^{-1/2}. \quad (14.40)$$

Equation (14.40) means that the magnetic field is strongly damped in a superconducting medium: \mathbf{B} can penetrate into the body of the superconductor only to a depth of λ , called the London penetration length. With the parameters appropriate for the lead, for instance, and assuming that each atom provides one conduction electron, $\rho \sim 3 \times 10^{22} / \text{cm}^{-3}$, one finds that

$$\lambda \sim \sqrt{\frac{1}{8\pi} \frac{mc^2}{e^2} \frac{1}{10^{22}}} \sim \sqrt{\frac{1}{25} \frac{1}{3 \times 10^{-13}} \frac{1}{10^{22}}} \sim O(10^{-5}) \text{ cm}.$$

This phenomenon, that the magnetic field is expelled from the interior of the superconductor, is known as the *Meissner effect*.⁶

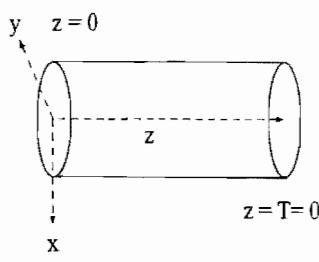


Fig. 14.5 Coordinates of the torus. The surface $z = T$ is identified with that at $z = 0$.

Flux quantization Something very interesting happens when the superconducting material has the form of a torus. As z , where z is the coordinate along the circle of the torus (Figure 14.5), is an angular variable, eqn (14.38) now admits a nontrivial solution,

$$\theta(x, y, z) = cz, \quad c = \frac{2\pi n}{T}, \quad n \in \mathbb{Z}, \quad (14.41)$$

where T is the period, i.e., the perimeter of the circle.

In this case, $\mathbf{j} \neq \mathbf{A}$, but the relation

$$\nabla^2 \mathbf{j} = -\frac{\rho q}{2mc} \nabla^2 \mathbf{A} = \frac{1}{\lambda^2} \mathbf{j} \quad (14.42)$$

still holds. Equations (14.41) and (14.42) imply that the current \mathbf{j} in the direction of z circulate only on the surface of the torus, i.e., within a thin layer of the depth of the order of λ ; vice versa, in the interior of the torus we have $\mathbf{j} = 0$.

This last fact means that along the center circle of the torus (curve C in Figure 14.6)) the relation

$$\hbar \nabla \theta = \frac{q}{c} \mathbf{A}$$

holds, so that by integrating this along curve C one gets (eqn (14.41))

$$\frac{q}{c} \oint dx_i A_i = \hbar \int d\theta = 2\pi n \hbar.$$

The last equality follows from the requirement for single-valuedness of the wave function Ψ . On the other hand,

$$\oint dx_i A_i = \int d\mathbf{S} \cdot \nabla \times \mathbf{A} = \int d\mathbf{S} \cdot \mathbf{B} = \Phi :$$

$\oint dx_i A_i$ is equal to the magnetic flux trapped by the torus. It follows that the magnetic flux through the "hole" of the torus is quantized as follows:

$$\Phi = \frac{2\pi n c \hbar}{q}, \quad n \in \mathbb{Z}. \quad (14.43)$$

14.3 The Landau levels

Consider now an electron, or any charged particle, moving in a plane (xy), under the influence of an applied magnetic field in the perpendicular direction, z , $\mathbf{H} = (0, 0, B)$. The spectrum of this system has some extraordinary features. Neglecting the spin, one finds that the Hamiltonian is given by

$$H = \frac{\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2}{2m},$$

where \mathbf{A} is the vector potential.

Let us first take the gauge

$$\mathbf{A} = (-B y, 0, 0). \quad (14.44)$$

In this gauge the Hamiltonian is

$$H = \frac{\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2}{2m} = \frac{\left(p_x - \frac{eB}{c}y\right)^2}{2m} + \frac{p_y^2}{2m}.$$

As the operator p_x commutes with H , it is possible to construct the eigenstates of H in the basis of plane waves,

$$\Psi(x, y) = e^{ipx/\hbar} \psi(y),$$

where p is an arbitrary eigenvalue of p_x . Substituting this into Schrödinger's equation,

$$H \Psi(x, y) = E \Psi(x, y),$$

we get the equation for $\psi(y)$:

$$\left[\frac{p_y^2}{2m} + \frac{\left(\frac{eB}{c}y - p\right)^2}{2m} \right] \psi(y) = E \psi(y),$$

which is just the equation for a harmonic oscillator, with the Larmor frequency,

$$\omega = \frac{eB}{mc},$$

and with the center of oscillation at

$$y = y_0 = \frac{pc}{eB}. \quad (14.45)$$

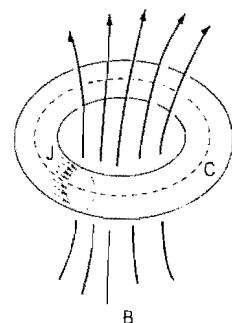


Fig. 14.6 A schematic view of a toroidal superconducting ring. The quantized flux is linked to the circumference C . Trapped magnetic flux is quantized.

The energy level is given by

$$E_n = \omega \hbar \left(n + \frac{1}{2} \right), \quad (14.46)$$

which is independent of p . This means that each oscillator level (14.46) is infinitely degenerate, with corresponding eigenstates

$$\Psi_{n,p}(x, y) = e^{ipx/\hbar} \psi_n(y), \quad (14.47)$$

where ψ_n is the normalized n -th harmonic oscillator eigenstate, (3.32). This level structure is known as *Landau levels*. The frequency $\omega = \frac{eB}{mc}$ corresponds to the circular, classical motion of a charged particle entering the uniform magnetic field \mathbf{B} ,

$$\frac{d}{dt} \mathbf{p} = \frac{e}{c} \mathbf{v} \times \mathbf{B}.$$

It is instructive to solve the spectrum by using another ("symmetric") gauge,

$$\mathbf{A} = \left(-\frac{By}{2}, \frac{Bx}{2}, 0 \right).$$

The Hamiltonian in this gauge is

$$H = \frac{(\mathbf{p} + \frac{e}{c}\mathbf{A})^2}{2m} = \frac{(p_x - \frac{eB}{2c}y)^2}{2m} + \frac{(p_y + \frac{eB}{2c}x)^2}{2m},$$

or by setting $\hbar = \frac{eB}{c} = m = 1$,

$$H = \frac{1}{2} \left(-i \frac{\partial}{\partial x} - \frac{y}{2} \right)^2 + \frac{1}{2} \left(-i \frac{\partial}{\partial y} + \frac{x}{2} \right)^2.$$

As often happens in a two-dimensional physical problem, both in classical and quantum mechanics, the introduction of complex coordinates turns out to be a powerful way to solve the problem. In fact, make the change of variables

$$z \equiv x + iy, \quad \bar{z} \equiv x - iy;$$

$$\partial_z = \frac{1}{2}(\partial_x - i\partial_y), \quad \partial_{\bar{z}} = \frac{1}{2}(\partial_x + i\partial_y),$$

($\partial_z \equiv \frac{\partial}{\partial z}$, etc). One finds that

$$[z, \partial_z] = [\bar{z}, \partial_{\bar{z}}] = -1, \quad [\bar{z}, \partial_z] = [z, \partial_{\bar{z}}] = 0.$$

Let us furthermore define the creation and annihilation operators by

$$a \equiv \sqrt{2} \left(\frac{\partial}{\partial z} + \frac{\bar{z}}{4} \right), \quad a^\dagger \equiv \sqrt{2} \left(-\frac{\partial}{\partial \bar{z}} + \frac{z}{4} \right),$$

which satisfy the usual commutation relation,

$$[a, a^\dagger] = 1.$$

A simple calculation shows that the Hamiltonian becomes

$$H = -2 \partial_z \partial_{\bar{z}} + \frac{z \bar{z}}{8} + \bar{z} \partial_z - z \partial_{\bar{z}} = \frac{1}{2}(a^\dagger a + a a^\dagger) = a^\dagger a + \frac{1}{2},$$

which is nothing but the harmonic oscillator Hamiltonian. The Landau levels (eqn (14.46)) follow immediately. The ground state is defined by

$$a \psi_0 = 0 :$$

it has an infinite number of solutions,

$$\psi_{0,m} = C_m \bar{z}^m e^{-\frac{1}{4}\bar{z}^2} = C_m (x - iy)^m e^{-\frac{1}{4}(x^2+y^2)}, \quad m = 0, 1, 2, \dots,$$

all with $E_0 = \frac{\omega \hbar}{2}$. These states are distinguished by the angular momentum

$$L = -i(x \partial_y - y \partial_x), \quad L \psi_{0,m} = m \psi_{0,m}$$

(note that L is the only component of the angular moment for a particle moving in a plane). L commutes with H .⁷

The excited states can be constructed by making a^\dagger act repeatedly on each of the ground state function $\psi_{0,m}$:

$$\psi_{N,m} = \frac{1}{\sqrt{N!}}(a^\dagger)^N \psi_{0,m}, \quad m = 0, 1, 2, \dots, \quad N = 0, 1, 2, \dots \quad (14.48)$$

It is interesting that in the stationary states found in this gauge, the electron is localized both in x and in y , while those in the asymmetric gauge (14.47) are localized only in one direction.

⁷The single-valuedness of the wave function requires m to be an integer. The regularity at the origin excludes the negative values for m .

14.3.1 The quantum Hall effect

A remarkable phenomenon, called the quantum Hall effect, was discovered in 1980, by von Klitzing, Dorda, and Pepper. Under certain conditions, the electrons moving in an effectively two-dimensional (xy) piece of material, subject to a strong perpendicular magnetic field, and to a weak electric field in the plane, lead to a conductivity tensor of the form

$$\sigma = \begin{pmatrix} 0 & -\frac{n e^2}{h} \\ \frac{n e^2}{h} & 0 \end{pmatrix},$$

where $h = 2\pi\hbar$ is Planck's constant, e is the electron charge, and n is a small integer. The diagonal conductivity vanishes and the current is in a perpendicular direction to the electric field: it is a dissipationless process. The non-diagonal conductivity is quantized in units of $\frac{e^2}{h}$ to an extremely high precision.

In a finite rectangular piece of material, $0 \leq x \leq L, 0 \leq y \leq W$, each Landau level can contain only a finite number of electrons. To see this, let us impose a periodic condition

$$\psi(x + L, y) = \psi(x, y),$$

working in the gauge (14.44). The momentum p is now quantized and takes values $p = 2\pi\hbar n/L$ only. As the eigenstates are localized in the y direction, with the oscillator centered at $y = y_0 = \frac{pc}{eB}$ (eqn (14.45)), it is reasonable to impose the restriction

$$0 \leq \frac{pc}{eB} \leq w, \quad \therefore n = 0, 1, 2, \dots, \frac{LW}{2\pi\ell^2}, \quad \ell \equiv \left(\frac{\hbar c}{eB}\right)^{1/2}.$$

As LW is the area of the rectangle, we conclude that the number of states per unit area is

$$n_B = \frac{1}{2\pi\ell^2} = \frac{eB}{hc}, \quad (14.49)$$

for a completely filled Landau level. In other words, an infinite degeneracy of each of the original Landau level in the xy plane has been replaced by a finite degeneracy. The degree of degeneracy (14.49) does not depend on the level. Suppose that all the Landau levels are completely filled up by the electrons up to a given, e.g., k -th level. There are then

$$kn_B = \frac{eBk}{hc}$$

electrons per unit area. Now if we apply an electric field \mathbf{E} in the (xy) plane, the electrons will move freely with a velocity perpendicular to the direction of \mathbf{E} as well as of \mathbf{B} , so that the electrostatic force cancels the Lorentz force,

$$e\mathbf{E} + \frac{e}{c}\mathbf{v} \times \mathbf{B} = 0,$$

that is, with a velocity

$$\mathbf{v} = \frac{c\mathbf{E} \times \mathbf{B}}{B^2}.$$

By multiplying the number of electrons kn_B we find that the current is given by

$$\mathbf{j} = \begin{pmatrix} 0 & -\frac{ke^2}{h} \\ \frac{ke^2}{h} & 0 \end{pmatrix} \mathbf{E}, \quad k = 1, 2, \dots$$

The conductivity tensor has purely non-diagonal elements only, and takes discrete values only, $\frac{ke^2}{h}$, $k = 1, 2, \dots$

Remarks

- The most remarkable feature of the quantum Hall effect is that the result, the quantized conductivity, is essentially exact: it holds independently of the shape, the details of the sample, temperature, impurities, etc. The result depends only on the ratio of the square of the electric charge unit and the Planck constant; it is measured with an accuracy of 10^{-8} or better, and in fact the QHE is now used as one of the metrological standards for fixing the value of e and/or of \hbar .

- A surprising development was that actually there are further finer effects observed at low temperatures, in which the Hall conductance is quantized in $\frac{f e^2}{h}$, where f is a rational fraction with an odd denominator. Such effects are called the *fractional quantum Hall effect* and involve subtle features of the two-dimensional multi-electron quantum states as a function of the magnetic field. See [Prange and Girvin (1990)], [Ezawa (2008)] for more discussions and for references.

14.4 Magnetic monopoles

One of the oldest questions in physics often troubles our mind: why is it that in Nature there are particles (electrons, protons, etc.) with a non-vanishing electric charge, while there seem to be no “particles” charged with a magnetic charge—magnetic monopoles. This asymmetry is somewhat bizarre, in view of the well-known elegant symmetry under the exchange of electric and magnetic fields,

$$\mathbf{B} \rightarrow \mathbf{E}; \quad \mathbf{E} \rightarrow -\mathbf{B}, \quad (14.50)$$

in classical electromagnetism. It is perhaps less well known that the vacuum Maxwell equations

$$\begin{aligned} \nabla \cdot \mathbf{B} &= -\frac{1}{c} \frac{\partial \mathbf{E}}{\partial t}; & \nabla \cdot \mathbf{E} &= 0; \\ \nabla \cdot \mathbf{E} &= \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}; & \nabla \cdot \mathbf{B} &= 0, \end{aligned}$$

are actually invariant under continuous transformations

$$\mathbf{E} + i\mathbf{B} \rightarrow e^{i\alpha} (\mathbf{E} + i\mathbf{B}), \quad (14.51)$$

which include the electromagnetic duality transformation (14.50). This invariance is broken by the presence of the electric sources, the first pair of Maxwell equations being replaced by

$$\nabla \cdot \mathbf{B} = -\frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi}{c} \mathbf{j}, \quad \nabla \cdot \mathbf{E} = -4\pi\rho, \quad (14.52)$$

where ρ and \mathbf{j} are the charge density and electric current density. As no magnetic sources seem to be there in Nature, this asymmetry destroys the electromagnetic duality.

But what if magnetically charged particles do exist somewhere in the universe?⁸ Can they exist in principle? Are they compatible with the idea of duality? Can a theory invariant under duality, or even under an extended duality symmetry (14.51), be constructed and find some applications in physics?

A partial (and affirmative) answer to these questions was given by Dirac in 1931. Dirac showed that magnetic monopoles can exist in principle, if the quantization condition

$eg = \frac{n}{2}, \quad n = 0, \pm 1, \pm 2, \dots$

(14.53)

⁸This and other questions below might sound rather extravagant. The fact is that the idea of electromagnetic duality and its various cousins turns out to be remarkably fertile. Many variants, such as the strong-weak coupling duality, the high and low temperature duality in the Ising model, etc. have found beautiful applications in statistical mechanics and condensed matter physics, as well as in quantum field theories and elementary particle physics.

is satisfied, where e is the electric charge of a particle present in the theory, say of the electron, and g is the magnetic charge of a possible magnetic monopole. Equation (14.53) is known as *Dirac's quantization condition*.

To see how such a quantization arises, recall that in the usual situation, where only electrically charged particles are present, the magnetic field is divergenceless, and can be generated from the vector potential,

$$\mathbf{B} = \nabla \times \mathbf{A}. \quad (14.54)$$

In the presence of a (point-like) magnetically charged particle, the magnetic field must satisfy Poisson's equation

$$\nabla \cdot \mathbf{B} = -4\pi g \delta^3(\mathbf{r}), \quad \mathbf{B} = \nabla \frac{g}{r},$$

analogous to the case of the electric field, and therefore no vector potential can exist, as eqn (14.54) implies that $\nabla \cdot \mathbf{B} = 0$. In fact eqn (14.54) implies that the total magnetic flux emanating from any point through the surface of a sphere vanishes:

$$\int d\mathbf{S} \cdot \mathbf{B} = \int dV \nabla \cdot \mathbf{B} = \int dV \nabla \cdot \nabla \times \mathbf{A} = 0.$$

while the presence of a magnetic charged particle requires

$$\int d\mathbf{S} \cdot \mathbf{B} = -4\pi g \neq 0,$$

if the integral is taken over a sphere surrounding the magnetic pole. How can this difficulty be avoided? Suppose that the theory is modified by the addition of an infinitely thin line with a magnetic flux confined to it (see Figure 14.7). Suppose that the flux carried by the string (called a *Dirac string*) is such that it exactly cancels the total flux emanating radially from the magnetic monopole, $4\pi g$. The field due to such a string can be explicitly written as

$$\mathbf{b} = -4\pi g \int_0^\infty dt \frac{ds(t)}{dt} \delta(\mathbf{r} - \mathbf{s}(t)) \quad (14.55)$$

where $\mathbf{s}(t)$, $t : 0 \rightarrow \infty$ parametrizes the Dirac string position, with $\mathbf{s}(0) = 0$, $\mathbf{s}(\infty) = \infty$ along some direction. The exact direction or the shape of the curve $\mathbf{s}(t)$ is immaterial to our discussion. It is an easy exercise to show that

$$\nabla \cdot \mathbf{b} = +4\pi g \delta^3(\mathbf{r}),$$

so that the total magnetic field $\mathbf{B} + \mathbf{b}$ is divergenceless. Therefore a vector potential exists which generates the total magnetic field

$$\mathbf{B} + \mathbf{b} = \nabla \times \mathbf{A},$$

and the electrically charged particles can be described in the standard way in terms of the minimal coupling.

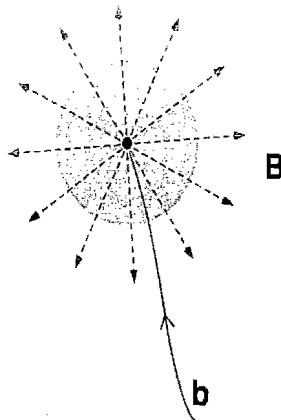


Fig. 14.7

We have, however, apparently done something suspicious. If the Dirac string had observable effects, we would have modified the theory nontrivially, something we did not intend to nor wish to do. At first sight, there might seem to be no problem at all: as the Dirac string is infinitely thin the probability that the electron passes into the region where the extra magnetic flux is present can be considered to be zero almost everywhere (i.e. except for regions with zero measure).

But in quantum mechanics, electrically charged particles interact with the magnetic field through the vector potential: even if the electron never penetrates the region with non-vanishing magnetic field there may be nontrivial observable effects. This should remind the reader of something familiar: the Aharonov-Bohm effect! Let us then consider a tiny loop s around the Dirac string. See Figure 14.8. Going through such a circle, the electron wave function will acquire a phase (we set $c = 1, \hbar = 1$)

$$\exp ie \int_s dx^i A_i = \exp ie \int_\sigma d\mathbf{S} \cdot \nabla \times \mathbf{A}.$$

But

$$\int_\sigma d\mathbf{S} \cdot \nabla \times \mathbf{A} = \int_\sigma d\mathbf{S} \cdot (\mathbf{B} + \mathbf{b}) \simeq \int_\sigma d\mathbf{S} \cdot \mathbf{b} = 4\pi g,$$

where we have neglected the contribution from \mathbf{B} . The flux through an infinitesimal solid angle σ due to \mathbf{B} (which is uniformly distributed over the surface of the sphere) can be safely neglected, and the above integral can be reliably calculated by taking into account the flux carried by the Dirac string only. The condition that the Dirac string is unobservable is then that the phase acquired by the electron wave function is a multiple of 2π :

$$4\pi i e = 2\pi i n, \quad n \in \mathbb{Z},$$

which is precisely Dirac's quantization condition (14.53).

Remarks

- This is an example of a *topological quantization* which occurs in various fields of physics. The “topology” relevant here is the first homotopy group of $U(1)$ (the group of the phase transformation of the wave function of the charged particles), that is, the classes of maps from S^1 to S^1 . As we have mentioned on a few occasions, they are classified by an integer “winding number”. The flux quantization, eqn (14.43), is another example of topological quantization.
- Dirac's quantization condition in a sense explains the quantization of the electric charge in Nature. If there is a magnetic monopole somewhere in the universe, then the consistency of electromagnetism requires the electric charge to be quantized.
- The electric charge unit is “small”: in the dimensionless combination it is the fine-structure constant $\frac{e^2}{\hbar c} \simeq \frac{1}{137}$. It follows that the magnetic coupling is very large, $\frac{g^2}{\hbar c} \simeq 37$. It is quite possible that

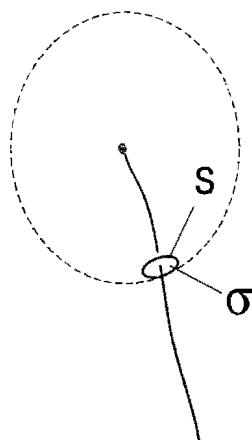


Fig. 14.8

all magnetic charges are tightly bound to form magnetically neutral systems, explaining the apparent absence of isolated magnetic monopoles.

- Although monopoles as introduced by Dirac may not exist as elementary, point-like particles, they can arise as topological excitations in various field-theoretic models (from condensed matter physics to elementary particle physics) and there are reasons to believe that they play an important role in our understanding of Nature in some subtle ways.

Guide to the Supplements

In Supplement 22.3 we give a derivation of Thomas precession at lowest order in v/c . In 22.4 and 22.5 the Hamiltonian for a system of charged particles is computed up to order v^2/c^2 . Spin interactions, mass polarization terms, and time delay effects are included in H . They are used in several problems and applications in this book. Finally in

Supplement 22.6 we give a short, elementary quantization procedure for the radiation field.

Also, the analytical solution for the Aharonov–Bohm scattering problem and some generalizations of the result are given in the solution (CD) to the numerical problem NB-14.1.

Problems

- (14.1) Compute the lifetime of the excited state $2p$ of the hydrogen atom in the dipole approximation. Why does the spin not affect the computation?
- (14.2) Let us consider an ensemble of hydrogen atoms in a $2p$ state, polarized along an axis, say, the z axis. Compute the angular distribution of the emitted photons in the transition $2p \rightarrow 2s$ and their polarizations.
- (14.3) Use the Wigner–Eckart theorem to write the hyperfine splitting structure for a level with arbitrary (L, S) . The nucleus has spin I .

Numerical analyses

- (14.1) Solve Schrödinger's equation for the Aharonov–Bohm process, with a line-shaped solenoid or a finite cylinder-shaped solenoid.

15

Atoms

The attempt to explain atomic structure was one of the main motives for the genesis of quantum mechanics (Bohr's atomic model, spectral lines, etc.); at the same time it represented the first true testing ground for the new theory. The explanation of the existence of discrete atomic levels, their quantitative prediction, understanding of the periodic structure of the elements, the correct interpretation of chemical bonds, etc., can be regarded without exaggeration as one of the greatest achievements of the scientific thought of our time. A door to an entirely new world—that of the atomic and subatomic phenomena—opened, triggering an impressive advance in basic scientific knowledge and modern technology, unprecedented in human history. The very concepts and many of the mathematical tools of quantum mechanics have, in many cases, sprung from the efforts to solve these problems. In this chapter, we study atomic structure, and try to illustrate some of these features.

15.1 Electronic configurations

In a first approximation the Hamiltonian of an atomic system has the form

$$H = \sum_{i=1}^Z \left(\frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (15.1)$$

In eqn (15.1) the nucleus is assumed to possess an infinite mass, \mathbf{r}_i is the position of the i -th electron; all relativistic corrections and spin-dependent interaction terms are neglected for the moment: they will be considered later.

The eigenvalues of H correspond to the stationary states of the atom, the atomic levels, with associated eigenfunction $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_Z)$. It is quite unrealistic to think of solving the eigenvalue problem associated with H exactly, even numerically; even if each coordinate is replaced by a discrete lattice, with e.g., 100 points, we need 100^{3Z} numbers just to write the wave function. Some approximation scheme must be developed. The basic idea is to consider in a first approximation the motion of each electron in an effective, spherically symmetric potential, due to the nucleus and to the mean charge density generated by all other electrons. In this way, Schrödinger's equation for a single electron has the form

$$h_i \psi_i = \epsilon_i \psi_i; \quad h_i = \frac{\mathbf{p}_i^2}{2m} - \frac{Z}{r_i} + V_i(r_i). \quad (15.2)$$

15.1 Electronic configurations	405
15.2 The Hartree approximation	412
15.3 Multiplets	418
15.4 Slater determinants	424
15.5 The Hartree-Fock approximation	427
15.6 Spin-orbit interactions	433
15.7 Atoms in external electric fields	438
15.8 The Zeeman effect	443
Further reading	450
Guide to the Supplements	451
Problems	451
Numerical analyses	452

The original problem can be treated perturbatively, by writing

$$\begin{aligned} H &= \sum_i h_i + \left(H - \sum_i h_i \right) \\ &\equiv H_0 + H_{ee} = H_0 + \left(\sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i V_i(r_i) \right), \end{aligned}$$

where

$$H_0 = \sum_i h_i,$$

and the second term describes the deviation from the approximation of a spherically symmetric effective potential (or simply the central field approximation).

The central field approximation corresponds to keeping H_0 as the Hamiltonian. H_0 is separable, each of h_i depending only on the coordinates of the i -th electron. The quantum numbers of the states are fixed by those of the single electrons. The latter are the principal quantum number, n , the orbital angular momentum ℓ, ℓ_z and the z component of the spin, s_z . The eigenstates of H_0 are constructed by taking into account Pauli's exclusion principle. Each state cannot be occupied by more than one electron. The ground state of a system with Z electrons can be obtained by filling all the single-particle states starting from the bottom. As Z varies, various possible atoms are described in this way:

1	H	$1s$	1 electron, spin s_z
2	He	$1s^2$	2 electrons, spin: \uparrow, \downarrow
3	Li	$1s^2 2s$	3 electrons, spin: $\uparrow, \downarrow, s_z$

and so on. The set of all quantum numbers such as $1s^2 2s^2 2p^2 \dots$ is called the *electronic configuration*. The notation borrowed from the hydrogen atom, such as

$$n\ell^b; \quad n = 1, 2 \dots, \quad \ell = s, p, d, \dots; \quad b = 1, 2, \dots, 2(2\ell + 1)$$

is used, where b is the number of electrons in a given shell, (n, ℓ) . The classification can be used for excited states also, for instance, $1s2s$ represents an excited state of the helium atom.

This scheme implies that as Z is varied, the electronic configurations exhibit a structure made of shells (n, ℓ) . We expect regular structures corresponding to the filled (closed) shells. If the potential were purely Coulomb, the energy would depend only on n and each shell would have a $2n^2$ -fold degeneracy (the factor 2 is due to the spin). In a more realistic case of a generic spherically symmetric potential, the states with different values of ℓ are not degenerate, and the filling pattern would be more like

$$\begin{aligned} &1s^2, (1s^2, 2s^2), (1s^2, 2s^2, 2p^6), (1s^2, 2s^2, 2p^6, 3s^2), \\ &(1s^2, 2s^2, 2p^6, 3s^2, 3p^6), (1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}), \dots \end{aligned}$$

It turns out that the configurations ns and np are almost degenerate, and lead to a pattern of the following type

Config.	external electrons	Atom
$1s^2$	2	He
$[He]2s^2 2p^6$	8	Ne
$[Ne]3s^2 3p^6$	8	Ar

A glance at the periodic table of the elements will convince the reader that such a filling pattern of various shells precisely corresponds to the periodicity observed in the chemical behavior of the elements. In particular, the closed shells $s-p$ yield particularly stable configurations, corresponding to chemically inert *noble gases*.

An interesting characteristic of the filling pattern concerns the d shell. As can be seen from the table of electronic configurations at the end of the book, the orbitals $4s$ are occupied first, in the elements potassium (K) and calcium (Ca) (which have the typical characteristics of alkali elements and alkaline Earth metals, respectively, as in Na and Mg) and then the ten $3d$ orbitals are occupied one by one, with ten elements Sc-Zn, and finally the $4p$ orbitals with six elements Ga-Kr. The elements corresponding to the filling of the $3d$ shell are called *transition metals* and have various chemical and magnetic properties in common. These similarities led us to think that the $3d$ shell corresponds to "more interior" orbits of the atom, and the peripheral electrons are the ones in the $4s$ orbitals which determine, approximately, their chemical properties.

The same situation is found for the sequence Y-Cd, corresponding to the filling of the $4d$ orbitals. An even more notable analogous situation occurs in the filling of the $4f$ shell, corresponding to the rare earth elements, La-Lu, and the $5f$ shell, Ac-No. In theory the periodic table could continue, but the nuclei above Uranium, $Z = 92$, are unstable. The corresponding elements are not found in Nature, and when they are produced artificially, they decay.

Degeneracy

An important point in the scheme of classification used is the degeneracy of the levels. These can be discovered experimentally, by use of external electric or magnetic fields, which lift the degeneracy, and the number of sublevels found this way is in accord with the scheme adopted above.

A configuration in which all possible states corresponding to a given principal quantum number are occupied is called a *closed shell*, for example, $1s^2, 2p^6$, etc. Such a configuration is obviously non-degenerate. This is the situation for the noble gases (He, Ne, Ar, Kr, etc.). In other atoms the degeneracy is determined by the number of ways the electrons can be arranged in the partly filled shell, respecting Pauli's principle. Electrons belonging to the same atomic orbitals are called *equivalent electrons*. For example, carbon in its ground state has the configuration $1s^2 2s^2 2p^2$, with two equivalent electrons in the $2p$ orbit. A p orbit can contain up to six electrons, according to different values of ℓ_z and of s_z . There are $\binom{6}{2} = 15$ ways to arrange the two electrons in six possible

states. It is clear that the only shell which matters for degeneracy is the incomplete one, and in the following we shall list only these incomplete shells. As a second example, take nitrogen (N): in the ground state, $2p^3$, the degree of degeneracy is $\binom{6}{3} = 20$, while in the excited state $2p^23s$ it is $\binom{6}{2} \times 2 = 30$. Other examples are to be found in the exercises at the end of this chapter.

We note that, by virtue of the well-known property of binomials $\binom{n}{k} = \binom{n}{n-k}$, to determine the degeneracy one can count the electrons or the *holes*, that is, the missing electrons which would fill the shell. Thus oxygen's $2p^4$ orbital has the same degeneracy as carbon's $2p^2$; fluoride's $2p^5$ has the same degeneracy as boron's $2p$. Such a symmetry between electrons and holes will sometimes be encountered in the following.

Let us briefly review the main experimental facts which confirm the validity of the scheme outlined above.

15.1.1 The ionization potential

A quantitative measure of the stability of an atomic system is provided by the ionization potential, I , defined as the minimum energy required to extract an electron from the atom. The experimental values in eV are given in a table at the end of the book. In Figure 15.1 I is shown as a function of atomic number. The shell structure and the strong stability of noble gases are clearly seen. The relatively flat parts correspond to the filling of d and f orbitals.

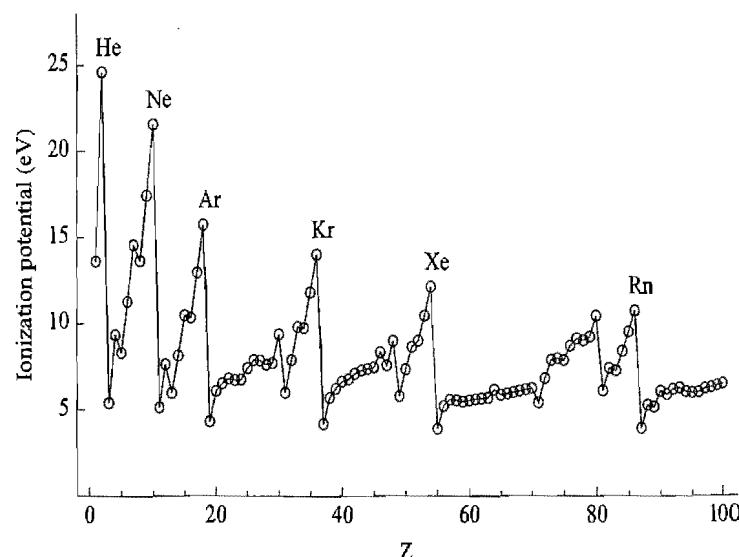


Fig. 15.1 Ionization potential in eV versus Z .

Intuitively the situation can be outlined as follows. Let us imagine going from one element to the next by increasing the nuclear charge by 1 and by adding an electron. In passing from He to Li ($Z = 2 \rightarrow Z = 3$),

the new electron would have an energy $-1/(2 \cdot 2^2)$ a.u. if the two $1s$ electrons screen the nuclear charge completely, and the ionization potential of about $13.6/4 \sim 3.4$ eV, if the screening due to the other two electrons were perfect. Instead, the ionization potential of Li is about 5.39 eV, implying that the screening is not complete, and the third electron feels an effective charge a little larger than 1, $Z_1^2 \sim 5.39/3.4 \sim 1.584$, i.e., $Z_1 \sim 1.3$. Even more so the next electron will see an effective charge not equal to Z_1 , but $Z_2 \sim (1 + \alpha)Z_1$, where $\alpha > 0$ represents the ineffectiveness of the screening of the first electron $2s$. For α sufficiently small and for a given shell the energy of the additional electron, proportional to Z_k^2 , behaves as

$$E_k \propto -Z_k^2 \sim -(C_1 + C_2 k); \quad I_k \sim C_1 + C_2 k.$$

Therefore for a given shell we expect an increase in the ionization potential roughly linear in Z . When the shell is filled up, the next electron must find a place in an orbit with a larger principal quantum number, and with a smaller ionization potential, and the cycle restarts. This picture is confirmed in broad outline by Figure 15.1. Note in particular the sharp discontinuities at the filling of the p shells (noble gases) and the relatively small discontinuities corresponding to the completion of the s shell (Be, Mg etc.).

In a given orbital, hence with a fixed radial function, at most half of the states have the same spin projection s_z , due to Pauli's principle. For instance if four p electrons were to have $s_z = +\frac{1}{2}$ then at least two of them would have the common eigenvalue of ℓ_z , which has only three possible eigenvalues, $1, 0, -1$, which is therefore impossible. In a configuration with an almost complete shell, the maximum possible value of S is $n_g/2$, if n_g is the maximal number of the electrons. The spin wave function in this case is completely symmetric, and according to Pauli's principle the orbital wave function must be completely antisymmetric and hence vanishes if two orbital quantum numbers coincide. For continuity the probability of finding two electrons "nearby" is therefore small. But the interactions between two electrons are repulsive, so the more distant the electrons are the less their energy becomes. As we shall see (*Hund's rule*), for a given atom, the ground state corresponds to the maximum possible value of the total spin. For an almost filled shell the configuration with all spins parallel is the ground state. For the reasons just outlined we expect that this configuration, being able to minimize the Coulomb repulsion, is particularly stable, and has an abnormally large ionization energy, a fact which can indeed be observed experimentally.

This same mechanism is responsible for a strange feature of the filling of the $3d$ shell: in the passage from vanadium ($3d^34s^2$) to chromium the configuration changes not to $3d^44s^2$ but to $3d^54s^1$: the configuration with the orbitals d^5 has less energy. A similar situation is realized for the orbital $4f^7$ of gadolinium (see Table 24.5 at the end of the book).

15.1.2 The spectrum of alkali metals

As expected intuitively the approximation of a spherically symmetric effective potential is particularly good for completely filled (closed) shells. For the alkali atoms then the optical spectrum should be well described by the transitions of the outer electron, an s electron, which moves in a Coulomb potential of the nucleus, screened by the spherical cloud of negative charge. Such an approximation must be particularly good for excited states, corresponding to large orbits. The energy levels of these atoms are in fact described well by a formula, due to Rydberg, which resembles that of the hydrogen atom,

$$E = -\frac{1}{(n - \delta)^2} \text{ Ry.} \quad (15.3)$$

The constant δ , called the Rydberg *defect*, describes the deviation from a purely Coulomb-type potential and depends on the angular momentum ℓ . An example of formula (15.3) is given in Table 15.1.

Orb.	E	δ	Orb.	E	δ	Orb.	E	δ
1s	-79.4		2p	-2.80		3d	-0.112	0.010
2s	-5.2		3p	-0.223	0.883	4d	-0.063	0.012
3s	-0.378	1.373	4p	-0.101	0.867	5d	-0.040	0.013
4s	-0.143	1.357	5p	-0.058	0.861	6d	-0.027	0.014
5s	-0.075	1.353	6p	-0.037	0.859			
6s	-0.046	1.351						
7s	-0.031	1.350						

Table 15.1 Energy levels of sodium, with the associated defect

Such an agreement provides a strong support in favor of the idea of the central field and, together with the explanation of the X-ray spectrum, was one of the main motivations for this kind of approximation.

15.1.3 X rays

Electromagnetic rays of extremely short wavelengths, 10^{-2} – 10^2 Å, known as X rays, are emitted when various substances are bombarded by very energetic electron beams. In the X ray spectra there are a set of discrete series, specific to the element, called characteristic X rays. These spectral lines form the series indicated by $K, L, M \dots$, a little like the Lyman, Balmer, etc. series in the visible region of the spectrum of the hydrogen atom. The K X rays appear clearly starting from sodium ($Z = 11$); the X rays belonging to the L series starts about $Z \geq 30$; and so on. Apart from the much shorter wavelengths as compared to visible light (which has a wavelength somewhere between 3000 and 8000 Å), this group of spectral lines has some remarkable properties which are not shared by visible light. The first is that the square root of the frequencies of a

given series (for instance, K) depends linearly on Z and is basically universal, in clear contrast to the periodic property of the spectral lines in the visible (Figure 15.1). Another curious property is that these lines are seen in the *emission spectra*, but not in the *absorption spectra*, a fact which suggests a different mechanism for X ray emission from that associated with visible light.

Always assuming that the photon is emitted upon transition of a single electron from a level i to another level f , with frequency

$$\nu = \frac{E_i - E_f}{h},$$

these mysterious properties of X rays can be explained (Kossel), supposing that such a ray is emitted when one of the electrons in the innermost orbits is removed (for instance, by bombarding electrons), and subsequently an electron in a higher orbit falls into the orbit which became empty.

Indeed if, for instance, a $1s$ electron is removed this way, this will be followed by transitions which bring down a $2p$ (or $3p, 4p, \dots$) electron to the $1s$ orbit, by emission of a photon. The energy at stake is normally much larger than 1 eV, and this can be understood as the innermost electron feeling the Coulomb potential of the nucleus, $V \sim -\frac{Z^2 e^2}{r}$, un-screened by other electrons: its binding energy is much larger than the typical value of 1 Ry of the outer electrons, by roughly a factor Z^2 . The frequency of the emitted rays in this manner naturally falls in the typical range of X rays, for $Z \geq 10$. For historical reasons the innermost orbits are called $K, L, M \dots$ orbits, corresponding to the principal quantum number, $n = 1, 2, 3 \dots$. The associated series of spectral lines are called $K, L, M \dots$ also, according to the lowest energy level involved in the transition. Corresponding to the separation of the levels $2s, 2p$ there will be a multiplet of lines L , etc. The energy of the electron is, as in the case of visible spectra, related to the limit of the series, for instance the K series is related to the transitions

$$2p \rightarrow 1s, 3p \rightarrow 1s, 4p \rightarrow 1s, \dots, np \rightarrow 1s, \dots,$$

so the limiting frequency of this series corresponds to the energy required to extract the $1s$ electron, which can be verified to be equal to the energy measured by the method of electron bombardment.

As already mentioned, the structure of the X ray spectrum is approximately universal, reflecting the fact that the mechanism involves the innermost electrons, and hence the problem reduces to one of Coulomb binding. In fact, the energy levels of $K, L \dots$ electrons are well represented by the expression

$$E_K = -\frac{(Z-s)^2}{1^2} \text{ Ry}, \quad E_L = -\frac{(Z-s')^2}{2^2} \text{ Ry} \dots \quad (15.4)$$

$s, s' \dots$, represent the effect of residual screening and are approximately constant (in Z). Obviously s' is somewhat larger than s . The quantity

$Z - s$ is called the effective charge. For example, from the levels of sodium in Table 15.1 one finds that

$$Z_{\text{eff}}(1s) = 8.91; \quad Z_{\text{eff}}(2s) = 4.56; \quad Z_{\text{eff}}(2p) = 3.35.$$

¹ See J. C. Slater *Phys. Rev.* **98**, 1039, (1955), and J. C. Slater, *Quantum theory of atomic structure*, vol.1.

In Table 15.2¹ the experimental values for the orbitals of light elements, obtained from optical and X ray spectra. The data $\sqrt{|E|/Ry}$ for the innermost levels is given in Figure 15.2 as a function of Z . The linear behavior predicted by eqn (15.4) is well verified. The curves are drawn by using Table 15.2 (experimental): K stands for the energy of the $1s$ electron; the two curves L represent the energy for the $2s$ and $2p$ electrons, and M the electrons in the $3s$, $3p$, $3d$ orbits. In the figure the points are the result of a numerical calculation, made with one of the Mathematica programs, given in Problems for Numerical Analysis at the end of the chapter. The agreement is rather good.

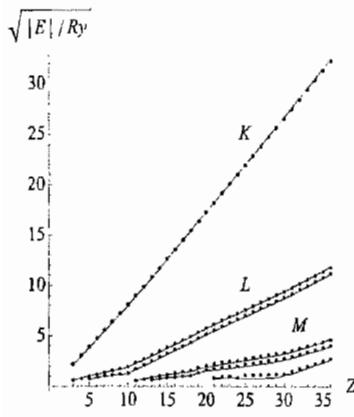


Fig. 15.2 $\sqrt{|E|/Ry}$ plotted against Z .

15.2 The Hartree approximation

The basic properties of the spherically symmetric effective potentials are contained in a very intuitive model elaborated by Hartree. Classically one can think of an electron moving in an effective electrostatic potential generated by the nucleus and by the charge density of other electrons, and therefore a reasonable approximation to Schrödinger's equation for the i -th electron would be

$$-\frac{1}{2m} \nabla^2 \psi_i(\mathbf{r}) - \frac{Ze^2}{r} \psi_i(\mathbf{r}) + e^2 \int d^3 \mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}') = \varepsilon_i \psi_i(\mathbf{r}), \quad (15.5a)$$

$$\rho(\mathbf{r}) = \sum_{j \neq i} |\psi_j(\mathbf{r})|^2. \quad (15.5b)$$

We look for solutions corresponding to a spherically symmetric potential: this can be achieved by considering an angular average of the electron motion:

$$\frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \rightarrow \frac{\overline{\rho(\mathbf{r}')}}{|\mathbf{r} - \mathbf{r}'|} = \int \frac{d\Omega_{\mathbf{r}}}{4\pi} \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (15.6)$$

With this substitution the solution of eqn (15.5) can be written in the form

$$\psi(\mathbf{r}) = R_{nl}(r) Y_{lm}(\Omega) \chi_s(\sigma), \quad (15.7)$$

and eqn (15.5) becomes a system of equations for the radial functions only. It is simpler to perform the average by summing over the projections of the angular momentum, instead of integrating over the angular variables; each electron contributes a potential

$$\int d^3 \mathbf{r}' \frac{R_{nl}^2(r') |Y_{lm}|^2}{|\mathbf{r} - \mathbf{r}'|} \rightarrow \frac{1}{2l+1} \sum_m \int d\Omega' r'^2 dr' R_{nl}^2(r') |Y_{lm}|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|}.$$

Z	1s	2s	2p	3s	3p	3d	4s	4p
H	1							
He	2	1.81						
Li	3	4.77	0.40					
Be	4	8.9	0.69					
B	5	14.5	1.03	0.42				
C	6	21.6	1.43	0.79				
N	7	30.0	1.88	0.95				
O	8	39.9	2.38	1.17				
F	9	51.2	2.95	1.37				
Ne	10	64.0	3.56	1.59				
Na	11	79.4	5.2	2.80	0.38			
Mg	12	96.5	7.0	4.1	0.56			
Al	13	115.3	9.0	5.8	0.83	0.44		
Si	14	135.9	11.5	7.8	1.10	0.57		
P	15	158.3	14.1	10.1	1.35	0.72		
S	16	182.4	17.0	12.5	1.54	0.86		
Cl	17	208.4	20.3	15.3	1.86	1.01		
Ar	18	236.2	24.2	18.5	2.15	1.16		
K	19	266.2	28.2	22.2	3.0	1.81	0.32	
Ca	20	297.9	32.8	26.1	3.7	2.4	0.45	
Sc	21	331.1	37.3	30.0	4.2	2.6	0.59	0.55
Ti	22	366.1	42.0	34.0	4.8	2.9	0.68	0.52
V	23	402.9	46.9	38.3	5.3	3.2	0.74	0.55
Cr	24	441.6	51.9	43.0	6.0	3.6	0.75	0.57
Mn	25	482.0	57.7	47.8	6.6	4.0	0.57	0.50
Fe	26	524.3	63.0	52.8	7.3	4.4	0.64	0.53
Co	27	568.3	69.0	58.2	8.0	4.9	0.66	0.53
Ni	28	614.1	75.3	63.7	8.7	5.4	0.73	0.55
Cu	29	662.0	81.3	69.6	9.6	6.1	0.79	0.57
Zn	30	712.0	88.7	76.2	10.5	7.0	1.28	0.69
Ga	31	764.0	96.4	83.0	11.8	7.9	1.6	0.93 0.44
Ge	32	818.2	104.6	90.5	13.5	9.4	2.4	1.15 0.55
As	33	874.5	113.0	98.5	15.4	10.8	3.4	1.30 0.68
Se	34	932.6	122.1	106.8	17.3	12.2	4.5	1.54 0.80
Br	35	993.0	131.7	115.6	19.9	13.8	5.6	1.80 0.93
Kr	36	1055.5	142.0	124.7	22.1	15.9	7.1	2.0 1.03

Table 15.2 The energies of different orbitals, (absolute value is in Rydberg) found from optical and X ray spectra.

By using the identity

$$\frac{1}{2\ell+1} \sum_m |Y_{\ell m}(\Omega)|^2 = \frac{1}{4\pi},$$

one obtains the Coulomb potential due to a spherically symmetric distribution of charge,

$$\int d^3 r' \frac{R_{n\ell}^2(r')}{4\pi} \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \quad (15.8)$$

The charge contained within a shell of radius r is

$$Q(r) = \int_{r' < r} d^3\mathbf{r}' \frac{R_{n\ell}^2(r')}{4\pi} = \int_0^r dx P_{n\ell}^2(x), \quad (15.9)$$

where $P_{n\ell}$ is the reduced radial function: $R_{n\ell} = P_{n\ell}/r$. The radial electric field associated with the charge (15.9) is $Q(r)/r^2$ and the corresponding potential which vanishes at infinity is²

$$V_{n\ell}(r) = \int_r^\infty ds \frac{Q(s)}{s^2} = \int_r^\infty ds \frac{1}{s^2} \int_0^s dt P_{n\ell}^2(t). \quad (15.10)$$

We then have an equation for each orbital. Passing to radial coordinates and using atomic units $m = 1, e = 1$, eqn (15.5) takes the form

$$\begin{aligned} -\frac{1}{2} \frac{d^2}{dr^2} P_a(r) + \left(\frac{\ell_a(\ell_a+1)}{2r^2} - \frac{Z}{r} \right) P_a(r) \\ + \left(\sum_{b \neq a} q_b V_b(r) + (q_a - 1)V_a(r) \right) P_a(r) = \varepsilon_a P_a(r), \end{aligned} \quad (15.11)$$

² Below it will sometimes be necessary to distinguish the sum over the particles from the sum over the orbitals. We shall use i, j, \dots , for the particles, reserving the letters a, b, \dots , for the orbitals.

where q_a stands for the number of the electrons in the a orbital.³

For example for carbon which involves three shells ($1s$), ($2s$), ($2p$), system (15.11) can be written as

$$\begin{aligned} -\frac{1}{2} P_{1s}''(r) - \frac{Z}{r} P_{1s}(r) + (V_{1s} + 2V_{2s} + 2V_{2p}) P_{1s}(r) &= \varepsilon_{1s} P_{1s}(r); \\ -\frac{1}{2} P_{2s}''(r) - \frac{Z}{r} P_{2s}(r) + (2V_{1s} + V_{2s} + 2V_{2p}) P_{2s}(r) &= \varepsilon_{2s} P_{2s}(r); \\ -\frac{1}{2} P_{2p}''(r) + \left[\frac{2}{2r^2} - \frac{Z}{r} \right] P_{2p}(r) + (2V_{1s} + 2V_{2s} + V_{2p}) P_{2p}(r) &= \varepsilon_{2p} P_{2p}(r). \end{aligned}$$

Equation (15.11) is a system of integro-differential equations (the unknown functions enter the potential) which can be solved numerically by iteration: one starts from an initial estimate for $P_{n\ell}$, which for instance can be taken to be hydrogenoid wave functions. We calculate the potential in terms of these wave functions on the right-hand side, and then solve the linear equations. With the solutions obtained, we calculate the potentials again, which are then used on the right-hand side, to obtain a second approximation for the wave functions, and so on. In a few steps we find a stable solution for the system.

A subtle question concerns the definition of the energy levels. In a normal separable Schrödinger equation the eigenvalue of the total Hamiltonian is the sum of the energies of the single particles, but here eqn (15.5a) is not the usual Schrödinger equation (not even linear), as the wave functions play a double role, both of solutions and at the same time of the source of the potentials. Multiplying eqn (15.5a) by ψ_i^* (normalized) and integrating one gets

$$\left\langle \frac{\mathbf{p}^2}{2m} - \frac{Ze^2}{r_i} \right\rangle + \int |\psi_i(\mathbf{r})|^2 V_i(\mathbf{r}) = \varepsilon_i.$$

The second term of the left-hand side is the interaction of the charge distribution in the potential generated by other electrons. If we now sum over all the electrons and write V_i explicitly this contribution produces

$$\sum_i \int_{\mathbf{r}_i} \rho(\mathbf{r}_i) \sum_{j \neq i} \sum_{\mathbf{r}_j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \rho(\mathbf{r}_j).$$

The interactions between each pair $i-j$ appears twice: once when the i -th electron moves in the field created by the j -th electron, and vice versa, thus leading to twice the potential energy. In conclusion⁴

$$\sum_i \varepsilon_i = E + \frac{1}{2} \int \rho_i(\mathbf{r}) V_i(\mathbf{r}). \quad (15.12)$$

The sense of eqn (15.12) is in fact that of considering the expectation value of the full Hamiltonian (15.1) in a state represented by the factorized form. As $H = H_0 + H_I$ this would be equivalent to a first-order calculation if the potentials V_i were ordinary external potentials.

Taking into account the fact that the radial wave functions are identical for electrons in a given orbital, the sum over the particles can be substituted by a sum over the orbitals, and one has

$$\begin{aligned} \Psi &= \prod_i \psi_i(\mathbf{r}_i); \\ \langle \Psi | H | \Psi \rangle = E &= \sum_i \left\langle i \left| \frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{r} \right| i \right\rangle + \frac{1}{2} \sum_{i \neq j} \int |\psi_i|^2 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} |\psi_j|^2 \\ &= \sum_a q_a \mathcal{L}_a + \frac{1}{2} \sum_{a \neq b} q_a q_b U_{ab} + \sum_a \frac{q_a(q_a - 1)}{2} U_{aa}, \end{aligned} \quad (15.13)$$

where q_a is the quantum number of the electrons in the orbit a , $q_a(q_a - 1)/2$ the number of pairs of electrons in the orbital, \mathcal{L}_a the expectation value of the single-particle operators, and U_{ab} the expectation value, averaged over the orientations ℓ_z , of the pairwise potential.

From eqn (15.11) it follows that, by multiplying each equation by $q_a P_a$ and integrating

$$\begin{aligned} \sum_{i \in \text{partic.}} \varepsilon_i &= \sum_a q_a \varepsilon_a = \sum_a q_a \mathcal{L}_a + \sum_{a \neq b} q_a q_b U_{ab} + \sum_a q_a(q_a - 1) U_{aa} = \\ &= E + \frac{1}{2} \sum_{a \neq b} q_a q_b U_{ab} + \frac{1}{2} \sum_a q_a(q_a - 1) U_{aa} \equiv E + \frac{1}{2} \sum_i \int \rho_i V_i, \end{aligned} \quad (15.14)$$

confirming the result, eqn (15.12).

⁴ This additional factor of $\frac{1}{2}$ is exactly the same as the one in the classical formula for the energy of an induced dipole, $-\frac{1}{2}\alpha E^2$, where $d = \alpha E$, while the energy of a permanent dipole is simply $-dE$.

15.2.1 Self-consistent fields and the variational principle

The Hartree equation (15.5a) can be obtained from a variational principle, which clarifies the meaning of the *self-consistent field*. Suppose

that we want to approximate our N -body problem (here the atom) by a system described by N independent electrons in a mean external field. What provides the best approximation? If the particles are independent the wave function can be written in a factorized way:

$$\Psi = \psi_{i_1}(q_1) \dots \psi_{i_N}(q_N); \quad (15.15)$$

i_k is an index describing the states in the field which is still to be found, q_k stands for all of the orbital variables and of spin of the k -th particle. Equation (15.15) does not take into account Pauli's principle, and is incompatible with quantum mechanics, but this will be remedied below.

We know that the eigenstates of Schrödinger's equation are the solution of a variational principle (see Chapter 10), and therefore eqn (15.15) can be interpreted as a restriction on the space of the functions over which the variational method is applied. In other words, the best field for our problem capable of generating a wave function of type (15.15) is the one defined by the variational principle, restricted to such functions.

Given Hamiltonian (15.1) one has⁵

$$\begin{aligned} \langle \Psi | H | \Psi \rangle &= \sum_i \int_q \psi_i^* \left(-\frac{1}{2} \nabla^2 - \frac{Z}{r_i} \right) \psi_i \\ &\quad + \sum_{i < j} \int_{q, q'} \psi_i^*(q) \psi_j^*(q') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_i(q) \psi_j(q'). \end{aligned} \quad (15.16)$$

According to the variational principle in eqn (15.16) we vary the functions ψ_i subject to the constraint $\|\psi_i\| = 1$, which can be imposed by use of a Lagrange multiplier,

$$\frac{\delta H}{\delta \psi_i^*} - \varepsilon_i \frac{\delta}{\delta \psi_i^*} \left(\int_q |\psi_i|^2 - 1 \right) = 0. \quad (15.17)$$

Performing the variation, one obtains

$$-\frac{1}{2} \nabla^2 \psi_i - \frac{Z}{r_i} \psi_i + \sum_{j \neq i} \int_{q'} |\psi_j(q')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_i(q) = \varepsilon_i \psi_i(q), \quad (15.18)$$

which coincides with eqn (15.5), the spin-dependent part of the wave function being factorized does not play any role. The variational principle then says that among all possible fields the optimal one is

$$V_i(r_i) = \sum_{j \neq i} \int_{q'} |\psi_j(q')|^2 \frac{1}{|\mathbf{r}_i - \mathbf{r}'|}.$$

The “energy” ε_i appears here as a Lagrange multiplier. A calculation identical to what has led to eqns (15.12) and (15.14) shows that the expectation value of H thus defined is just that quantity called E in those formulas.

The approximation of a spherically symmetric effective potential is a special case of eqn (15.18) obtained, as we have already seen, by averaging over the angles. The variational principle suggests another way to

⁵Here and below, we shall use always the atomic unit, unless otherwise stated.

get to the same result: if we are looking for a spherically symmetric field the wave function must be of the form of eqn (15.7), with a factorized radial part; we can then insert it directly into the variational expression and obtain the equation for the radial functions. This point of view is what will be adopted in the derivation of the Hartree–Fock equation.

15.2.2 Some results

The eigenvalues ε_a in eqn (15.11) are, approximately, the binding energy of the electrons and so must be compared with the data in Table 15.2. As an example, we list in Table 15.3 some values calculated⁶ made by our programs dedicated to the Hartree equation.

Z	1s	2s	2p	3s	3p	3d	4s	4p
Li	-4.99	-0.35						
Be	-9.50	-0.58						
B	-15.49	-0.89	-0.45					
C	-22.84	-1.21	-0.61					
N	-31.55	-1.57	-0.75					
O	-41.63	-1.97	-0.90					
F	-53.11	-2.40	-1.07					
Ne	-65.97	-2.87	-1.25					
Na	-81.27	-4.35	-2.44	-0.33				
Ar	-237.13	-22.20	-17.84	-1.91	-0.84			
K	-266.80	-26.28	-21.54	-2.69	-1.47	-0.26		
Zn	-706.14	-84.61	-75.59	-9.33	-6.23	-0.99	-0.54	

Table 15.3 Electron energies in Rydberg, calculated in the Hartree approximation.

The comparison between the two series of results is quite encouraging. The experimental results are reproduced within 5–10%, which, given the scheme, can be considered satisfactory. In any case the important point is the qualitative aspect: the approximation of the central field captures the gross structure of the levels.

Another feature to be underlined is the confirmation of the sequence of the filling pattern of the d levels. As an example, the graphs of the wave functions $4s$ and $3d$ for zinc are shown in Figure 15.3. One can see how the $3d$ wave function corresponds to a distribution more interior than that of $4s$, as expected. As another example consider potassium, K , with an external electron structure $3p^64s$. From the result of calculations in Table 15.3 the energy of the $4s$ electron is -0.265 Ry. Calculation of the energy of the electronic configuration $3p^63d$, instead, gives $\varepsilon_{3d} = -0.113$ Ry, that is, higher. Actually, we must verify that the total energy is smaller in the case of $4s$ as compared with the case of $3d$: this can be verified numerically but the major contribution to the difference of the energy comes from terms related to Pauli's principle; we shall come back to this later.

In Figure 15.4 the effective potentials for the $3p$ and $3d$ electrons

⁶For a discussion of the numerical analysis and for the programs, see the Mathematica notebooks given in the accompanying CD.

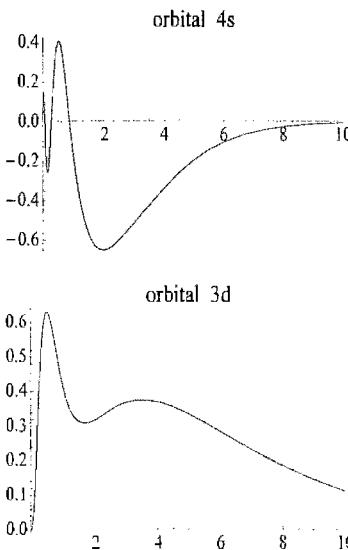


Fig. 15.3 Wave functions for the orbitals 4s and 3d of zinc

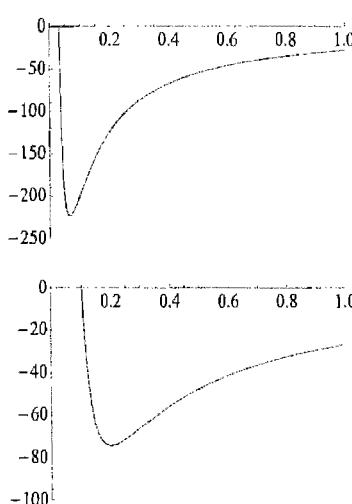


Fig. 15.4 The effective potentials for the orbits 3p and 3d of zinc.

are shown. Note the relatively shallow potential for the 3d orbital. The position of the well approximately determines the region where the wave function is appreciably different from zero. For the 3p orbital the well is obviously much deeper, and shifted towards smaller values of r : it describes an electron bound much more tightly and in the interior region.

As a final example we calculate the levels of sodium in the Hartree approximation. Using the numerical program given on CD accompanying this book the reader can convince her- or himself self that the energy level of the external electron can be calculated in two ways: either by making the calculation ab initio, or by keeping the closed core $1s^2 2s^2 2p^6$ fixed and solving the equation for the peripheral electron. We find compatible results. This confirms the intuitive idea that in a first approximation, a filled core is a closed shell, around which the exterior electrons orbit.

Table 15.4 summarizes the results obtained by keeping the “core” fixed; they must be compared with the experimental data in Table 15.1. Also in this case there is a qualitative agreement and the goodness of Rydberg’s formula, eqn (15.3).

Orb.	E	δ	Orb.	E	δ	Orb.	E	δ
1s	-81.270		2 p	-2.440		3 d	-0.111	0.001
2 s	-4.350		3 p	-0.193	0.725	4 d	-0.063	0.002
3 s	-0.325	1.245	4 p	-0.093	0.713	5 d	-0.040	0.002
4 s	-0.131	1.235	5 p	-0.054	0.708	6 d	-0.028	0.002
5 s	-0.070	1.232	6 p	-0.036	0.706	7 d	-0.020	0.002
6 s	-0.044	1.231	7 p	-0.025	0.705	8 d	-0.016	0.002
7 s	-0.030	1.230	8 p	-0.019	0.705	9 d	-0.012	0.002

Table 15.4 Energy levels of sodium and the corresponding defects in the Hartree approximation

15.3 Multiplets

To take the next step in refining our treatment of atomic structure, it is necessary to take into account the first relativistic corrections, and study how the degeneracy we found above in the central field approximation is removed. The total Hamiltonian for an atom, including relativistic corrections will have the form

$$\begin{aligned}
 H &= \sum_{i=1}^N \left(\frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + H_{rel} \\
 &= \sum_{i=1}^N h_i + \left(\sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i V_i \right) + H_{rel} = H_0 + H_{ee} + H_{rel} ;
 \end{aligned}$$

$$h_i = \frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{r_i} + V_i .$$

The relativistic correction H_{rel} contains spin-orbit interactions of the form $\ell \cdot \mathbf{s}$ as well as magnetic spin-spin interactions. As before we have separated the part corresponding to the central field approximation as H_0 , the “perturbation” term being given by $H_{ee} + H_{rel}$.

In the central field approximation, we found that the atomic states corresponding to a given electronic configuration had a characteristic degeneracy, d_g . This degeneracy is removed when the non-central corrections are taken into account; the resulting atomic level structure is known as *multiplets*.

The non-centrally-symmetric perturbation consists of two parts, the static electric repulsion terms H_{ee} and the relativistic corrections H_{rel} . Two extreme situations occur when one of these terms dominates over the other. The average velocity of the electrons increases with Z , and for light atoms the electrostatic repulsion terms turn out to be the main contribution, while for heavier elements the two contributions are of the same order of magnitude. The two cases require two different strategies for the diagonalization of the Hamiltonian: Russell-Saunders (also known as LS) coupling in the first case, for the light elements, and the jj coupling for heavier elements. In this section we shall be mainly dealing with the first case.

15.3.1 Structure of the multiplets

We first neglect H_{rel} and the Hamiltonian is then

$$\begin{aligned} H &= \sum_{i=1}^N \left(\frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &= \sum_{i=1}^N h_i + \left(\sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i V_i \right) . \end{aligned} \quad (15.19)$$

H is invariant under rotations and so commutes with the total angular momentum \mathbf{L} , and being independent of the spin, commutes with the total spin \mathbf{S} also. We can thus take H, L^2, L_z, S^2, S_z as the maximal set of observables that characterize each state. For a given electronic configuration (i.e., for given radial quantum numbers n_i , and for fixed ℓ_i) rotational invariance ensures that each level is characterized by L, S ,

$$E = E(\alpha, L, S) ,$$

and each of these levels have a residual degeneracy, $(2L + 1)(2S + 1)$. These degeneracies might be removed by applying external fields. α is an additional index for distinguishing levels with the same L, S .

Obviously, for a given degeneracy d_g of the electronic configuration we have

$$d_g = \sum (2L + 1)(2S + 1) .$$

This immediately suggests how to find the levels and states: it suffices to diagonalize L^2, S^2, L_z, S_z ; if there is no residual degeneracy we shall have the eigenstates of H ; otherwise, we must further diagonalize in the space of the degenerate levels.

Remarks

- Conservation of the quantum numbers L, S, L_z, S_z is an exact property of the full Hamiltonian, eqn (15.19): it does not depend on taking the electronic configuration as the zeroth-order approximation. In the case of mixing of configurations, one can take the distinct configurations (giving rise to the same L, S, L_z, S_z) as labeling the zeroth-order states.
- Another exactly conserved quantum number is parity. If we start with a given electronic configuration it can be written as

$$P = (-1)^{\ell_1 + \dots + \ell_n}.$$

Note that, in general, $\sum \ell_i \neq L$.

- In the following we shall consider a single electronic configuration to construct various states (L, S, L_z, S_z) so parity is automatically assigned. In the case of mixing, only states with the same parity will mix to form the eigenstates of H . Furthermore, when a level is resolved into multiplets due to the electrostatic repulsions, as we shall see below, all the members of a given multiplet have the same parity: this in particular implies that the dipole transitions among them are forbidden.

In the next section we shall see that the global quantum numbers L, S, L_z, S_z depend only on the electrons in incomplete shells; therefore the problem is to determine which values of L, S can be formed by these electrons via the addition rule of angular momentum and spin, taking into account Pauli's principle.

For inequivalent electrons, for instance in an excited state of carbon, $1s^2 2s^2 2p3p$, there are no problems: the possible values of L, S are found by applying the usual rule, the orbital wave functions of the two inequivalent electrons being distinct. Pauli's principle just tells us that the orbital functions must be symmetrized or antisymmetrized, according to the symmetry property of the spin wave function. Thus as the two electrons both have $\ell = 1, s = \frac{1}{2}$ the possible values of (L, S) are $L = 0, 1, 2, S = 0, 1$. For instance the state $L = 0, S = 1, S_z = 1$ will have the form,

$$\{R_{21}(r_1)R_{31}(r_2) - R_{21}(r_2)R_{31}(r_1)\} \hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2 \chi_+(1)\chi_+(2), \quad (15.20)$$

where the antisymmetrization is realized by the radial part of the wave function. As a check, let us compute the total number of states: two inequivalent electrons in p will have a total of $6 \times 6 = 36$ possible states. Each level with a given L has four states corresponding to spin states, a singlet $S = 0$ and a triplet $S = 1$, for a total of

$$\sum 4 \cdot (2L+1) = 4 \times 1 + 4 \times 3 + 4 \times 5 = 36$$

states, as expected. The Hamiltonian is diagonalized in this basis, and the original level split into different multiplets

$$^1D, ^3D, ^1P, ^3P, ^1S, ^3S.$$

In general, the notation

$$^{2S+1}A \quad A = S, P, D, F, G, \dots \quad \text{for } L = 0, 1, 2, 3, 4, 5, \dots$$

is used to indicate each multiplet.

In the case with equivalent electrons the situation is more complicated, as Pauli's principle excludes some of the combinations. For instance the state (15.20) would identically vanish if the principal quantum numbers of the two electrons were the same, and consequently the multiplet ($L = 0, S = 1, S_z = 1$) would not exist.

To construct all the possible states we proceed in order. For two equivalent electrons in the s orbit, $n s^2$, there are no problems: the only possible combination is the spin antisymmetric state, and hence the only possible multiplet is 1S .

In the case with higher angular momenta the simplest way to proceed is to write the states and list the possible ways to occupy them. Let us consider, for instance, the case of two equivalent p electrons. The six possible single-particle states are (showing the quantum numbers m, s):

$$\psi_{(1,\frac{1}{2})}^{(1)}; \quad \psi_{(0,\frac{1}{2})}^{(2)}; \quad \psi_{(-1,\frac{1}{2})}^{(3)}; \quad \psi_{(1,-\frac{1}{2})}^{(4)}; \quad \psi_{(0,-\frac{1}{2})}^{(5)}; \quad \psi_{(-1,-\frac{1}{2})}^{(6)}.$$

We then write the possible ways to occupy them, marking the eigenvalues of L_z, S_z (restricting ourselves to non-negative eigenvalues: those with negative eigenvalues can be immediately found from those with positive eigenvalues):

$$\Phi^{(1,2)} = |1, 1\rangle; \quad \Phi^{(1,3)} = |0, 1\rangle; \quad \Phi^{(1,4)} = |2, 0\rangle; \quad \Phi^{(1,5)} = |1, 0\rangle;$$

$$\Phi^{(2,4)} = |1, 0\rangle; \quad \Phi^{(2,5)} = |0, 0\rangle; \quad \Phi^{(1,6)} = |0, 0\rangle, \quad \Phi^{(3,4)} = |0, 0\rangle.$$

Consider first the state with $L_z = 2$. This state has a unique value for $S_z = 0$, and therefore $S = 0$ (and $L = 2$): it is the multiplet 1D . One of the states $|1, 0\rangle$ and one of $|0, 0\rangle$ serve to complete this multiplet. Of the remaining five states, four are members of 3P . The last remaining $|0, 0\rangle$ state must form its own multiplet, 1S .

As an exercise, for three equivalent p electrons the possible states are

$$\Phi^{(1,2,4)} = |2, \frac{1}{2}\rangle; \quad \Phi^{(1,3,4)} = |1, \frac{1}{2}\rangle; \quad \Phi^{(1,2,3)} = |0, \frac{3}{2}\rangle; \quad \Phi^{(1,2,5)} = |1, \frac{1}{2}\rangle;$$

$$\Phi^{(1,2,6)} = |0, \frac{1}{2}\rangle; \quad \Phi^{(1,3,5)} = |0, \frac{1}{2}\rangle; \quad \Phi^{(2,3,4)} = |0, \frac{1}{2}\rangle.$$

They are members of three multiplets: $^4S, ^2D, ^2P$.

Proceeding this way, and remembering that holes are equivalent to electrons in constructing the multiplets (L, S) , we arrive at the results in Table 15.5 below.

The prefactors [2] (or [3]) which appear in Table 15.5 starting from the d^3 configurations indicate that there are two (or three) multiplets

p, p^5	2P	
p^2, p^4	$^1S, ^1D;$	3P
$p^3,$	$^2P, ^2D;$	4S
d, d^9	2D	
d^2, d^8	$^1S, ^1D, ^1G;$	$^3P, ^3F$
d^3, d^7	$^2P, [2] ^2D, ^2F, ^2G, ^2H$	$^4P, ^4F$
d^4, d^6	$[2] ^1S, [2] ^1D, ^1F, [2] ^1G, ^1I$	$[2] ^3P, ^3D, [2] ^3F, ^3G, ^3H$
d^5	$[2] ^2S, ^2P, [3] ^2D, [2] ^2F, [2] ^2G, ^2H, ^2I$	5D
		$^4P, ^4D, ^4F, ^4G$
f, f^{13}	2F	
f^2, f^{12}	$^1I, ^1G, ^1D, ^1S$	$^3H, ^3F, ^3P$

Table 15.5 Multiplets

of those quantum numbers. A more complete table can be found in the book *Quantum theory of atomic structure* by Slater, and similar tables can be generated by using the symbolic programs given in the present book's accompanying CD.

To each multiplet there corresponds an atomic level. The electrostatic repulsion potential has split the degenerate levels present in the spectrum of H_0 into sub-levels having definite L, S . As can be verified in Table 24.3 given at the end of the book, the energy differences among various multiplets are of the order of $10^4 \hbar c/\text{cm} \simeq 1.2 \text{ eV}$, in agreement with what is expected from an electrostatic perturbation of the order of e^2/r_B .

The degenerate levels in a multiplet are finally split by the relativistic corrections (of which one is the spin-orbit interaction discussed in Section 15.6; the other corresponds to the spin-spin interaction). The resulting structure of the atomic levels is known as *fine structure*. Each single sub-level is characterized by L, S and the total angular momentum J , and denoted by a symbol of the type

$$^{2S+1}A_J, \quad (15.21)$$

which is called the *spectral term*. The states of an atom are thus determined by the electronic configuration, together with the global quantum numbers, eqn (15.21). For instance, the ground states of some of the light

elements are as follows:

He :	$1s^2$	${}^1S_0;$
Na :	$1s^2 2s^2 2p^6 3s$	${}^2S_{1/2};$
Cl :	$1s^2 2s^2 2p^6 3s^2 3p^5$	${}^2S_{1/2};$
Ar :	$1s^2 2s^2 2p^6 3s^2 3p^6$	${}^1S_0;$
Fe :	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$	${}^5D_4;$

etc. The only degeneracy which survives is the $2J + 1$ -fold degeneracy related to the conservation of total angular momentum, corresponding to the states $J_z = J, J - 1, \dots, -J$. A detailed discussion of fine structure and hyperfine structure of the hydrogen atom was given in Section 21.2.

Two equivalent electrons in generic orbital

Consider two equivalent electrons in a generic ℓ orbital. Consider the state with $\{\ell_z = \ell, \ell_z = \ell\}$ which is necessarily the state with the largest L , $L = 2\ell$. The orbital wave function is necessarily symmetric (even) and Pauli's principle requires that the spin must in an antisymmetric state ($S = 0$). The orbital state $L = 2\ell - 1$ and $L_z = 2\ell - 1$ is necessarily antisymmetric, as it must be orthogonal to the state $L = 2\ell$, $L_z = 2\ell - 1$, which is symmetric. Thus for the states $L = 2\ell - 1$ the associated spin wave function must be symmetric: $S = 1$. Repeating these considerations for other values of L we arrive at the general conclusion for the allowed values of (L, S) :

$$L + S = \text{even} \quad (15.22)$$

Hund's rule

An empirical fact, which can be justified by a numerical calculation, is a rule known as *Hund's rule*. It states that the ground state of the atom corresponds to the multiplet with the highest value of the total spin S , and among the multiplets with the same value of S , the one with the largest possible L . We remark that such a rule obviously holds only for the ground state.

Intuitively, the state with the maximum spin has a spin wave function as symmetric as possible; the orbital wave function must then be maximally antisymmetric and the electrons tend to occupy space regions as separate as possible. In this way the Coulomb repulsion is minimized and the energy is lowered.

Configuration mixing

It is important to know the extent to which the discussion so far applies. Let us think in an abstract fashion that one has all possible single-particle solutions, and that one constructs the eigenfunctions of H_0 , Ψ_k (see the Section 15.4). As these form a complete set of functions the exact solution of Schrödinger's equation for n electrons can be written

as

$$\Psi = \sum_k \Psi_k . \quad (15.23)$$

Up to now we have considered only a small subspace of solutions, of dimension d_g corresponding to a given electronic configuration. The Hamiltonian H will in general have non-vanishing matrix elements among states with different electronic configurations, which means that wave function (15.23) can be written as a “sum over configurations”. For instance, the ground state of carbon will have a more general form,

$$c_0 |1s^2 2s^2 2p^2\rangle + c_1 |1s^2 2s^2 2p3p\rangle + \dots$$

If the Hartree approximation, or the Hartree–Fock approximation, which we are going to study below, is a good approximation, it means that the coefficients c_1, \dots , are small. But if one wants to calculate the atomic levels to great precision these coefficients must be calculated. The existence of such a mixing, together with the spin–spin coupling, has an important qualitative consequence: it helps explain some electromagnetic transitions which would otherwise be forbidden.

15.4 Slater determinants

As has already been emphasized, an important ingredient in the quantum mechanical analysis of atomic structure is the Pauli’s principle. In this section we analyze how, starting from single-particle states, completely antisymmetric states can be constructed: it makes use of Slater determinants, already encountered in Chapter 5.

The single-particle Hamiltonian (15.2) does not explicitly depend on spin. The solution of Schrödinger’s equation for a single particle in a central field therefore has the form

$$\psi = R_{n\ell}(r) Y_{\ell,m}(\Omega) \chi_s(\sigma). \quad (15.24)$$

The electron carries spin $\frac{1}{2}$, and hence the quantum numbers needed to describe the state completely are the ones listed in eqn (15.24): n is the principal (radial) quantum number, ℓ the orbital angular momentum, m the eigenvalue of ℓ_z , and s the eigenvalue of s_z . Ω stands for the variables θ, φ , whereas σ stands for the spin variables, $\pm \frac{1}{2}$. χ_s is the spin wave function. For instance, if $s = \pm$ indicates the spin components,

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

The electronic configuration is determined by the values n, ℓ , the various wave functions corresponding to the quantum numbers ℓ_z, s_z .

In the zeroth-order approximation, $H = H_0$, the wave function of N electrons can be obtained from the Slater determinants, constructed as

the antisymmetrized products out of the single-particle wave functions:

$$\Psi = \begin{vmatrix} \psi_{a_1}(q_1) & \psi_{a_1}(q_2) & \dots \\ \psi_{a_2}(q_1) & \psi_{a_2}(q_2) & \dots \\ \dots & \dots & \dots \\ \psi_{a_n}(q_1) & \psi_{a_n}(q_2) & \dots \end{vmatrix}. \quad (15.25)$$

a_i are the states and q_i are the variables of the N particles. For a single-particle wave function in a central field, $\psi_{a_i}(q_i)$, a_i stands for $\{n \ell m s\}$.

From the structure of the Slater determinant, it is easy to see the following properties:

Property 1. *The state corresponding to a closed shell has the quantum numbers $(L, S) = (0, 0)$.*

In a completely filled shell, all possible single-particle states corresponding to the given electronic configuration are occupied, and consequently a unique Slater determinant describes this state. Thus each possible value of m_i appears once, and hence $\sum m_i = 0$ and $L_z|\Psi\rangle = 0$. Act on this state with $L_+ = \sum \ell_+$, where the summation is over the particles. Each ℓ_+ acting on one of the electrons either annihilates the state (if $m_i = \ell_i$) or raises m_i by one so that the same value of m now appears twice. Now two rows of the determinant become identical and the determinant vanishes. For the same reason the action of $L_- = \sum \ell_-$ annihilates the state. A state annihilated by both L_+ and L_- is a state with $L = 0$. The same reasoning applied to the spin shows that it is a state with $S = 0$.

Property 2. *The rotational properties of a Slater determinant depends only on the electrons in partially filled shells.*

This is a simple application of the preceding result, and is a consequence of the distribution property of the operators. When \mathbf{L} acts on a closed shell it yields zero while when it acts on an incomplete shell it generates a linear combination of Slater determinants corresponding to the same electron configuration. In other words, the set of Slater determinants associated with a fixed set of quantum numbers of an incomplete shell form an (in general, reducible) representation of the rotation group. Which angular momenta appear depends on the usual addition rule of angular momentum and Pauli's principle.

Property 3. *The transformation property of a configuration with N_1 external electrons is equivalent to that of a configuration with $N_0 - N_1$ external electrons, where N_0 stands for the number of electrons in the complete shell.*

This property follows from the first two discussed above. Instead of indicating the orbitals occupied by the electrons we can specify the empty orbitals. Thus in the case of a p^5 state, instead of specifying the

states of five electrons it is sufficient to indicate the hole (the empty orbit) to get to the same result. The set of possible hole states also forms a representation of the rotational group; they are equivalent to those formed by the electrons, and there is a unique correspondence between the two possible ways to describe the same states.

As an explicit example, consider carbon with the electronic configuration $1s^2 2s^2 2p^2$. As a p shell has six possible states, there are $\binom{6}{2} = 15$ ways of choosing the two states occupied by the outer electrons. There are 15 Slater determinants (atomic states) in this case. For instance if the external electrons occupy $(1, \frac{1}{2}), (1, -\frac{1}{2})$ or $(1, \frac{1}{2}), (-1, -\frac{1}{2})$, the respective states are

$$\Psi_1 = \begin{vmatrix} R_{10}(r_1)Y_{00}\chi_+(\sigma_1) & R_{10}(r_2)Y_{00}\chi_+(\sigma_2) & \dots & R_{10}(r_6)Y_{00}\chi_+(\sigma_6) \\ R_{10}(r_1)Y_{00}\chi_-(\sigma_1) & R_{10}(r_2)Y_{00}\chi_-(\sigma_2) & \dots & R_{10}(r_6)Y_{00}\chi_-(\sigma_6) \\ R_{20}(r_1)Y_{00}\chi_+(\sigma_1) & R_{20}(r_2)Y_{00}\chi_+(\sigma_2) & \dots & R_{20}(r_6)Y_{00}\chi_+(\sigma_6) \\ R_{20}(r_1)Y_{00}\chi_-(\sigma_1) & R_{20}(r_2)Y_{00}\chi_-(\sigma_2) & \dots & R_{20}(r_6)Y_{00}\chi_-(\sigma_6) \\ R_{21}(r_1)Y_{11}\chi_+(\sigma_1) & R_{21}(r_2)Y_{11}\chi_+(\sigma_2) & \dots & R_{21}(r_6)Y_{11}\chi_+(\sigma_6) \\ R_{21}(r_1)Y_{11}\chi_-(\sigma_1) & R_{21}(r_2)Y_{11}\chi_-(\sigma_2) & \dots & R_{21}(r_6)Y_{11}\chi_-(\sigma_6) \end{vmatrix}$$

$$\Psi_2 = \begin{vmatrix} R_{10}(r_1)Y_{00}\chi_+(\sigma_1) & R_{10}(r_2)Y_{00}\chi_+(\sigma_2) & \dots & R_{10}(r_6)Y_{00}\chi_+(\sigma_6) \\ R_{10}(r_1)Y_{00}\chi_-(\sigma_1) & R_{10}(r_2)Y_{00}\chi_-(\sigma_2) & \dots & R_{10}(r_6)Y_{00}\chi_-(\sigma_6) \\ R_{20}(r_1)Y_{00}\chi_+(\sigma_1) & R_{20}(r_2)Y_{00}\chi_+(\sigma_2) & \dots & R_{20}(r_6)Y_{00}\chi_+(\sigma_6) \\ R_{20}(r_1)Y_{00}\chi_-(\sigma_1) & R_{20}(r_2)Y_{00}\chi_-(\sigma_2) & \dots & R_{20}(r_6)Y_{00}\chi_-(\sigma_6) \\ R_{21}(r_1)Y_{11}\chi_+(\sigma_1) & R_{21}(r_2)Y_{11}\chi_+(\sigma_2) & \dots & R_{21}(r_6)Y_{11}\chi_+(\sigma_6) \\ R_{21}(r_1)Y_{11}\chi_-(\sigma_1) & R_{21}(r_2)Y_{11}\chi_-(\sigma_2) & \dots & R_{21}(r_6)Y_{11}\chi_-(\sigma_6) \end{vmatrix}$$

Remarks

- (1) If d_g is the degeneracy associated with a given electronic configuration, the calculation of the energy eigenvalues will be a typical problem of degenerate perturbation theory, with a $d_g \times d_g$ matrix associated with such a configuration.
- (2) The Slater determinant is the product of single-particle wave functions, *antisymmetrized* with respect to exchange of particles. As a result of such an antisymmetrization, it will not be an eigenstate of ℓ_z or s_z of single particles. For instance, for a p^2 state with $(\ell_z, s_z) = (0, \frac{1}{2}), (1, \frac{1}{2})$

$$\Psi = \begin{vmatrix} R(r_1)Y_{11}(\Omega_1)\chi_+(\sigma_1) & R(r_2)Y_{11}(\Omega_2)\chi_+(\sigma_2) \\ R(r_1)Y_{10}(\Omega_1)\chi_+(\sigma_1) & R(r_2)Y_{10}(\Omega_2)\chi_+(\sigma_2) \end{vmatrix} \\ = R(r_1)R(r_2)\chi_+(\sigma_1)\chi_+(\sigma_2)[Y_{11}(\Omega_1)Y_{10}(\Omega_2) - Y_{10}(\Omega_1)Y_{11}(\Omega_2)],$$

and the action of $\ell_z^{(1)}$ yields

$$\ell_z^{(1)}\Psi = R(r_1)R(r_2)\chi_+(\sigma_1)\chi_+(\sigma_2)Y_{11}(\Omega_1)Y_{10}(\Omega_2),$$

which is not proportional to Ψ , although, naturally, it is an eigenstate of $\ell_z = \ell_z^{(1)} + \ell_z^{(2)}$, as can be readily checked. In general, such a situation is a consequence of the fact that the physical states belong to particular space, $\mathcal{A}(\mathcal{H}^N)$, whose basis is the set of completely antisymmetric states, and not simply the space \mathcal{H}^N .

- (3) As we have already noted, each Slater determinant is in general not even an eigenstate of

$$\mathbf{L} = \ell_1 + \dots \ell_N; \quad \mathbf{S} = \mathbf{s}_1 + \dots \mathbf{s}_N.$$

It will be seen that it is possible to diagonalize L^2, L_z, S^2, S_z in terms of suitably chosen linear combinations of the Slater determinants; such a step will be important in the classification of the spectrum.

15.5 The Hartree–Fock approximation

Starting with a set of single-particle wave functions, with the method of the preceding sections, we constructed the Slater determinants, which have the correct quantum numbers (L, S). They can be regarded as a first approximation of the wave function of the atom. For instance, the solution of Hartree's equations, ψ_i , can be taken as the zeroth order single-particle wave functions.

A further refinement in the analysis of atomic structures is due to Hartree and Fock. A Hartree–Fock approximation makes use of the central fields already discussed, but with wave functions which are constructed in terms of the Slater determinants. Pauli's principle is incorporated from the beginning in this approach.

Let us start with a simple case: let us try to describe a system with a single Slater determinant, Ψ , made from the products of single-particle wave functions, $\psi_a(q_i)$. What is the best choice for the single-particle wave functions? The answer can be found by considering the whole question from a variational point of view: among the class of functions which has the form of Ψ , the best choice is the one for which the energy is minimized. Let us for simplicity consider a set of orthogonal functions, so that the constraint of normalization can be written by use of a set of Lagrange multipliers, $\varepsilon_i(\|\psi_i\|^2 - 1)$; the variational principle tells us that

$$\frac{\delta}{\delta\psi_i(q_i)} \left(\langle \Psi | H | \Psi \rangle - \sum_k \varepsilon_k (\|\psi_k\|^2 - 1) \right) = 0.$$

The Hamiltonian has the following operatorial form:

$$H = \sum_i f_i + \sum_{i < j} g_{ij},$$

where f_i are operators acting only on the variables of a single particle, and g_{ij} contains the interaction terms between the two particles, i, j . For instance they can be of the form

$$f_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i}; \quad g_{ij} = \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}.$$

The matrix element of the Hamiltonian H can then have the form,

$$\langle \Psi | H | \Psi \rangle = \sum_i \langle i | f | i \rangle + \sum_{i < j} (\langle ij | g | ij \rangle - \langle ij | g | ji \rangle). \quad (15.26)$$

More⁷ explicitly,

⁷In eqn (15.26) the summation is over the states which compose the determinant Ψ . By Pauli's principle there is one state per particle so it is equivalent to summing over the particles.

$$\langle i|f|i\rangle = \int_q \psi_i^*(q) \left(-\frac{1}{2} \nabla^2 - \frac{Z}{r} \right) \psi_i(q) : \quad (15.27a)$$

$$\begin{aligned} \langle ij|g|ij\rangle - \langle ij|g|ji\rangle &= \int_{q_1 q_2} \psi_i^*(q_1) \psi_j^*(q_2) \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} \psi_i(q_1) \psi_j(q_2) \\ &\quad - \int_{q_1 q_2} \psi_i^*(q_1) \psi_j^*(q_2) \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} \psi_j(q_1) \psi_i(q_2) . \end{aligned} \quad (15.27b)$$

q stands for the coordinates as well as spin, the integration symbol means space integrals as well as sums over spin variables. The first term of eqn (15.27b) is called the *direct term*, while the second term is referred to as the *exchange term*, or exchange integral.

By using eqn (15.27) we see that the variational equation, with respect to $\psi_i^*(q)$, takes the form

$$\begin{aligned} \varepsilon_i \psi_i(q) &= \left(-\frac{1}{2} \nabla^2 - \frac{Z}{r} \right) \psi_i(q) \\ &\quad + \sum_{j \neq i} \int_{q'} \left[\psi_j^*(q') \frac{1}{|\mathbf{x} - \mathbf{x}'|} \psi_j(q') \psi_i(q) - \psi_j^*(q') \frac{1}{|\mathbf{x} - \mathbf{x}'|} \psi_i(q') \psi_j(q) \right] . \end{aligned} \quad (15.28)$$

We note that in the exchange term, the unknown function ψ_i appears under the integration symbol. In the summation over particles, the term $i = j$ can be included, as it cancels out between the direct and exchange terms.

Equation (15.28) constitutes an eigenvalue problem of a system of integro-differential equations, and these are the Hartree–Fock equations for a single Slater determinant. Numerical solutions for this equation are given in the Problems for numerical analysis at the end of this chapter. For now we note some of the properties of this system of equations.

Exchange term

The Coulomb interaction in the exchange integral gives

$$\psi_j^*(q') \frac{1}{|\mathbf{x} - \mathbf{x}'|} \psi_i(q') :$$

it is independent of spin. The integral is therefore proportional to the simple product of the spin wave functions,

$$\sum_{\sigma'} \chi_{s_j}^*(\sigma') \chi_{s_i}(\sigma') = \delta_{s_i s_j} ; \quad (15.29)$$

in other words, the exchange term vanishes for orbitals with different eigenvalues s_z : only for the two particles with parallel spins does Pauli's principle give rise to an additional interaction term.

Orthogonality

We have not explicitly discussed the orthogonality condition among the functions ψ_i , but this is a consequence of system (15.28). As in the usual

proof of the orthogonality of eigenfunctions, we multiply the equation for ψ_i by ψ_j^* and the ψ_j equation by ψ_i^* , and subtract term by term the complex conjugate of the second from the first. We find that

$$(\varepsilon_i - \varepsilon_j)(\psi_j|\psi_i\rangle = 0,$$

and therefore the eigenfunctions corresponding to different eigenvalues are orthogonal to each other.

Eigenvalues ε_i

The Lagrange multipliers ε_i have the interpretation as the extraction energy of the i -th electron. Let us number the particles so that the one we are interested in is the N -th electron, multiply the associated equation (15.28) by $\psi_N^*(q)$, and integrate. Using the notation in eqn (15.27) we get

$$\varepsilon_N = \langle N|f|N\rangle + \sum_{j < N} (\langle jN|g|jN\rangle - \langle jN|g|Nj\rangle). \quad (15.30)$$

The energy of N particles is given by eqn (15.26) (call it U_N): isolating the part depending on the N -th particle, it is possible to separate the energy of $N-1$ particles and the remaining part:

$$U_N = U_{N-1} + \langle N|f|N\rangle + \sum_{j < N} (\langle jN|g|jN\rangle - \langle jN|g|Nj\rangle),$$

that is, formally,

$$\varepsilon_N = U_N - U_{N-1}.$$

Suppose now that, in a first approximation, extraction of the N -th particle leaves the other wave functions approximately invariant. Then U_{N-1} is indeed the energy of the system of $N-1$ particles, and ε_N is the energy for extracting the N -th particle. This assertion, which is approximately valid, is known as Koopman theorem. (Koopman's theorem is more than this, but this will be discussed in Supplement 22.7.11.)

Now multiplying eqn (15.28) by $\psi_i(q)$ and integrating and summing over the particles, one finds that

$$\begin{aligned} \sum_i \varepsilon_i &= \sum_i \langle i|f|i\rangle + \sum_{i \neq j} (\langle ij|g|ij\rangle - \langle ij|g|ji\rangle) \\ &= \langle \Psi|H|\Psi\rangle + \sum_{i < j} (\langle ij|g|ij\rangle - \langle ij|g|ji\rangle), \end{aligned}$$

that is

$$E = \langle \Psi|H|\Psi\rangle = \sum_i \varepsilon_i - \sum_{i < j} (\langle ij|g|ij\rangle - \langle ij|g|ji\rangle). \quad (15.31)$$

As in the case of the Hartree approximation, the second term in eqn (15.31) describes the correction to first order in perturbation theory, with respect to the independent-particle approximation.

15.5.1 Examples

To see how the Hartree–Fock (HF below) approximation works let us study a few simple examples in this section. The relatively simple form of the HF equation (15.28) is valid in the case of a closed shell, with a unique Slater determinant, or in the case of only one outer electron (as we shall see in this case the multiplicity due to spin or orbital angular momentum does not present a problem).

Let us start with helium in the ground state configuration, $1s^2$. The unique Slater determinant is

$$\begin{aligned}\Psi &= \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_{1s}(\mathbf{x}_1)\chi_+(\tilde{\sigma}_1) & \psi_{1s}(\mathbf{x}_2)\chi_+(\tilde{\sigma}_2) \\ \psi_{1s}(\mathbf{x}_1)\chi_-(\tilde{\sigma}_1) & \psi_{1s}(\mathbf{x}_2)\chi_-(\tilde{\sigma}_2) \end{vmatrix} \\ &= \psi_{1s}(\mathbf{x}_1)\psi_{1s}(\mathbf{x}_2) \frac{1}{\sqrt{2}} (\chi_+(\tilde{\sigma}_1)\chi_-(\tilde{\sigma}_2) - \chi_+(\tilde{\sigma}_2)\chi_-(\tilde{\sigma}_1)) .\end{aligned}$$

The two electrons are in a spin-singlet state, and therefore by virtue of eqn (15.29) there are no exchange terms in the HF equation. It is easy to compute

$$\begin{aligned}\langle \Psi | H | \Psi \rangle &= 2 \int d^3x \psi_{1s}^*(\mathbf{x}) \left(-\frac{1}{2} \nabla^2 - \frac{Z}{|\mathbf{x}|} \right) \psi_{1s}(\mathbf{x}) \\ &\quad + \int d^3x d^3x' |\psi_{1s}(\mathbf{x})|^2 \frac{1}{|\mathbf{x} - \mathbf{x}'|} |\psi_{1s}(\mathbf{x}')|^2 ,\end{aligned}$$

and the variational principle yields the Hartree equation,

$$\left(-\frac{1}{2} \nabla^2 - \frac{Z}{|\mathbf{x}|} \right) \psi_{1s}(\mathbf{x}) + \int d^3x' |\psi_{1s}(\mathbf{x}')|^2 \frac{1}{|\mathbf{x} - \mathbf{x}'|} \psi_{1s}(\mathbf{x}) = \varepsilon \psi_{1s}(\mathbf{x}) .$$

A more interesting case is that of an excited state of helium, $1s2s$. We know from the general discussion of Section 15.3 that there are two possible spectral terms, the spin triplet 3S and the singlet, 1S . Let us see in some detail how these states come about, and how the electron-electron interactions split these two levels.

There are four Slater determinants:

$$\begin{aligned}\Psi_1 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1s}(\mathbf{x}_1)|+\rangle & \psi_{1s}(\mathbf{x}_2)|+\rangle \\ \psi_{2s}(\mathbf{x}_1)|+\rangle & \psi_{2s}(\mathbf{x}_2)|+\rangle \end{vmatrix} ; \quad \Psi_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1s}(\mathbf{x}_1)|-\rangle & \psi_{1s}(\mathbf{x}_2)|-\rangle \\ \psi_{2s}(\mathbf{x}_1)|-\rangle & \psi_{2s}(\mathbf{x}_2)|-\rangle \end{vmatrix} ; \\ \Psi_3 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1s}(\mathbf{x}_1)|+\rangle & \psi_{1s}(\mathbf{x}_2)|+\rangle \\ \psi_{2s}(\mathbf{x}_1)|-\rangle & \psi_{2s}(\mathbf{x}_2)|-\rangle \end{vmatrix} ; \quad \Psi_4 = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1s}(\mathbf{x}_1)|-\rangle & \psi_{1s}(\mathbf{x}_2)|-\rangle \\ \psi_{2s}(\mathbf{x}_1)|+\rangle & \psi_{2s}(\mathbf{x}_2)|+\rangle \end{vmatrix} .\end{aligned}$$

Obviously the states Ψ_1 and Ψ_2 correspond to the two states of the triplet with $S_z = 1$ and $S_z = -1$ respectively; Ψ_3 and Ψ_4 are linear combinations of the two states with $S_z = 0$, one in the triplet and the other in the singlet. Let us consider the HF equation for Ψ_1 . Equation (15.28) gives, after multiplying it by the spin wave function and

simplifying

$$\begin{aligned}\varepsilon_{1s}\psi_{1s}(\mathbf{x})\chi_+(\sigma) &= \left(-\frac{1}{2}\nabla^2 - \frac{Z}{|\mathbf{x}|}\right)\psi_{1s}(\mathbf{x})\chi_+(\sigma) \\ &+ \sum_{\sigma'} \int_{\mathbf{x}'} \frac{1}{|\mathbf{x} - \mathbf{x}'|} \left(\psi_{2s}^*(\mathbf{x}')\chi_+^*(\sigma')\psi_{2s}(\mathbf{x}')\chi_+(\sigma')\psi_{1s}(\mathbf{x})\chi_+(\sigma) \right. \\ &\quad \left. - \psi_{2s}^*(\mathbf{x}')\chi_+^*(\sigma')\psi_{1s}(\mathbf{x}')\chi_+(\sigma')\psi_{2s}(\mathbf{x})\chi_+(\sigma) \right).\end{aligned}$$

By summing over σ' and with a further simplification we find that

$$\begin{aligned}\varepsilon_{1s}\psi_{1s}(\mathbf{x}) &= \left(-\frac{1}{2}\nabla^2 - \frac{Z}{|\mathbf{x}|}\right)\psi_{1s}(\mathbf{x}) \\ &+ \int_{\mathbf{x}'} \frac{1}{|\mathbf{x} - \mathbf{x}'|} \left(|\psi_{2s}(\mathbf{x}')|^2\psi_{1s}(\mathbf{x}) - \psi_{2s}^*(\mathbf{x}')\psi_{1s}(\mathbf{x}')\psi_{2s}(\mathbf{x}) \right); \\ \varepsilon_{2s}\psi_{2s}(\mathbf{x}) &= \left(-\frac{1}{2}\nabla^2 - \frac{Z}{|\mathbf{x}|}\right)\psi_{2s}(\mathbf{x}) \\ &+ \int_{\mathbf{x}'} \frac{1}{|\mathbf{x} - \mathbf{x}'|} \left(|\psi_{1s}(\mathbf{x}')|^2\psi_{2s}(\mathbf{x}) - \psi_{1s}^*(\mathbf{x}')\psi_{2s}(\mathbf{x}')\psi_{1s}(\mathbf{x}) \right),\end{aligned}$$

where the equation for ψ_{2s} , which can be obtained in the same way, is also written. Suppose that these equations have been solved. The energy of the states can be written by using eqn (15.26) as

$$\begin{aligned}\langle \Psi_1 | H | \Psi_1 \rangle &= I_{1s} + I_{2s} + J - K; \quad (15.32) \\ I_a &\equiv \int_{\mathbf{x}} \psi_a^* \left(-\frac{1}{2}\nabla^2 - \frac{Z}{|\mathbf{x}|}\right) \psi_a; \\ J &\equiv \int_{\mathbf{x}, \mathbf{x}'} |\psi_{1s}(\mathbf{x})|^2 \frac{1}{|\mathbf{x} - \mathbf{x}'|} |\psi_{2s}(\mathbf{x}')|^2; \\ K &\equiv \int_{\mathbf{x}, \mathbf{x}'} \psi_{1s}^*(\mathbf{x}')\psi_{2s}^*(\mathbf{x}') \frac{1}{|\mathbf{x} - \mathbf{x}'|} \psi_{1s}(\mathbf{x})\psi_{2s}(\mathbf{x}).\end{aligned}$$

J, K are the direct integral and exchange integral, respectively. The same result holds for Ψ_2 .

We now consider the determinants Ψ_3 and Ψ_4 . In these cases there are no exchange terms, as the spins are in opposite directions, and we find easily that

$$\langle \Psi_3 | H | \Psi_3 \rangle = \langle \Psi_4 | H | \Psi_4 \rangle = I_{1s} + I_{2s} + J.$$

The four determinants are degenerate eigenstates in the approximation of independent particles; therefore it is necessary to consider the non-diagonal matrix elements of H . As S^2 and S_z both commute with H the only non-vanishing elements are $\langle \Psi_3 | H | \Psi_4 \rangle$ and its complex conjugate.

Equation (15.26) cannot be used to compute these matrix elements but we can expand the states and write, in compact form,

$$\begin{aligned}\langle \Psi_3 | H | \Psi_4 \rangle &= \sum \psi_{1s}^*(\mathbf{x}_1)\psi_{2s}^*(\mathbf{x}_2)\chi_+(\sigma_1)\chi_-(\sigma_2)H \\ &\quad \left(\psi_{1s}(\mathbf{x}_1)\psi_{2s}(\mathbf{x}_2)\chi_-(\sigma_1)\chi_+(\sigma_2) - \psi_{1s}(\mathbf{x}_2)\psi_{2s}(\mathbf{x}_1)\chi_-(\sigma_2)\chi_+(\sigma_1) \right).\end{aligned}$$

The first term in the bracket vanishes by the orthogonality of the spin wave functions; in the second term the single-particle terms vanish by the orthogonality of the radial wave functions, as for instance the kinetic term associated with the variable \mathbf{x}_1 is multiplied by

$$\int_{\mathbf{x}_2} \psi_{2s}(\mathbf{x}_2) \psi_{1s}(\mathbf{x}_2) = 0.$$

The term of Coulomb interaction is just the exchange integral, and therefore

$$\langle \Psi_3 | H | \Psi_4 \rangle = -K.$$

The Hamiltonian can therefore be written, in the subspace Ψ_3, Ψ_4 , as

$$\begin{pmatrix} I_{1s} + I_{2s} + J & -K \\ -K & I_{1s} + I_{2s} + J \end{pmatrix},$$

with eigenvalues and corresponding eigenstates

$$\begin{aligned} I_{1s} + I_{2s} + J - K : & \quad \frac{1}{\sqrt{2}} (\Psi_3 + \Psi_4) ; \\ I_{1s} + I_{2s} + J + K : & \quad \frac{1}{\sqrt{2}} (\Psi_3 - \Psi_4) . \end{aligned}$$

With some algebra, the eigenstates can be found to be

$$\begin{aligned} \frac{\Psi_3 + \Psi_4}{\sqrt{2}} &= \frac{\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)}{\sqrt{2}} \cdot \frac{\chi_+(1)\chi_-(2) + \chi_-(1)\chi_+(2)}{\sqrt{2}} ; \\ \frac{\Psi_3 - \Psi_4}{\sqrt{2}} &= \frac{\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1)}{\sqrt{2}} \cdot \frac{\chi_+(1)\chi_-(2) - \chi_-(1)\chi_+(2)}{\sqrt{2}} . \end{aligned}$$

As expected, one of these states is what is needed to complete the triplet, with the same energy as $\Psi_{1,2}$. The other state is the singlet.

It can easily be shown that $K > 0$ and therefore for excited helium the triplet (the ground state of ortho-helium) is lower in energy than the singlet (the first excited state of para-helium).

An observation which could be useful in more complicated cases is the following. We have computed the eigenvalues of non-degenerate states relatively straightforwardly, eqn (15.32). On the other hand, we know a priori that one of the states with $S_z = 0$ must be the third member of the multiplet and so must have the same energy. The $(S, S_z) = (1, 0)$ and the singlet $(S, S_z) = (0, 0)$ states are related to $\Psi_{3,4}$ by a unitary transformation, but as any unitary transformation leaves the trace of H in this 2×2 subspace, the energy eigenvalue for the singlet could have been found from the known value for

$$\text{Tr } H = \langle \Psi_3 | H | \Psi_3 \rangle + \langle \Psi_4 | H | \Psi_4 \rangle = 2(I_{1s} + I_{2s} + J).$$

In fact, by subtracting the eigenvalue of the triplet, we find that

$$2(I_{1s} + I_{2s} + J) - (I_{1s} + I_{2s} + J - K) = (I_{1s} + I_{2s} + J + K),$$

in agreement with what we found by diagonalization. This observation, in general cases, is known as Slater's theorem.

15.6 Spin-orbit interactions

The interactions due to the electron spin are in general rather complicated, see eqn (22.67):

$$U_{so} = \sum_a \frac{Ze^2}{2m^2c^2r_a^3} \boldsymbol{\ell}_a \cdot \mathbf{s}_a ; \quad (15.33a)$$

$$U_{soo} = \sum_{a < b} \frac{e^2}{2m^2c^2r_{ab}^3} [(\mathbf{s}_b + 2\mathbf{s}_a) \cdot (\mathbf{r}_{ab} \times \mathbf{p}_b) - (\mathbf{s}_a + 2\mathbf{s}_b) \cdot (\mathbf{r}_{ab} \times \mathbf{p}_a)] ; \quad (15.33b)$$

$$U_{ss} = \sum_{a < b} \frac{e^2}{m^2c^2r_{ab}^3} \left[\mathbf{s}_a \cdot \mathbf{s}_b - \frac{3(\mathbf{s}_a \cdot \mathbf{r}_{ab})(\mathbf{s}_b \cdot \mathbf{r}_{ab})}{r_{ab}^2} \right] . \quad (15.33c)$$

Equation (15.33a) represents the “spin-orbit interactions” with the electric field of the nucleus, eqn (15.33b) the interactions between the spin of an electron and the fields of other orbiting electrons; eqn (15.33c) the spin-spin interactions. In eqn (15.33c) we have neglected a contact term, proportional to $\mathbf{s}_a \mathbf{s}_b \delta^3(\mathbf{r}_{ab})$, which is invariant under space rotations as well as spin rotations, and does not influence the following analysis.

Order of magnitude

It is important to have an idea of the order of magnitude of various terms in eqn (15.33), and above all, their dependence on Z . The spin-orbit interaction U_{so} feels the field of the nucleus directly. We know that the characteristic length in a Coulomb field with charge Z is $a_Z = r_B/Z$, where r_B is the Bohr radius, and hence the order of magnitude of the matrix elements of U_{so} is

$$\frac{Ze^2 \hbar^2}{m^2 c^2 a_Z^3} |\psi(a_Z)|^2 a_Z^3 . \quad (15.34)$$

The last factor is the probability of finding an electron at a distance $r \sim a_Z$. $\psi(a_Z)$ can be estimated either by a semi-classical argument (see Section 22.7.1) or by a scaling argument. If in the Hartree-Fock or Hartree equation, we pass to the rescaled variable $x = Z r$, $\tilde{\psi} = \psi/\sqrt{Z}$, we have an equation in which each term is of order $1/Z$ but there are Z of them. The characteristic range in these variables, in atomic units, is $x \sim 1$ and in this region $\tilde{\psi} \sim 1$, which corresponds in the usual variables to $r \sim 1/Z$, $\psi \sim 1/\sqrt{Z}$. Therefore $|\psi(a_Z)|^2 a_Z^3 \sim 1/Z^2$, that is, the probability of finding an electron near the nucleus decreases as $1/Z^2$. Substitution of this into eqn (15.34) gives

$$\langle U_{so} \rangle \sim Z^4 \frac{1}{Z^2} \frac{e^2 \hbar^2}{m^2 c^2 r_B^3} = Z^2 \alpha^2 \frac{e^2}{r_B} .$$

The dimensionless constant

$$\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137}$$

is called the *fine-structure constant*: it characterizes the splitting of the levels. As we shall see only the peripheral electrons contribute to the matrix elements responsible for the splitting of fine-structure sub-levels, so there is no extra factor Z due to the summation over the electrons.

The terms U_{soo} and U_{ss} are large for $r \sim r_B$, as they have no factors Z to multiply it, and therefore⁸

$$\langle U_{soo} \rangle \sim \langle U_{ss} \rangle \sim \alpha^2 \frac{e^2}{r_B}.$$

We see therefore that all the contributions give corrections of the order of $\mathcal{O}(\alpha^2)$ to the energy, but the LS term is dominant for large Z . For large Z , that is, $Z\alpha \sim 1$, the corrections due to the spin-orbit interactions become of the same order of magnitude as a Coulomb energy, and this invalidates the Russell-Saunders model for constructing the states.

We further note that for highly excited states the external electron orbits are basically in the simple Coulomb potential, with the typical energy $e^2/n^2 r_B$, where n is the principal quantum number. In this regime the spin-orbit interactions certainly prevail over Coulomb interactions.

In what follows we shall treat only the Russell-Saunders case in which simple symmetry considerations allow us to find the effect of the spin interactions.

In a purely electrostatic approximation each level (multiplet) has a degeneracy, $d_{LS} = (2S + 1)(2L + 1)$, which will be lifted by the spin-orbit interactions, H_{LS} .

We are in fact faced with a classic problem of degenerate perturbation theory: we must diagonalize H_{LS} in the subspace with given E_{LS} , i.e., we must find a basis in which H_{LS} is diagonal.

Within each multiplet, one can choose either of the two natural bases: the first is the one in which $|L, S, L_z, S_z\rangle$ are diagonal, the second is the one in which the total angular momentum is diagonal, $|L, S, J, J_z\rangle$. As \mathbf{J} commutes with H_{LS} and in fact with the full Hamiltonian, in the second basis H_{LS} is automatically diagonal, with each level being degenerate $(2J + 1)$ times.

In conclusion the basis $|L, S, J, J_z\rangle$ is the one which diagonalizes H , whose eigenvalues will be denoted as $E(L, S, J)$, or sometimes simply as E_J . The remaining degeneracy can be removed only by rotationally non-invariant perturbations (e.g., external electric field).

The sub-levels coming from the original multiplet are called *spectral terms* and are indicated by

$$^{2S+1}L_J.$$

The possible terms correspond to the possible values of J : we know from the theory of angular momentum that

$$|L - S| \leq J \leq L + S.$$

In cases $S \leq L$, i.e., when the number of terms is equal to $2S + 1$, the last number is called the *multiplicity* of the multiplet. We talk

⁸ Here also only the outer electrons in incomplete shells matter, so that there is no factor $Z(Z - 1)/2$, counting the electron pairs.

about singlets, doubles, triplets, etc., for multiplets of types 1L , 2L , 3L , etc. The classification with symbols such as $^{2S+1}L_J$ is used even when the Russell-Saunders model is qualitatively inadequate. In the latter cases J is always a good quantum number but not so L and S , and the eigenstates of H are combinations of states with different (L, S) . In such a case the notation is a purely formal one.

The central field

As a simple case we shall first of all consider the central field approximation, neglecting the spin-spin interactions among the electrons. Each electron moves in a mean field generated by the nucleus and by the other electrons. Let V_i be the field the i -th electron feels. We find the spin dependent part of the Hamiltonian, neglecting the relativistic corrections such as those proportional to p^4 , by applying eqn (14.25) directly

$$H_{LS} = \sum_i \frac{e}{2m^2 c^2} \frac{1}{r_i} \frac{dV_i}{dr} \mathbf{s}_i \cdot (\mathbf{r}_i \times \mathbf{p}_i) \equiv \sum_i A_i(r) \ell_i \cdot \mathbf{s}_i . \quad (15.35)$$

In this effective Hamiltonian are included the effects of the terms in eqn (15.33a) and eqn (15.33b).

Within each multiplet, the Wigner-Eckart theorem tells us that the matrix elements of a vector dependent on the orbital variables are proportional to the matrix elements of \mathbf{L} , while those of \mathbf{s}_i are proportional to the matrix elements of \mathbf{S} . Therefore the Hamiltonian takes a very simple form;

$$H_{LS} = A \mathbf{L} \cdot \mathbf{S} , \quad (15.36)$$

and by using the relation

$$2\mathbf{L} \cdot \mathbf{S} = \mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2 ,$$

we get for the eigenvalues of H_{LS}

$$E_J = \frac{A}{2} [J(J+1) - L(L+1) - S(S+1)] . \quad (15.37)$$

Within a multiplet L, S are constant so eqn (15.37) is a statement about the difference of the various terms of fine structure,

$$E_{J+1} - E_J = AJ . \quad (15.38)$$

Equation (15.38) is known as *Landé's rule*.

In a configuration with only closed shells, there are no fine structures, as $S = 0, L = 0$. This means that for each closed shell

$$\sum_{i \in \text{orb.compl.}} \ell_i \cdot \mathbf{s}_i = 0 \quad (15.39)$$

and therefore it is natural to understand that the matrix elements of eqn (15.35) depend, in the central field approximation, solely on the partially filled shells.

Depending on whether $A > 0$ or $A < 0$ the energies of the terms of the multiplet increase or decrease with J ; in the first case we talk about a *normal multiplet*, in the second case an *inverted multiplet*.

For the electron $e < 0$ and, for an attractive central field, $e dV/dr > 0$; therefore the sign of the constant A depends on the sign of the matrix element $\ell_i \cdot \mathbf{s}_i$, summed over the incomplete orbitals.

It is actually easy to determine the sign of A for atoms with only one incomplete shell in the ground state (and this is a very common case). Let $d_\ell = 2(2\ell+1)$ be the maximum number of particles which the orbital can host. If the actual number of electrons n is such that $n \leq d_\ell/2$ then Hund's rule tells us that all the spins are parallel and for all purposes we can put $\mathbf{s}_a = \mathbf{S}/n$. As all the particles have the same radial wave functions all the matrix elements of $A_i(r)$ in eqn (15.35) are equal and their value can be factorized, and hence

$$\langle U_{so} \rangle = \langle A_i \rangle \sum_i \mathbf{s}_i \cdot \ell_i = \langle A_i \rangle \frac{1}{n} \mathbf{S} \cdot \sum_i \ell_i = \langle A_i \rangle \frac{1}{n} \mathbf{S} \cdot \mathbf{L},$$

and as a result, we get $A > 0$.

For shells with $n > d_\ell$ it suffices to add and subtract the sum over the empty orbitals (holes),

$$\sum_i A_i \ell_i \cdot \mathbf{s}_i = \sum_{\text{orb.compl.}} A_i \ell_i \cdot \mathbf{s}_i - \sum_{\text{holes}} A_i \ell_i \cdot \mathbf{s}_i;$$

the coefficients A_i depend only on the orbitals, while for holes the spin and the orbital angular momenta are inverted with respect to the electrons. The first term vanishes by eqn (15.39), so only the negative term remains, i.e., $A < 0$.

Comparison with data

A way to check Landé's rule is to consider the ratios

$$\Delta_J = \frac{E_J - E_{J-1}}{J}. \quad (15.40)$$

These ratios must be independent of J , if Landé's rule holds.

The data for some typical cases are listed in Table 15.6. The energies are given in cm^{-1} . We note the presence of both normal multiplets with $\Delta_J > 0$ and inverted multiplets, with $\Delta_J < 0$, depending on the electronic configuration, in agreement with the general discussion above. There is also a qualitative agreement with Landé's rule. The main corrections are due to the inapplicability of Russell-Saunders and to the mixing among different electronic configurations.

The reader will find in the exercises closer examination of some of the issues, such as explicit writing of the LS coupling in the HF approximation, in the cases of two electrons.

15.6.1 The hydrogen atom

The hydrogen atom presents some particularities due to the accidental degeneracy. This degeneracy has no effect on the calculation of the ma-

Config.	Elem.	Multip.	Δ_J	Δ_{J-1}
$2p^2$	C	3P	13.5	16.42
$2p^4$	O	3P	-79.13	-68.71
$3p^2$	Si	3P	73.02	77.11
$3p^4$	S	3P	-198.	-177.6
$3d^2 4s^2$	Ti	3F	54.19	56.71
$3d^8 4s^2$	Ni	3F	-333.	-294.8
$4s^2 4p^2$	Ge	3P	426.4	557.1

Table 15.6 Estimates of A for triplets of fine structure

trix elements for the LS coupling but the Coulomb degeneracy remains to certain extent even after the relativistic corrections and maintains the degeneracy among the states with different ℓ, s but with the total angular momentum j , with the same principal quantum number n . (See Supplement 21.2.)

For simplicity we shall deal only with the $2p$ state here, which has a $(2S+1)(2L+1) = 6$ -fold degeneracy. In the presence of LS interactions the conserved quantum number can have values $j = \frac{1}{2}, \frac{3}{2}$, so there are two levels, with degrees of degeneracies 2 and 4, respectively: $2p_{1/2}$ and $2p_{3/2}$. Interactions (15.33a), in the case of hydrogenoid atoms, take the form

$$H_{FS} = Z \frac{e^2}{2m^2 c^2 r^3} \boldsymbol{\ell} \cdot \mathbf{s},$$

and the shift of the levels is given by eqn (15.36) with $L = 1, S = \frac{1}{2}$:

$$\Delta E(2p_{1/2}) = -A; \quad \Delta E(2p_{3/2}) = \frac{A}{2};$$

$$A = Z \frac{e^2 \hbar^2}{2m^2 c^2} \left\langle 2p \left| \frac{1}{r^3} \right| 2p \right\rangle.$$

For the hydrogenoid states

$$\left\langle nl \left| \frac{1}{r^3} \right| nl \right\rangle = \frac{Z^3}{r_B^3} \frac{1}{n^3} \frac{1}{\ell(\ell + \frac{1}{2})(\ell + 1)},$$

and hence for $n = 2, \ell = 1$

$$A = Z^4 \frac{e^2 \hbar^2}{2m^2 c^2 r_B^3} \frac{1}{24} = \frac{1}{24} Z^4 \alpha^2 \left(\frac{e^2}{2r_B} \right).$$

The factorized energy is the Rydberg energy. Note the characteristic dependence $Z^2\alpha^2$ of the corrections with respect to the unperturbed energy, Z^2 Ry. As $A > 0$ the level with the larger value of j is raised and vice versa. The difference, called fine-structure separation, is

$$F_{2p} = \Delta E(2p_{3/2}) - \Delta E(2p_{1/2}) = \frac{1}{16} Z^2 \alpha^2 \times Z^2 \text{ Ry} = Z^4 4.53 \times 10^{-5} \text{ eV}. \quad (15.41)$$

Numerically, the associated frequency for the hydrogen, F_{2p}/h , is

$$\frac{1}{h} F_{2p} = 10.95 \text{ GHz}.$$

Consider a line in the Balmer series, for instance the spectral line $3s \rightarrow 2p$. The transition frequency is about

$$\nu = \left(\frac{1}{4} - \frac{1}{9}\right) \text{ Ry}/h \simeq 4.57 \times 10^5 \text{ GHz}.$$

A spectral line such as this, observed at high resolution, reveals a tiny structure, that is fine structure. The splitting is given by eqn (15.41), i.e., one part in 10^4 . The doubling is due to the splitting of two possible transitions, $3s_{1/2} \rightarrow 2p_{1/2}$ and $3s_{1/2} \rightarrow 2p_{3/2}$.

15.7 Atoms in external electric fields

We now want to study the effects of a static external electric field on the atomic levels. For simplicity, we shall consider neutral atoms and neglect the effects of the order of m/M . In typical atomic distances, $\Delta x \sim 10^{-8}$ cm, macroscopic electric fields can be approximately regarded as constant. We shall therefore expand the electrostatic potential about the atomic center of mass, which approximately coincides with the position of the nucleus. Apart from a possible additive constant, the atom-external field interaction energy is given, by expanding to the second order (see Chapter 14)

$$H_I = -\mathbf{d} \cdot \mathbf{E} + \frac{1}{6} Q_{ij} \partial_i \partial_j V. \quad (15.42)$$

V is the external static field; the derivative of V and the electric field are calculated at the center of mass, the position of the nucleus, which is taken as the origin. \mathbf{d} is the electric dipole, and Q_{ij} the quadrupole moment,

$$\mathbf{d} = \sum_a e_a \mathbf{r}_a; \quad Q_{ij} = \sum_a e_a (3r_{a,i}r_{a,j} - r_a^2 \delta_{ij}). \quad (15.43)$$

$e_a = -|e|$ is the charge and \mathbf{r}_a is the position of the a -th particle.

15.7.1 Dipole interaction and polarizability

The shift of atomic levels due to a static electric field is known as the *Lo Surdo-Stark* effect. For a homogeneous field, the interaction is described

by the first term of eqn (15.42), and the Hamiltonian is given by

$$H = H_0 + H_I = \sum_a \frac{p^2}{2m} - \sum_a \frac{Ze^2}{r_a} + \sum_{a < b} \frac{e^2}{r_{ab}} + H_{LS} - d_z \mathcal{E}. \quad (15.44)$$

H_{LS} stands for generic relativistic corrections. The direction of the external field \mathcal{E} is taken to be the z direction. The Hamiltonian H_0 is invariant under rotations and under parity,

$$\mathbf{r}_a \rightarrow -\mathbf{r}_a; \quad \mathbf{p}_a \rightarrow -\mathbf{p}_a. \quad (15.45)$$

Normally the energy levels have as the sole $2J + 1$ -fold degeneracy that due to the orientation of the total angular momentum, J , and each level corresponds to the subspaces spanned by $|n, J, J_z\rangle$, con $J_z = -J, \dots + J$.

Perturbation theory with H_I in this subspace is, however, simple: if the quantization axis is taken to be z then H_I is invariant under rotations around the z axis, so H_I commutes with J_z and is automatically diagonal in the basis of states (J, J_z) . In other words the effect is

$$\delta E_n = -\mathcal{E} \langle n, J, J_z | d_z | n, J, J_z \rangle.$$

But parity commutes with H_0 ; barring accidental degeneracy, the energy eigenstate is also a parity eigenstate,

$$P|n, J, J_z\rangle = \eta_P |n, J, J_z\rangle; \quad (15.46)$$

$\eta_P = \pm 1$. On the other hand, the dipole operator is odd under parity,

$$P\mathbf{d}P^\dagger = -\mathbf{d}, \quad (15.47)$$

and thus

$$\begin{aligned} \langle \psi | \mathbf{d} | \psi \rangle &\equiv \langle \psi | P^{-1} P \mathbf{d} P^{-1} P | \psi \rangle = \langle \psi | P^\dagger P \mathbf{d} P^\dagger P | \psi \rangle \\ &= |\eta_P|^2 \langle \psi | P \mathbf{d} P^\dagger | \psi \rangle = -\langle \psi | \mathbf{d} | \psi \rangle, \end{aligned} \quad (15.48)$$

so that $\delta E_n = 0$: a linear Stark effect vanishes for a non-degenerate state.

The only exception occurs when there is an accidental degeneracy (i.e., not related to the angular momentum), as in the hydrogen case. This last case has been treated in Chapter 9. In a generic case, instead, we must go to the second order in perturbation theory, and according to the general formula, eqn (9.15), the correction to the energy for a stationary state $|\psi_0\rangle$ is

$$\delta E^{(2)} = \sum'_n \langle \psi_0 | \mathbf{d} \cdot \mathcal{E} | n \rangle \frac{1}{E_0 - E_n} \langle n | \mathbf{d} \cdot \mathcal{E} | \psi_0 \rangle \equiv -\frac{1}{2} \alpha_{ij} \mathcal{E}_i \mathcal{E}_j, \quad (15.49)$$

where the polarization tensor

$$\alpha_{ij} = \sum'_n \langle \psi_0 | d_i | n \rangle \frac{1}{E_n - E_0} \langle n | d_j | \psi_0 \rangle + (j \leftrightarrow i) \quad (15.50)$$

has been defined.

The energy in an electric field is therefore, to the second order in \mathcal{E} ,

$$E = E_0 - \frac{1}{2} \alpha_{ij} \mathcal{E}_i \mathcal{E}_j. \quad (15.51)$$

As can be seen from the preceding formulas the order of magnitude for the effect considered is

$$\alpha \sim \frac{e^2 a^2}{\Delta E}; \quad [\alpha] = \text{cm}^3.$$

If the binding energy is of electrostatic type we expect that $\Delta E \sim e^2/a$ and so $\alpha \sim a^3$, i.e., the polarizability is proportional to the volume of the system.

The dipole of the system is defined through the response of the system to the variation of the external electric field,

$$D_i = -\frac{\partial E}{\partial \mathcal{E}_i} = \alpha_{ij} \mathcal{E}_j. \quad (15.52)$$

The absence of the constant term in eqn (15.52) indicates the absence of a permanent dipole: the term shown is called the *induced dipole*.

Decomposition of the tensor α_{ij}

The tensor α_{ij} is symmetric. It can be decomposed into a part proportional to an identity and a traceless part,

$$\alpha_{ij} = \alpha_{kk} \frac{1}{3} \delta_{ij} + \left(\alpha_{ij} - \alpha_{kk} \frac{1}{3} \delta_{ij} \right) \equiv \alpha \delta_{ij} + \beta_{ij}, \quad (15.53a)$$

$$\alpha = \frac{2}{3} \sum'_n \langle \psi_0 | d_i | n \rangle \frac{1}{E_n - E_0} \langle n | d_i | \psi_0 \rangle. \quad (15.53b)$$

The operator which appears in eqn (15.53b),

$$\sum'_n d_i | n \rangle \frac{1}{E_n - E_0} \langle n | d_i |$$

is obviously invariant under rotations as the summation is done over all states and therefore over all different projections of the states $|n\rangle$, and the energies E_n are not supposed to depend on J_z : the unperturbed system is invariant under rotations.

Vice versa, the tensor β_{ij} is a symmetric traceless tensor, so it transforms as an irreducible second-rank tensor.

The level shift

We have seen that the energy in the quadratic Stark effect is of the order of $\alpha \mathcal{E}^2$. If \mathcal{E} is measured in volt/cm one can estimate this parameter:

$$\begin{aligned} \mathcal{E} &= f \frac{\text{V}}{\text{cm}}; \quad \alpha \sim 1 \text{\AA}^3; \\ \alpha \mathcal{E}^2 &\sim \frac{\text{\AA}^2}{\text{cm}^2} \frac{\text{\AA}}{e^2} (e \cdot \text{V})^2 f^2 \sim 10^{-16} \frac{(e \text{ V})^2}{10 \text{ eV}} f^2 \sim 10^{-17} \text{ eV} f^2. \end{aligned} \quad (15.54)$$

Therefore excluding the cases with very large fields or exceedingly small fine structure, the Stark effect is a small perturbation with respect to H_{LS} . In this case the Wigner–Eckart theorem tells us immediately the form that the operator α_{ij} takes among the states with fixed J :

$$\alpha_{ij} = \alpha \delta_{ij} + \beta \left(J_i J_k + J_k J_i - \frac{2}{3} \mathbf{J}^2 \delta_{ij} \right). \quad (15.55)$$

The second term is the second-rank traceless symmetric tensor formed by J , so we get

$$\delta E(J, J_z) = -\frac{1}{2} \mathcal{E}^2 \left[\alpha + 2\beta \left(J_z^2 - \frac{1}{3} J(J+1) \right) \right]. \quad (15.56)$$

We note that α represents the center of mass of the energy shift: taking the trace and summing over J_z are equivalent, so the sum over various terms proportional to β vanishes, which can be also verified directly:

$$\frac{1}{2J+1} \sum_{J_z=-J}^{J_z=+J} J_z^2 = \frac{1}{3} J(J+1).$$

We note furthermore that the states with opposite J_z are degenerate. This is a consequence of the fact that the full Hamiltonian, including the perturbation, is invariant under the reflection with respect to a plane including z , e.g., the xz plane. Under such a reflection, J_z changes sign, so the two states differing by J_z are necessarily degenerate.

The constant α, β depends on the state, i.e., on L, S, J for an atom, but it is clear that, α_{ij} being a tensor constructed from the orbital variables only, the dependence on J is indirect, through the construction in terms of Clebsch–Gordan coefficients. The Wigner–Eckart theorem then imposes the condition

$$\alpha_{ij} = a \delta_{ij} + b \left(L_i L_k + L_k L_i - \frac{2}{3} \mathbf{L}^2 \delta_{ij} \right). \quad (15.57)$$

The coefficients a, b depend only on the multiplet considered, i.e., on L, S . Expressing now the tensor (15.57) in terms of these in eqn (15.56) we find the relation between α, β and a, b . The result is

$$\alpha = a; \quad \beta = b \frac{3(\mathbf{JL})[(2\mathbf{JL})-1] - 2J(J+1)L(L+1)}{J(J+1)(2J-1)(2J+3)}, \quad (15.58)$$

where \mathbf{JL} can be found from the identity

$$2\mathbf{JL} = -(\mathbf{J} - \mathbf{L})^2 + \mathbf{J}^2 + \mathbf{L}^2 = J(J+1) + L(L+1) - S(S+1).$$

See Problem 15.6.

If the Stark effect is of the order of fine-structure separation, it is necessary to simultaneously diagonalize the two perturbations, i.e.,

$$A \mathbf{L} \cdot \mathbf{S} - \frac{1}{2} \mathcal{E}^2 \left[a + 2b \left(L_z^2 - \frac{1}{3} L(L+1) \right) \right],$$

on the multiplet in question. An analogous calculation was done for the hydrogen atom in Chapter 9.

15.7.2 Quadrupole interactions

For an inhomogeneous field, there is a quadrupole coupling in eqn (15.42):

$$H_Q = \frac{1}{6} Q_{ij} \partial_i \partial_j V ; \quad Q_{ij} = \sum_a e_a (3r_{a,i} r_{a,j} - \mathbf{r}_a^2 \delta_{ij}) . \quad (15.59)$$

To calculate the effects on the levels it is necessary to evaluate the matrix elements of the tensor Q_{ij} among the unperturbed wave functions. We begin by noting that for a state with $J = 0, J = \frac{1}{2}$,

$$\langle n, J = 0 | Q_{ij} | n, J = 0 \rangle = 0 ; \quad \langle n, J = \frac{1}{2} | Q_{ij} | n, J = \frac{1}{2} \rangle = 0 . \quad (15.60)$$

In fact, Q_{ij} transforms as an angular moment 2, and the matrix element (15.60) vanishes by the selection rules. Thus only the states with angular momenta $J \geq 1$ can have a quadrupole moment.

For $J > \frac{1}{2}$ there is some simplification if the Wigner-Eckart theorem is used again. The average of the traceless tensor Q_{ij} must be proportional, on a multiplet with fixed J , to the same type of tensor constructed from J , so for $|\psi\rangle = |n, J, J_z\rangle$, where n stands for additional quantum numbers,

$$\langle \psi | Q_{ij} | \psi \rangle = \frac{3Q_J}{2J(2J-1)} \langle \psi | \left(J_i J_j + J_j J_i - \frac{2}{3} \mathbf{J}^2 \delta_{ij} \right) | \psi \rangle . \quad (15.61)$$

The normalization in eqn (15.61) has been chosen so that Q_J coincides with the expectation value of Q_{zz} on the states with the maximum value of J_z . For compactness eqn (15.61) will be written as

$$Q_{ij} = \frac{3Q_J}{2J(2J-1)} \left(J_i J_j + J_j J_i - \frac{2}{3} \mathbf{J}^2 \delta_{ij} \right) , \quad (15.62)$$

and Q_J is what is called the *quadrupole moment* of the state.

Let us note that Q_{ij} , in contrast to the dipole, is even under parity, and therefore the matrix elements between the states of opposite parity vanish.

For example, consider an external field having an axial symmetry around the z axis: as the Laplace equation must be satisfied by the field Φ we must have

$$\partial_x^2 \Phi = \partial_y^2 \Phi = A ; \quad \partial_z^2 \Phi = -2A ,$$

with other derivatives vanishing. The Hamiltonian reduces to the form

$$H_Q = \frac{1}{6} (Q_{xx} + Q_{yy} - 2Q_{zz}) A = -\frac{1}{2} Q_{zz} A .$$

In the last passage, use was made of the fact that Q_{ij} is traceless. By using eqn (15.61) one gets

$$\delta E = \frac{Q_J}{2J(2j-1)} (J(J+1) - 3J_z^2) .$$

As indicated by the notation, the number Q_J depends on J . On the other hand, the operator Q_{ij} is made solely of the orbital variables. If the fine-structure separation is larger than the quadrupole shift, which we shall assume to be the case, L, S are good quantum numbers and Q_J must be expressible in terms of these, by using the Wigner-Eckart theorem only for the orbital angular momentum:

$$Q_{ij} = \frac{3Q_L}{2L(2L-1)} \left(L_i L_j + L_j L_i - \frac{2}{3} \mathbf{L}^2 \delta_{ij} \right). \quad (15.63)$$

Equation (15.63) is understood as an expectation value in an orbital wave function, spin averaged over.

The relation between the two expressions depends on the Wigner-Eckart theorem only, and not on the particular tensor operator considered, and is indeed the same as that encountered in the case of the polarization tensor

$$\frac{3Q_J}{2J(2J+1)} = \frac{3Q_L}{2L(2L-1)} \cdot d(J, L, S);$$

the constant $d(J, L, S)$ is the same as the one appearing in eqn (15.58). In particular, for a doublet, $S = \frac{1}{2}$, one finds that

$$Q_J = \begin{cases} Q_L & \text{for } J = L + \frac{1}{2} \\ \frac{(L-1)(2L+3)}{L(2L+1)} Q_L & \text{for } J = L - \frac{1}{2}. \end{cases}$$

15.8 The Zeeman effect

External magnetic fields also have nontrivial effects on the atomic spectrum. To begin with, let us briefly review the situation in classical mechanics. Classically a spectral line with frequency ω_0 is associated with an electron moving in a periodic motion. A magnetic field adds a Lorentz force term to the equation of motion,

$$m \ddot{\mathbf{x}} = -m \omega_0^2 \mathbf{x} + \frac{e}{c} \mathbf{v} \times \mathbf{B} \equiv -m \omega_0^2 \mathbf{x} - \frac{|e|}{c} \mathbf{v} \times \mathbf{B}. \quad (15.64)$$

Let us choose the reference system such that \mathbf{B} is in the z direction. System (15.64) describes two oscillations, one in the xy plane perpendicular to the field, and the other parallel to it. To intuitively see the influence of the field on the motion, we recall that the equation of motion in the system of reference, rotating with an angular velocity, Ω , is given by

$$m \dot{\mathbf{v}} = \mathbf{F} + 2m \mathbf{v} \times \Omega + m \Omega \times (\mathbf{x} \times \Omega),$$

the second term being the Coriolis force. For small magnetic fields therefore an oscillator in a magnetic field is equivalent to an oscillator seen in the rotating system, with angular velocity

$$\Omega = -\omega_L \hat{\mathbf{z}}; \quad \omega_L = \frac{|e|B}{2mc},$$

to the first order in the angular velocity. This statement is obviously valid in any system, not only for an oscillator, and is known as *Larmor's theorem*. The angular velocity ω_L is called the *Larmor frequency*. We note that the rotation is anti-clockwise as the electron charge is negative.

A circular, clockwise or anti-clockwise motion is described by the vector

$$\mathbf{x}_+ = A(\cos \omega_0 t, \sin \omega_0 t); \quad \mathbf{x}_- = A(\cos \omega_0 t, -\sin \omega_0 t);$$

a linear oscillation, e.g., along the x direction, can be seen as a linear combination of the two circular motions:

$$A(\cos \omega_0 t, 0) = \frac{1}{2}(\mathbf{x}_+ + \mathbf{x}_-).$$

If we now go to the system rotating in a clockwise sense (with angular velocity ω_L) then an anti-clockwise motion has an angular velocity $\omega_0 + \omega_L$ while a clockwise motion has $\omega_0 - \omega_L$.

Therefore the effect of the magnetic field is to separate the three oscillation modes into three distinct frequencies, $\omega_0, \omega_0 \pm \omega_L$. Classically, each spectral line should split, in a magnetic field, in three components, with the separation given by $\omega_L = |e|B/2mc$. Another important consequence is the following. Classically the intensity of emission is proportional to the square of the acceleration of the charge in the direction perpendicular to that of the line of observation. In an oscillator the acceleration is proportional to the dipole of the system $e\mathbf{a} = \ddot{\mathbf{d}} = -\omega^2 \mathbf{d}$. Thus if one observes the light in the z direction the dipole oscillating in this direction does not contribute, and one would observe only *two* lines, at frequencies $\omega_0 \pm \omega_L$, with circular polarizations, the motion being that of a dipole rotating in the xy plane. More precisely the dipole in an anti-clockwise motion has frequency $\omega_0 + \omega_L$ and emit left polarized light with the same frequency, while the clockwise dipole will emit light with frequency $\omega_0 - \omega_L$. In other words the light with left polarization has the higher frequency.

Vice versa, if the line of observation is in a direction orthogonal to the field, e.g., in the x direction, then one would observe only the effects of the dipoles oscillating in the z and y directions, and as a consequence, linearly polarized (in the z direction) light at a frequency ω_0 and two lines at frequencies $\omega_0 \pm \omega_L$, linearly polarized along the y axis. In a generic direction one expects to observe a line of linearly polarized light along the z direction and two lines of elliptically polarized light, with frequencies $\omega_0 \pm \omega_L$. These are known as the (*normal*) Zeeman effect.

15.8.1 The Zeeman effect in quantum mechanics

In *quantum mechanics* the effect of a magnetic field is an additional term in the Hamiltonian,

$$H_B = -\frac{e}{2mc}(\ell + g\mathbf{s}) \cdot \mathbf{B}. \quad (15.65)$$

g is the gyromagnetic ratio of the electron, and we shall set $g = 2$ for simplicity. The magnetic field is taken in the z direction, and by measuring the angular momenta in units of \hbar , $\ell = \hbar \mathbf{L}$ etc., we see that eqn (15.65) can be written as

$$\frac{|e|B\hbar}{2mc}(L_z + 2S_z) \equiv \hbar\omega_L(L_z + 2S_z). \quad (15.66)$$

We see therefore that Larmor frequency appears here also, and can be written by using the Bohr magneton as

$$\hbar\omega_L = |\mu_B|B.$$

Equation (15.66) holds for any number of electrons, as \mathbf{B} acts on all electrons in the same way; \mathbf{L}, \mathbf{S} represent the total orbital angular momentum and total spin.

In general, \mathbf{L} and \mathbf{S} are not separately conserved, due to $\mathbf{L} \cdot \mathbf{S}$ interactions, and this implies that the effect of the magnetic field somehow depends on the fine structure of the system. We note that

$$|\mu_B| \simeq 5.788\,381\,749 \times 10^{-5} \text{ eV T}^{-1} \sim 5.8 \times 10^{-5} \text{ eV T}^{-1}. \quad (15.67)$$

The tesla, (T), that is 10^4 gauss in CGS units, is the unit of magnetic field. The order of magnitude of the fine structure is α^2 a.u. $\sim 10^{-4}$ – 10^{-5} eV, so for weak fields, much less than a tesla, the fine structure is not negligible; vice versa for a much stronger field the latter may be neglected. The criterion of the division is provided by the ratio between the Larmor frequency ω_L and the fine-structure separation frequency ω_{FS} . Sometimes, for weak fields, $\omega_L \ll \omega_{FS}$, and the effect is called *Zeeman effect*, while for stronger magnetic field $\omega_L \sim \omega_{FS}$, or $\omega_L \gg \omega_{FS}$, and it is called the *Paschen-Back effect*.

States with $S = 0$

Let us begin with a simple case with $S = 0$. This is neither the case for hydrogen, nor for alkali atoms, but it is useful to see the connection between the classical theory and what happens in the atomic world (quantum mechanics). We must first of all recall the selection rule for dipole emission, discussed in Chapter 9. The most intense spectral lines are those associated with the dipole transition, just as in the classical case,

$$\langle f | \mathbf{d} | i \rangle; \quad \text{transition } i \rightarrow f. \quad (15.68)$$

Taking z as the quantization axis of angular momentum, the three independent components of the dipole are

$$d_z; \quad d_+ = d_x + id_y; \quad d_- = d_x - id_y.$$

The dipole \mathbf{d} behaves as a vector under spatial rotations so the selection rules for \mathbf{L} in eqn (15.68) are $\Delta L = 0, \pm 1$, and the transition $\Delta L = 0$ is forbidden in the case of a single electron by parity, the state having

parity $(-1)^L$ only in the case of a single electron. The transition $0 \rightarrow 0$ is forbidden. For each component

$$d_z \quad \text{light polarized linearly in the } z \text{ direction} \quad (15.69a)$$

$$d_- \quad \text{light with circular polarization +} \quad (15.69b)$$

$$d_+ \quad \text{light with circular polarization -} \quad (15.69c)$$

The preceding rules are easy to understand: a left-circular polarized photon along the z direction has an angular momentum $+\hbar$ along the same direction; this angular momentum is taken away from the atom, through the matrix element of d_- , which lowers L_z of the system by unity. In absorption the role of d_+ and d_- in eqns (15.69b) and (15.69c) are exchanged.

In the absence of spin Hamiltonian (15.66) can be diagonalized immediately:

$$H_B = \hbar \omega_L L_z; \quad (15.70)$$

therefore we have a series of equally spaced levels, the separation between the adjacent levels being $\hbar \omega_L$, and the total number of sub-levels $2L+1$.

Let us consider now the transition between two levels i, f . Let $\hbar \omega_0 = E_i - E_f$ be the frequency of the associated line, in the absence of a magnetic field. If the level i has spin 0, then the final state f also has spin 0, since the dipole operator does not act on spin. Therefore the splitting in the two levels due to the magnetic field is the same and is given by eqn (15.70). We find the situation illustrated in Figure 15.5, for $L_i = 2, L_f = 1$. The transitions take place, by virtue of the selection rule, only between adjacent levels, that is, with the same L_z , or with L_z differing by one. As can be seen from the figure, the allowed transitions take place as follows:

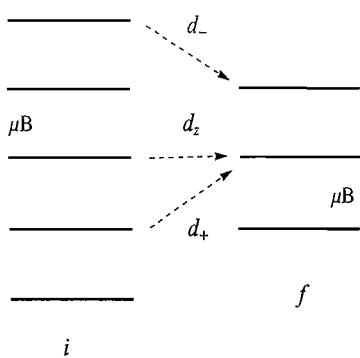


Fig. 15.5 The Zeeman effect

$$\begin{array}{lll} \Delta L_z = 0 & \text{operator: } d_z \rightarrow \text{lin. pol.} & \text{freq. } \hbar \omega = E_i - E_f \equiv \hbar \omega_0 \\ \Delta L_z = +1 & \text{operator: } d_+ \rightarrow \text{pol. -} & \text{freq. } \hbar \omega = \hbar(\omega_0 - \omega_L) \\ \Delta L_z = -1 & \text{operator: } d_- \rightarrow \text{pol. +} & \text{freq. } \hbar \omega = \hbar(\omega_0 + \omega_L) \end{array}$$

The situation is exactly the same as in classical mechanics outlined earlier. The number of lines, their separation, and the associated polarizations are as classically expected.

States with $S \neq 0$: strong magnetic fields

Let us now suppose that the two states have spin, but that the magnetic fields are strong enough to allow us to neglect the fine structure: we are in the regime of the Paschen-Back effect. The initial level has a $(2L+1)(2S+1)$ -fold degeneracy (it is considered degenerate, as we neglect the fine structure). In this case, the base states can be taken as $|L, L_z, S, S_z\rangle$ which is naturally a complete basis in the subspace in question. L_z and S_z are good quantum numbers as LS interactions are neglected. Hamiltonian (15.70) is diagonal in this basis with eigenvalue

$$\hbar \omega_L (L_z + 2S_z). \quad (15.71)$$

This spectrum is practically the same as the previous one, equally spaced ($\Delta E = \hbar\omega_L$) sub-levels goes from $-(L+2S)$ to $(L+2S)$ for a total of

$$\# \text{ levels} = 2(L+2S) + 1 \quad (L \neq 0); \quad \# \text{ levels} = 2S+1 \quad (L=0). \quad (15.72)$$

The center of mass of the levels is still the unperturbed energy E_0 as $\sum L_z = 0 = \sum S_z$. For instance, for $L=0, S=\frac{1}{2}$ the two levels are $\hbar\omega_0 \pm \hbar\omega_L$, the center of mass is zero, but none of the levels coincides with zero.

For $L > 0$, as L_z varies by integers and $2S_z$ is also an integer, the levels are separated by the same quantity, $\hbar\omega_L$: here, of course, the fact that $g=2$ is crucial. What is different from the case of spinless states is the number and multiplicity of the single levels. Eigenvalues (15.71) go from $-L-2S$ to $L+2S$, equally spaced. The multiplicity is given by the number of ways an integer can be formed by L_z and S_z . To count the degeneracy one can for instance start with a given L_z and add or subtract $2S_z$ for various S_z and count in how many ways we arrive at a given number. The situation is illustrated in Figure 15.6 for $L=2, S=\frac{1}{2}$.

In the case of $L=0$ there are simply $2S+1$ levels, with level spacing $2\hbar\omega_L$.

In a dipole transition spin does not change, so there will be three spectral lines, associated with the selection rules, $\Delta L_z = 0, \pm 1$; in the limit of a strong magnetic field we have the normal Zeeman effect even in the presence of spin.

$S \neq 0$: weak fields

Let us now consider the case of weak fields, i.e., $\hbar\omega_L \ll E_{FS}$. First of all, however, what we have seen up to now tells us that for weak fields that are nonetheless strong enough as compared with the hyperfine splitting, which we recall to be of the order of $10^{-3} E_{FS}$, we can continue to neglect the effects of the nucleus. This is a typical situation for magnetic fields between 1 tesla, which corresponds to about 5.8×10^{-5} eV, and $10^{-3} T = 10$ gauss, the value at which the effects related to the nucleus start to become important.

Let us assume, to be concrete, that $L \geq S$. We know then that a given level is split by virtue of the spin-orbit interactions into $2S+1$ levels with $J = L-S, L-S+1, \dots, L+S$. Assuming, as we have mentioned already, that $\hbar\omega_L \ll E_{FS}$, degenerate perturbation theory can be applied to each fine-structure level. This implies neglecting terms of the order of $\mu_B B / E_{FS} \ll 1$. By denoting all other quantum numbers by α we see that a basis of the $2J+1$ states in question is naturally $|\alpha, J, J_z\rangle$. The Hamiltonian

$$H_B = \hbar\omega_L(L_z + 2S_z)$$

is invariant under rotations around the z axis and so commutes with J_z and is diagonal in this basis. The problem then is to calculate the matrix elements $\langle \alpha, J, J_z | L_z | \alpha, J, J_z \rangle$ and the analogous ones for S_z .

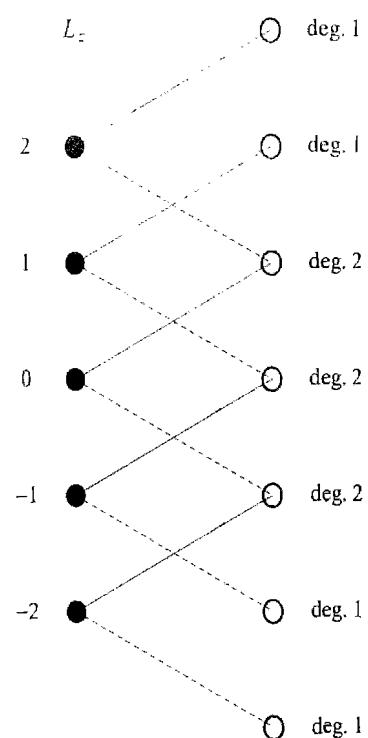


Fig. 15.6

The Wigner–Eckart theorem guarantees that within a multiplet all the vectors have matrix elements which are proportional, and in particular to \mathbf{J} . The matrix elements of H_B therefore have the form

$$H_B = \hbar \omega_L g_J J_z . \quad (15.73)$$

The coefficient g_J is called the *Landé factor*.

The calculation of g_J is a simple application of the Wigner–Eckart theorem: within a multiplet the matrix elements of *any* vector are proportional to the elements of \mathbf{J} , so that as a $(2J+1) \times (2J+1)$ matrix

$$\mathbf{L} = c \mathbf{J} ; \Rightarrow c \mathbf{J}^2 = (\mathbf{L} \cdot \mathbf{J}) . \quad (15.74)$$

By using $\mathbf{J} - \mathbf{L} = \mathbf{S}$ e $\mathbf{J}^2 + \mathbf{L}^2 - 2\mathbf{J} \cdot \mathbf{L} = \mathbf{S}^2$ one finds that

$$\mathbf{J} \cdot \mathbf{L} = \frac{1}{2} (\mathbf{J}^2 + \mathbf{L}^2 - \mathbf{S}^2) = \frac{1}{2} [J(J+1) + L(L+1) - S(S+1)] ,$$

and finally, from eqn (15.74), we find that

$$\begin{aligned} \mathbf{L} &= \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} \mathbf{J} ; \\ \mathbf{S} &= \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \mathbf{J} . \end{aligned}$$

For the matrix elements of \mathbf{S} the only thing to do is to exchange the role of \mathbf{L} and \mathbf{S} . From the preceding formulas we find the diagonal matrix elements of H_B :

$$\begin{aligned} \hbar \omega_L J_z &\left[\frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} \right. \\ &\quad \left. + 2 \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \right] \\ &= \hbar \omega_L J_z \left[1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \right] . \end{aligned}$$

Therefore the Landé factor is equal to

$$g_J = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} . \quad (15.75)$$

If the deviation from the value 2 of the gyromagnetic ratio of the electron is taken into account, then the answer is

$$g_J = 1 + [1 + (g - 2)] \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} .$$

For $g_J = 1$ (such as for $S = 0$) the level spacing predicted by eqn (15.73) is the classical one.

For $g_J \neq 1$ the levels are still equi spaced but with spacing $\hbar\omega_L g_J$. This is different from a classical interpretation of the effect.

The most remarkable effect is about the number of the lines: in the transition between two levels the factor g_J changes and so does the level spacing, within the multiplet. Let us take, as an example, a transition from a state with J^i to a state with J^f , $J^f < J^i$. The transition induced by d_z , with $\Delta J_z = 0$, has frequency

$$\hbar\omega = (E_i - E_f) + \hbar\omega_L (g_i J_z^i - g_f J_z^f) = \hbar\omega_0 + \hbar\omega_L J_z^i (g_i - g_f),$$

which depends on J_z . Similarly a transition due to d_- , which we recall gives rise to a left-polarized photon, yields $J_z^i = J_z^f + 1$ and the frequency

$$\hbar\omega = (E_i - E_f) + \hbar\omega_L (g_i J_z^i - g_f J_z^f) = \hbar\omega_0 + \hbar\omega_L [J_z^f (g_i - g_f) + g_i].$$

Here the frequency also varies within the Zeeman sub-levels. In conclusion there are more than three lines, and the effect was historically termed the *anomalous Zeeman effect*, although there is nothing anomalous about it.

It is easy to convince oneself that for a transition $i \rightarrow f$ in emission, with $J_i > J_f$, the shifts in frequency, number of the spectral lines and polarization are given by

d_z	$\hbar\omega_L (J_z(g_i - g_f)),$	# lines: $(2J_f + 1)$,	(15.76)
d_-	$\hbar\omega_L (J_z(g_i - g_f) + g_i),$	# lines: $(2J_f + 1)$ [$J_z \leq J_f - 1$ # = $2J_f$],	
d_+	$\hbar\omega_L (J_z(g_i - g_f) - g_i)$	# lines: $(2J_f + 1)$ [$J_z \geq -J_f + 1$ # = $2J_f$],	

where $-J_f \leq J_z \leq J_f$. The last column refers to the case $J_i = J_f$. An analogous table can be made easily for the cases $J_i < J_f$.

As a concrete example consider the yellow line of sodium. Sodium is an alkali metal with one peripheral electron in $3s$. The yellow line in absorption corresponds to the transition $3s \rightarrow 3p$, or to $3p \rightarrow 3s$, in emission. The other electrons act as "spectators", remain in the closed shell $L = 0, S = 0$, and are neglected in the determination of the quantum numbers of the atom. The state $3p$ has $L = 1$ and $S = \frac{1}{2}$ and it has a fine structure, with two levels, $J = \frac{1}{2}$ and $J = 3/2$. Actually the yellow line is made of two distinct lines with wavelengths

$$3p_{1/2} \rightarrow 3s_{1/2} : 5895.924 \text{ \AA}; \quad 3p_{3/2} \rightarrow 3s_{1/2} : 5889.950 \text{ \AA}. \quad (15.77)$$

The first line has a larger wavelength, in agreement with the fact that $A\ell \cdot \mathbf{s}$ is positive, having only one electron in the incomplete shell. We can easily estimate that the fine structure level spacing is

$$\Delta E/E \sim \Delta\lambda/\lambda \sim 10^{-3}.$$

For the value of the energy, it follows from eqn (15.77) that

$$E_{3/2} - E_{1/2} \simeq 2.1 \times 10^{-3} \text{ eV},$$

in perfect agreement with what is expected for a typical LS interaction. From eqn (15.67) it follows that up to some hundreds of gauss we are in the weak field regime.

The Landé factor can be obtained from eqn (15.75):

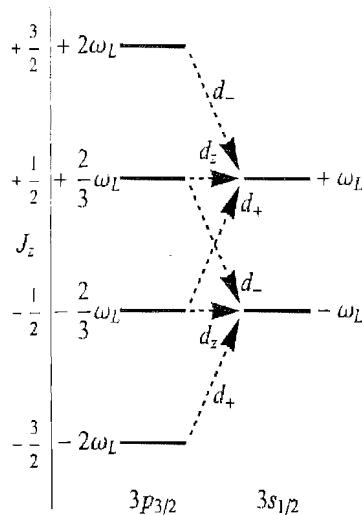
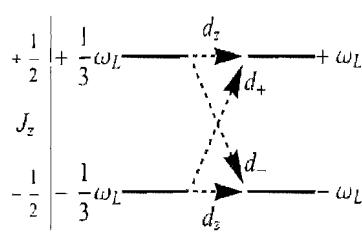


Fig. 15.7 The Zeeman effect for sodium

$$g(3s_{1/2}) = 2; \quad g(3p_{1/2}) = \frac{2}{3}; \quad g(3p_{3/2}) = \frac{4}{3},$$

and gives rise to the energy shifts (eqn (15.73))

$$\delta E(3s_{1/2}) = \pm \hbar \omega_L; \quad \delta E(3p_{1/2}) = \pm \frac{1}{3} \hbar \omega_L; \quad \delta E(3p_{3/2}) = (\pm \frac{2}{3}, 2) \hbar \omega_L.$$

The transition schemes are illustrated in Figure 15.7. From the figure the shifts in *frequencies* can be found:

$$3p_{1/2} \rightarrow 3s_{1/2} \quad d_z : (\frac{2}{3}, -\frac{2}{3}) \hbar \omega_L \quad d_- : \frac{4}{3} \hbar \omega_L \quad d_+ : -\frac{4}{3} \hbar \omega_L \\ 3p_{3/2} \rightarrow 3s_{1/2} \quad d_z : (\frac{1}{3}, -\frac{1}{3}) \hbar \omega_L \quad d_- : (\frac{5}{3}, 1) \hbar \omega_L \quad d_+ : -(\frac{5}{3}, 1) \hbar \omega_L$$

in agreement with eqn (15.76). The first line splits into four, the second into six substructures.

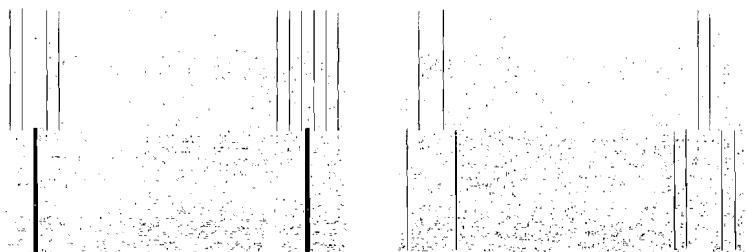


Fig. 15.8 Zeeman splitting for sodium $3p \rightarrow 3s$ transitions. In the second figure, the upper lines correspond to a transition induced by d_z , the lower ones induced by d_{\pm} .

Further reading

The books *Atomic Physics* [Born (1989)] and *Atomic Spectra and Atomic Structure* [Herzberg (1944)] are excellent introductory texts to the argument.

The general problem of atomic structure is touched on all textbooks on quantum mechanics, see e.g. [Landau and Lifshitz (1976 c)]. A more specific study on the Hartree-Fock approximation is in [Slater (1960)], [Condon and Shortley (1935)] and [Bethe and Jackiw (1986)]. A good

introduction to the numerical aspects of the problem is in [Fischer, Brage, and Jönsson (1997)].

Fermi's papers [Fermi (1927)], [Fermi and Amaldi (1934)] can be consulted for the Thomas-Fermi approximation. For the Gross-Pitaevski equation briefly touched in a supplement we refer to the review paper [Dalfonso, et al. (1999)].

Guide to the Supplements

In Supplement 22.7 some details of the analysis of atomic systems skipped in the main text are presented. Supplement 22.7.1 contains an exposition of the Thomas–Fermi approximation, a semi-classical model for atoms. This argument is expanded in numerical problems 15.19 and 15.20.

In Subsection 22.7.2 we review some aspects of the Hartree approximation, while Subsection 22.7.3 contains the main facts about the Slater determinants, in particular we give the explicit form of one-particle and two-particle operators. These results are used in Subsection 22.7.4 to write the effective Hamiltonian for closed shell atoms, the results are then generalized to non-complete shells. To handle the case of non-complete shells the useful concept of mean energy is introduced in Subsection 22.7.5. In the rest of the Supplement we write the Hamiltonian for the generic atom in the Hartree–Fock approximation.

These results are used to build an elementary theory for atomic multiplets (based on the Hartree–Fock equation for the mean energy) and then to write the explicit form of the Hartree–Fock equation for a single level. Some nontrivial aspects of the problem related to Koopman’s theorem are addressed in Subsection 22.7.11.

The theory exposed in the Supplement 22.7 forms part of the numerical procedures used in the numerical problems on the Hartree and Hartree–Fock approximations.

Finally in Subsection 22.9 we give a simple application of the Hartree–Fock procedure to bosonic systems and derive the Gross–Pitaevski equation, while in Supplement 22.8 we give an example of variational calculation for the simplest molecule, H_2^+ .

In the problems of this chapter some particular physical applications are briefly touched, for instance in Problem 15.7 the main points of the quantum theory of paramagnetic and diamagnetic effects for atoms are outlined.

Problems

- (15.1) Write the classical equation of motion for a plane harmonic oscillator and compute the shift in frequencies due to a magnetic field directed perpendicular to the plane.
- (15.2) Study the effect of a magnetic field on the $n = 2$ level of the hydrogen atom.
- (15.3) Consider a fine-structure doublet, $S = \frac{1}{2}$ and $L > 0$. Study the effect of a magnetic field on the system.
- (15.4) Parametrize the effect of spin–spin and spin–orbit interactions in the Russell–Saunders coupling approximation.
- (15.5) Compute the quadrupole moment for 2p states of the hydrogen atom and show that $Q = 0$ for the $2p_{1/2}$ state.
- (15.6) Write the Wigner–Eckart theorem for a vector and a symmetric tensor in subspaces with given orbital momentum L or with given J . Find the relation between the two, for a spin-independent operator and for an operator depending only on spin.
- (15.7) Sketch the classical theory of magnetism and point out its problems. Define the magnetization for a macroscopic homogenous medium in terms of the microscopic magnetic moment in quantum theory. Give an order of magnitude for the different contributions to the magnetic susceptibility.
- (15.8) Compute the magnetic susceptibility for an atom with and without fine-structure splitting. Discuss both the limits of low and high temperature.
- (15.9) Compute the magnetic susceptibility for an atom with $S = 0$ in the ground state, or in general for a single level of fine structure. Neglect diamagnetic contributions.

Numerical analyses

- (15.1) Study the effect of a magnetic field on an LS multiplet. Compute the splitting of spectral lines as a function of the magnetic field.
- (15.2) Compute the mean energy for an arbitrary electronic configuration.
- (15.3) Compute the possible multiplets for equivalent electrons and study the diagonalization of the Hamiltonian.
- (15.4) Compute the possible multiplets for a shell of equivalent electrons and one electron in another shell. Study the diagonalization of the Hamiltonian.
- (15.5) Use Clebsch-Gordan coefficients to directly write states with definite angular momentum and spin for a system of two electrons. Write the form of one- and two-electron operators. In particular consider the electrostatic interaction, LS coupling, and the interaction with an external magnetic field.
- (15.6) Study the problem of energy splitting in atoms with a configuration $s-p$ (or $s-d$). Deduce radial integrals and LS coupling from experimental data and check the consistency of the procedure.
- (15.7) Explore in Mathematica the discretization technique for ordinary differential equations.
- (15.8) Write a Mathematica procedure to compute the effective potentials appearing in the Hartree and Hartree-Fock equations.
- (15.9) Study the implementation of the Hartree equation in Mathematica.
- (15.10) Compute the ground state energy of the carbon in the Hartree approximation. Give an estimate of the energies of the (L, S) terms.
- (15.11) Compute the Rydberg series for alkali atoms in the Hartree approximation.
- (15.12) Study the implementation of Hartree-Fock equation in Mathematica.
- (15.13) Compute the ground state energy of carbon in the Hartree-Fock approximation. Give an estimate of the energies of the (L, S) terms and compare them with the results of the HF approximation for single levels.
- (15.14) Compute the Rydberg series for alkali atoms in the Hartree-Fock approximation. Compare the results with experimental data.
- (15.15) Study the variation of ionization potential with atomic number Z .
- (15.16) Study the filling sequence of shells p and d in HF approximation.
- (15.17) Study the HF approximation for He and compare the results with the variational approach of Hylleraas.
- (15.18) Study the X rays spectrum in the HF approximation.
- (15.19) Solve the Thomas-Fermi equation numerically.
- (15.20) Use the Thomas-Fermi potential to compute energy levels of atoms.
- (15.21) Give a variational computation of potential energy for H_2^+ molecule.

16

Elastic scattering theory

In this chapter we shall discuss in an elementary fashion the problem of elastic scattering in quantum mechanics. Several approximation methods specific to scattering problems are discussed. Some of the issues have been discussed in connection with particular approximation schemes (perturbation theory, the semi-classical approximation, and metastable states) in more specific terms: here we limit ourselves to the general features of the scattering problems.

16.1 The cross section

Consider the scattering of two distinguishable particles, with masses (m_1 and m_2). If the interactions depend only on the relative coordinate ($\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$) the problem reduces to one of a single particle with a reduced mass $\mu = m_1 m_2 / (m_1 + m_2)$, which moves in a potential $V(\mathbf{r})$.

In classical mechanics the scattering process is studied by determining the *trajectories* of the particle. Let $\theta(E, b)$ the angle between the direction of the momentum of the incident particle and the direction of the velocity of the particle at $t = \infty$, where E is the incident energy, b is an impact parameter. If the particle (at fixed E) enters with the impact parameter b it will be scattered and observed in the direction of the scattering angle $\theta(E, b)$. If the impact parameter is randomly distributed among the incident particles the probability that the particle is deflected at angles between θ and $\theta + d\theta$ will be proportional to the area $(2\pi b db)$ of the concentric rings with radius b and $b+db$. See Figure 16.1.

Let f be the flux of the incident particles, i.e., the number of particles which go through a unit area per second. Suppose that the flux is uniform in the (xy) plane. The number of particles observed in the directions between the angles θ and $\theta + d\theta$ will then be $2\pi b db \cdot f$. The cross section is defined by such a number per unit incident flux, i.e.,

$$d\sigma = 2\pi b(E, \theta) db = F(E, \theta) d\theta, \quad (16.1)$$

where b is the solution of $\theta = \theta(E, b)$

In quantum mechanics a flux of incoming particles is described by the current

$$\mathbf{j} = \frac{i\hbar}{2m} (\psi \nabla \psi^* - \psi^* \nabla \psi).$$

Such an interpretation follows naturally from the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0,$$

16.1 The cross section	453
16.2 Partial wave expansion	457
16.3 The Lippman–Schwinger equation	460
16.4 The Born approximation	461
16.5 The eikonal approximation	463
16.6 Low-energy scattering	465
16.7 Coulomb scattering: Rutherford's formula	468
Further reading	474
Guide to the Supplements	475
Problems	476
Numerical analyses	476

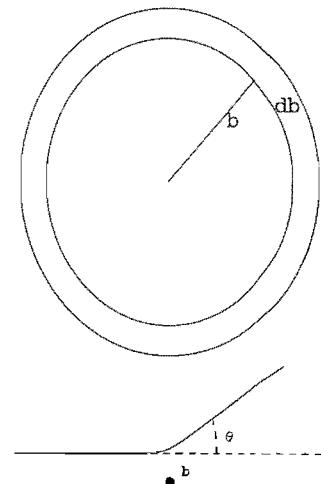


Fig. 16.1 Elastic scattering

$\rho = |\psi|^2$ being the particle (probability) density.

A free particle traveling along the z direction is described by a plane wave

$$\psi = e^{ikz}; \quad E = \frac{k^2 \hbar^2}{2m}.$$

ψ is an eigenstate of momentum with eigenvalue $\mathbf{p} = (0, 0, k\hbar)$. The corresponding current

$$\mathbf{j} = (0, 0, v), \quad v = \frac{p}{m} = \frac{k\hbar}{m}.$$

describes a stationary uniform flux with intensity $|\mathbf{j}|$.

We shall study the scattering process in a stationary condition, i.e., with a constant, uniform incident flux. The wave function describing such a system will be described by a divergent (expanding) spherical wave for the scattered particles, superimposed on the incoming, plane wave. Thus we look for a stationary solution which asymptotically (as $r \rightarrow \infty$) behaves as

$$\psi = e^{ikz} + f(\theta, \phi) \frac{e^{ikr}}{r}. \quad (16.2)$$

Up to an overall normalization, fixed by the incoming wave, eqn (16.2) is the most general solution of Schrödinger's equation (for potentials decreasing faster than $1/r$, see below) describing an incoming and a divergent wave. All dynamical information is encoded in the function $f(\theta, \phi)$, called the *scattering amplitude*.

In writing eqn (16.2) we have used the elasticity of the scattering, imposing the condition that the outgoing wave has the same momentum, $k = |\mathbf{k}|$, as the incoming wave.

The scattering cross section is defined through the ratio of scattered and incoming flux. Let us consider a small region of area $dS = r^2 d\Omega$ intersected by the solid angle $d\Omega = \sin \theta d\theta d\varphi$ on a large sphere of radius r . In this small region the spherical wave can be approximated by a plane wave and it is easy to show that the number of particles traversing this area per second is (with an incident flux v)

$$\frac{d\mathcal{N}}{dt} = \int \mathbf{j}_{fin} \cdot d\mathbf{S} = v \frac{|f|^2}{r^2} r^2 d\Omega = v |f|^2 d\Omega. \quad (16.3)$$

The differential cross section is *defined* by the ratio \mathcal{N}/j_{in} or

$$d\sigma = |f(\theta)|^2 d\Omega. \quad (16.4)$$

Note that the normalization of the incoming flux cancels in this definition; in other words if I is the number of particles traversing the unit surface in a second in the incoming beam, then

$$d\mathcal{N} = d\sigma I dt \quad (16.5)$$

is the number of particles scattered in a solid angle $d\Omega$ in a time dt .

In this chapter we will consider only spherical potentials; in this case by rotational symmetry around the z axis the wave function cannot depend on φ and $f = f(\theta)$.

The exact scattering amplitude is obtained by solving Schrödinger's equation with asymptotic condition (16.2). As this problem is usually very difficult a number of methods have been devised to get an approximate solution:

- (1) The Born approximation. This is perturbation theory applied to scattering, touched in Chapter 9.
- (2) The eikonal approximation.
- (3) The low-energy approximation.
- (4) The resonance approximation, some aspects of which have been studied in Chapter 13.
- (5) The semi-classical approximation, already encountered in Chapter 11.

The total cross section

Integrating eqn (16.4) over the solid angle one gets the *total cross section*

$$\sigma = \int |f(\theta)|^2 d\Omega, \quad (16.6)$$

which is particularly relevant as it describes the total number of scattered particles.

Let I be the intensity of the incoming beam. Following eqn (16.5) the probability per second for a particle to be scattered from a given scattering center is $I\sigma$. At each scattering the beam loses the scattered particles. Let z be the direction of the beam, A its section. The number of particles per second impinging on the target is IA , while the number of events (scatterings) per second in a length dz is

$$\text{num. of target particles} \times \text{prob. of scatt.} = n Adz I\sigma,$$

where n is the density of scattering centers (the number of target particles per unit volume). It follows that the number of scattered particles per second, i.e. the decrease in the total flux IA , is

$$d(IA) = -n Adz I\sigma nAdz,$$

or

$$\boxed{\frac{dI}{dz} = -I n\sigma; \quad I(z) = I_0 e^{-n\sigma z}.} \quad (16.7)$$

The length $\lambda = 1/(n\sigma)$ gives a measure of the beam attenuation and is called the *mean free path*.

The inadequacy of classical mechanics

Quantum mechanics solve a disturbing puzzle of classical mechanics. A particle scattered at an angle θ acquires a transverse momentum of order $p_{\perp} \sim \theta p$ (we can assume θ small in the following). In classical mechanics the process is described by an impact parameter b ,

$$\theta_{cl} \sim \frac{p_{\perp}}{p} \sim \frac{F_{\perp} \Delta t}{p} \sim \frac{V(b) \Delta t}{b} \sim \frac{V(b)}{p v} \sim \frac{V(b)}{E}.$$

This means that we have a small contribution to scattering for arbitrary large b , the only exception being the finite-range potential with $V(r) = 0$ for $r > r_0$. This implies that the classical total cross section, being the integral of $b db$, is always divergent (except for finite range V).

In quantum mechanics to define the notion of impact parameter b we need some instrument, like a circular aperture of radius b , which selects particles. Passage through this aperture causes a diffraction angle $\theta_d \sim \lambda/b$, where λ is the de Broglie wavelength. The measurement of the scattered angle clearly makes sense only if $\theta_{cl} > \theta_d$, i.e.

$$\frac{V(b)}{p v} \gg \frac{\hbar}{p b}; \quad \Rightarrow \quad V(b) \gg \frac{\hbar v}{b}. \quad (16.8)$$

This inequality is violated for potentials decreasing faster than $1/r$: this is why the classical estimate is wrong. The Coulomb potential $V = Ze^2/r$ is at the borderline of the inequality, satisfied only for $Ze^2/\hbar v \gg 1$.

In quantum mechanics the total cross section turns out to be finite for potentials decreasing faster than $1/r^2$ as $r \rightarrow \infty$.

Remarks

We will usually compute cross sections in the center-of-mass system, while sometimes it is necessary to know $d\sigma$ in the *laboratory system*, where the target is at rest.

Let m_1 be the mass of the incident particle and m_2 , the mass of the target particle. A simple kinematic argument gives the relations between the diffusion angles (θ, φ) in the center-of-mass system and the corresponding angles θ_0, ϕ_0 in the laboratory:

$$\tan \theta_0 = \frac{m_2 \sin \theta}{m_2 \cos \theta + m_1}, \quad \phi_0 = \phi.$$

The cross section transforms as a consequence, under the requirement that the number of scattered particles is the same in the two frames, i.e.

$$\sigma_0(\theta_0, \phi_0) \sin \theta_0 d\theta_0 d\phi_0 = \sigma(\theta, \phi) \sin \theta d\theta d\phi.$$

This follows from the Jacobian of the transformation:

$$d\sigma_0(\theta_0, \phi_0) = \frac{(1 + \eta^2 + 2\eta \cos \theta)^{3/2}}{|1 + \eta \cos \theta|} d\sigma(\theta, \phi), \quad \eta \equiv \frac{m_1}{m_2}.$$

16.2 Partial wave expansion

A general method of analysis for scattering processes is the *partial wave expansion*, i.e. the expansion in eigenstates of angular momentum. We will consider a central potential. The solution of Schrödinger's equation

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right) \psi = E\psi; \quad E = \frac{\hbar^2 k^2}{2\mu} > 0$$

can be expanded in partial waves:

$$\psi = \sum_{\ell=0}^{\infty} A_{\ell} P_{\ell}(\cos \theta) R_{\ell}(r). \quad (16.9)$$

Only $Y_{\ell 0} \propto P_{\ell}(\cos \theta)$ appears due to the symmetry for rotations around the z axis, directed along the incident wave.

The radial wave functions are solutions of

$$\left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{2m}{\hbar^2} (E - V(r)) - \frac{\ell(\ell+1)}{r^2} \right] R_{\ell}(r) = 0. \quad (16.10)$$

Equation (16.9) is a solution by construction, but we have to fix the coefficients A_{ℓ} by imposing boundary condition (16.2). Equation (16.10) is a standard one-dimensional Schrödinger problem and we must find the *regular* solution of this equation. If the potential goes to zero sufficiently fast as $r \rightarrow \infty$ asymptotically, Schrödinger's equation reduces to the free equation, whose general solution is

$$R_{\ell}(r) \sim 2k(c_1 j_{\ell}(kr) + c_2 n_{\ell}(kr)), \quad |c_1|^2 + |c_2|^2 = 1; \quad (16.11)$$

$j_{\ell}(kr), n_{\ell}(kr)$ are spherical Bessel functions, see Chapter 6. This is true also for the regular solution we are looking for.

From the asymptotic behavior of spherical Bessel functions

$$j_{\ell}(x) \sim \frac{1}{x} \cos \left(x - \frac{(\ell+1)\pi}{2} \right); \quad n_{\ell}(x) \sim \frac{1}{x} \sin \left(x - \frac{(\ell+1)\pi}{2} \right)$$

we have for R_{ℓ}

$$R_{\ell}(r) \simeq \frac{2}{r} \sin \left(kr - \frac{\ell\pi}{2} + \delta_{\ell} \right),$$

where δ_{ℓ} is the *phase shift* for the ℓ wave. We can recast this expression as

$$\begin{aligned} R_{\ell}(r) &\simeq \frac{1}{ir} \left[e^{i(kr-\ell\pi/2+\delta_{\ell})} - e^{-i(kr-\ell\pi/2+\delta_{\ell})} \right] \\ &= \frac{(-i)^{\ell}}{ir} e^{-i\delta_{\ell}} [e^{ikr} + (-)^{\ell+1} e^{-ikr} + (e^{2i\delta_{\ell}} - 1) e^{ikr}]. \end{aligned} \quad (16.12)$$

The effect of scattering is in the last term, the rest representing the solution in the absence of scattering ($\delta_{\ell} = 0$). In fact, by the partial wave expansion of a plane wave (see Chapter 6),

$$e^{ikz} = e^{ikr \cos \theta} = \sum_{\ell=0}^{\infty} (2\ell+1) i^{\ell} j_{\ell}(kr) P_{\ell}(\cos \theta), \quad (16.13)$$

with

$$j_\ell(x) \sim \frac{1}{x} \sin\left(x - \frac{\ell\pi}{2}\right) = \frac{(-i)^\ell}{2ikr} [e^{ikr} + (-)^{\ell+1} e^{-ikr}],$$

we see that the correct choice for A_ℓ is

$$A_\ell = \frac{1}{2k} (2\ell+1) i^\ell e^{i\delta_\ell}. \quad (16.14)$$

Substitution of (16.14) and (16.12) into eqn (16.9) finally gives (asymptotically)

$$\begin{aligned} \psi &\sim \sum_{\ell=0}^{\infty} \frac{2\ell+1}{2kri} P_\ell(\cos\theta) (e^{ikr+2i\delta_\ell} - (-1)^\ell e^{-ikr}) = \\ &= \sum_{\ell=0}^{\infty} \frac{2\ell+1}{2kri} P_\ell(\cos\theta) (e^{ikr} + (-)^{\ell+1} e^{-ikr} + (e^{2i\delta_\ell} - 1)e^{ikr}) \\ &= e^{ikz} + f(\theta, \phi) \frac{e^{ikr}}{r}, \end{aligned} \quad (16.15)$$

$$f(\theta) = \sum_{\ell=0}^{\infty} \frac{2\ell+1}{2ki} P_\ell(\cos\theta) (e^{2i\delta_\ell} - 1). \quad (16.16)$$

The cross section follows:

$$\begin{aligned} \sigma &= \int d\sigma = 2\pi \int_0^\pi d\theta \sin\theta |f(\theta)|^2 = \frac{2\pi}{4k^2} 2 \sum_{\ell} (2\ell+1) |e^{2i\delta_\ell} - 1|^2 \\ &= \frac{4\pi}{k^2} \sum_{\ell} (2\ell+1) \sin^2 \delta_\ell \equiv \sum_{\ell} \sigma_{\ell}. \end{aligned} \quad (16.17)$$

We have used here the orthogonality property of Legendre polynomials:

$$\int d\Omega P_\ell(\cos\theta) P_{\ell'}(\cos\theta) = \frac{4\pi}{2\ell+1} \delta_{\ell\ell'}.$$

σ_{ℓ} can be considered the cross section in the ℓ wave.

The total cross section is related to the imaginary part of the forward amplitude ($\theta = 0$) by the *optical theorem*

$$\sigma = \frac{4\pi}{k} \text{Im}f(0). \quad (16.18)$$

This relation is related to the unitarity, i.e. conservation of total probability. In the simple case of elastic scattering eqn (16.18) follows directly from eqn (16.16) and $P_\ell(\cos(0)) = 1$.

Remarks

- (1) The phase shifts δ_ℓ give both the differential and the total cross sections. δ_ℓ are real for elastic scattering.

- (2) The factor $S_\ell \equiv e^{2i\delta_\ell}$ gives the deviation from 1 of the coefficient of the divergent spherical wave. The property $|S_\ell| = 1$ shows that only the phase of the spherical wave is affected by scatterings, this is also an aspect of unitarity: the flux of convergent and divergent spherical waves is the same for each ℓ , as is evident from the first line in eqn (16.9).
- (3) From $\delta_\ell \in \mathbb{R}$, i.e. elastic unitarity, it follows that the ℓ -th cross section is bounded:

$$\sigma_\ell = \frac{4\pi}{k^2} (2\ell + 1) \sin^2 \delta_\ell(k) \leq \frac{4\pi}{k^2} (2\ell + 1),$$

independently of δ_ℓ .

- (4) Partial wave expansion is particularly useful at low energy. It will be shown below that for low k

$$\delta_\ell(k) \simeq \text{const. } k^{2\ell+1}, \quad (16.19)$$

and then at low energies only a limited number of waves are sufficient to reproduce with great accuracy the scattering amplitude.

16.2.1 The semi-classical limit

For each angular momentum ℓ the phase shifts δ_ℓ give the phase difference between the exact scattering solution and the free solution. We have found this difference in the semi-classical limit in Chapter 11; see eqn (11.82):

$$\begin{aligned} \delta_\ell &= \int_{\rho}^{\infty} \sqrt{k^2 - \frac{2mV(r)}{\hbar^2} - \frac{(\ell + \frac{1}{2})^2}{r^2}} dr - \int_{\rho_0}^{\infty} \sqrt{k^2 - \frac{(\ell + \frac{1}{2})^2}{r^2}} dr \\ &= \int_{\rho}^{\infty} \left\{ \sqrt{k^2 - \frac{2mV(r)}{\hbar^2} - \frac{(\ell + \frac{1}{2})^2}{r^2}} - k \right\} dr + \frac{\pi}{2} (\ell + \frac{1}{2}) - k\rho. \end{aligned} \quad (16.20)$$

ρ is the classical inversion point for the interacting case, ρ_0 for the free equation.

In this section we limit ourselves to showing the implications of eqn (16.20) on the finiteness of the total cross section. From eqn (16.17) it follows that possible divergences in σ can be due to the non-convergence of the series

$$\sigma = \frac{4\pi}{k^2} \sum_{\ell} (2\ell + 1) \sin^2 \delta_\ell. \quad (16.21)$$

The large- ℓ behavior (large quantum numbers) is under the control of the WKB approximation. From eqn (16.20) if $V(r)$ goes to zero faster than $1/r^2$ as $r \rightarrow \infty$,

$$\delta_\ell \simeq - \int_{\rho}^{\infty} \frac{mV(r) dr}{\hbar^2 \sqrt{k^2 - \frac{(\ell + \frac{1}{2})^2}{r^2}}}.$$

If the integral is finite (and it is if $V(r)$ goes to zero faster than $1/r$) its order of magnitude is

$$\delta_\ell \sim \frac{mV(\rho)\rho}{k\hbar^2}. \quad (16.22)$$

As $\ell \sim k\rho$ and $\rho \sim \ell/k$, from eqn (16.22) $\delta_\ell \rightarrow 0$ for large ℓ .

By substitution in eqn (16.21) one gets

$$\sigma \sim 4\pi \int d\rho 2k\rho \delta_\ell^2 \sim 4\pi \int d\rho 2k\rho \left(\frac{mV(\rho)\rho}{k\hbar^2} \right)^2 \sim \int d\rho V^2(\rho)\rho^3.$$

This integral converges if $V(r)$ goes to zero faster than $1/r^2$ as $r \rightarrow \infty$, so in this condition σ is finite.

16.3 The Lippman–Schwinger equation

From the discussion in Section 16.1 it follows that the solution of a scattering problem consists in solving Schrödinger's equation

$$(H_0 + V(r))\psi = E\psi, \quad H_0 = -\frac{\hbar^2}{2\mu}\nabla^2,$$

with the boundary condition

$$\psi \equiv \psi^{(+)} \simeq \psi_0 + f(\theta, \phi) \frac{e^{ikr}}{r}, \quad \psi_0 = e^{ikz},$$

for $r \gg d$, where d is the characteristic range of the potential.

This problem has the formal solution (or better can be transformed to an integral equation):

$$\psi^{(+)}(\mathbf{r}) = \psi_0(\mathbf{r}) + \int d\mathbf{r}' G^{(+)}(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi^{(+)}(\mathbf{r}'): \quad (16.23)$$

this is the *Lippmann–Schwinger* equation. Here $G^{(+)}(\mathbf{r}, \mathbf{r}')$ is the Green function

$$(H_0 - E)G^{(+)}(\mathbf{r}, \mathbf{r}') = -\delta^3(\mathbf{r} - \mathbf{r}')$$

with the correct boundary condition (a divergent spherical wave).

The free solution ψ_0 solves

$$(H_0 - E)\psi_0(\mathbf{r}) = 0.$$

In the bra-ket notation we have the relations

$$(H_0 + V)|\psi^{(+)}\rangle = E|\psi^{(+)}\rangle, \quad H_0|\psi_0\rangle = E|\psi_0\rangle,$$

$$|\psi^{(+)}\rangle = |\psi_0\rangle + \frac{1}{E - H_0 + i\epsilon} V|\psi^{(+)}\rangle \quad (\text{Lippman–Schwinger}),$$

$$G^{(+)}(\mathbf{r}, \mathbf{r}') = \langle \mathbf{r} | \frac{1}{E - H_0 + i\epsilon} | \mathbf{r}' \rangle.$$

In this notation the correct prescription is embodied in the “ $+i\epsilon$ ” prescription ($\epsilon > 0$). This prescription has been discussed in Chapter 13.

We remember that by inserting a complete set of momentum eigenstates and performing the integral in the complex plane, one computes (see eqn (13.25))

$$G^{(+)}(\mathbf{r}, \mathbf{r}') = -\frac{2m}{\hbar^2} \frac{e^{i\mathbf{k}\cdot\mathbf{R}}}{4\pi R}.$$

The Lippmann–Schwinger equation then has the explicit form

$$\psi^{(+)}(\mathbf{r}) = \psi_0(\mathbf{r}) - \frac{m}{2\pi\hbar^2} \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} e^{i\mathbf{k}|\mathbf{r}-\mathbf{r}'|} V(\mathbf{r}') \psi^{(+)}(\mathbf{r}'). \quad (16.24)$$

16.4 The Born approximation

The Lippman–Schwinger equation can be used to generate by iteration a perturbative solution for $\psi^{(+)}$. At lowest order if V is “small” we can use on the right-hand side of eqn (16.24) the zero order value ψ_0 : this is the first order *Born approximation*:

$$\begin{aligned} \psi_{\text{Born}}^{(+)}(\mathbf{r}) &\simeq \psi_0(\mathbf{r}) + \int d\mathbf{r}' G^{(+)}(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi_0(\mathbf{r}') \\ &= e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{4\pi} \int d\mathbf{r}' \frac{2m}{\hbar^2} \frac{e^{i\mathbf{k}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} V(\mathbf{r}') e^{i\mathbf{k}\cdot\mathbf{r}'}. \end{aligned} \quad (16.25)$$

By substitution of this expression into the right-hand side of eqn (16.24) one obtains the second order approximation and so on.

The amplitude for the first order Born approximation (for shortness simply the Born approximation) has a simple expression. For large r

$$|\mathbf{r} - \mathbf{r}'| \simeq r \left(1 - \frac{\mathbf{r} \cdot \mathbf{r}'}{r^2} + \dots \right),$$

and then

$$k |\mathbf{r} - \mathbf{r}'| \simeq k r - \frac{k \mathbf{r} \cdot \mathbf{r}'}{r} = k r - \mathbf{k}' \cdot \mathbf{r}', \quad (16.26)$$

where $\mathbf{k}' \equiv \mathbf{k}\mathbf{r}/r$. It follows for the scattering amplitude that

$$f(\theta) = -\frac{m}{2\pi\hbar^2} \int d\mathbf{r}' V(\mathbf{r}') e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}'}.$$

We see that $f(\theta)$ is (up to a constant) the Fourier transform of the potential computed at the momentum equal to the transferred momentum $\mathbf{k} - \mathbf{k}'$. If we denote momentum eigenstates by their wave numbers, then

$$f(\theta) = -\frac{m}{2\pi\hbar^2} \langle \mathbf{k}' | V | \mathbf{k} \rangle.$$

This formula is in perfect agreement with expectations from perturbation theory. Let us review this point in some detail. From eqn (16.3) the probability of scattering per unit time in the angle $d\Omega$ is

$$dW = v d\sigma.$$

In perturbation theory this quantity is computed by Fermi's rule (9.52):

$$dW = \frac{2\pi}{\hbar} |V_{fi}|^2 \delta(E_f - E_i) d\Phi.$$

Here the initial and final states are free particles with momentum $\hbar\mathbf{k}$ and $\hbar\mathbf{k}'$ respectively. Using eqn (9.54) for the density of final states

$$\delta(E_f - E_i) d\Phi = \frac{d\Omega}{(2\pi\hbar)^3} m p_f,$$

and the elasticity of the scattering ($p_f = p_i = mv$), we get

$$dW = \frac{2\pi}{\hbar} |\langle \mathbf{k}' | V | \mathbf{k} \rangle|^2 \frac{d\Omega}{(2\pi\hbar)^3} m p_f = v \left(\frac{m}{2\pi\hbar^2} \right)^2 |\langle \mathbf{k}' | V | \mathbf{k} \rangle|^2,$$

in agreement with a cross section given by the scattering amplitude (16.28).

Let us now study the validity of the Born approximation. The limitations depend on k , as we will see below. Let d be the range of the potential, i.e. the region where the integral over dr' can differ appreciably from zero.

- (1) If $k \ll 1/d$ we can approximate $|\exp i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}'| \sim 1$. For a reasonable approximation the first order in V , i.e. $\psi^{(1)} = f(\theta)e^{ikr}/r$, must be small with respect to 1 (the order of magnitude of the incoming wave):

$$|\psi^{(1)}| \sim \frac{m|V|d^3}{\hbar^2 d} \simeq \frac{m|V|d^2}{\hbar^2} \ll 1. \quad (16.29)$$

This is the condition for the validity of the Born approximation at low energy.

- (2) If $k \gg 1/d$ the correction can be small as the integral oscillates very rapidly. To give an estimate of the integral let us come back to Schrödinger's equation. With $\psi = \psi_0 + \psi^{(1)} + \mathcal{O}(V^2)$ we find to first order in V that

$$\Delta\psi^{(1)} + k^2\psi^{(1)} = \frac{2m}{\hbar^2} V e^{ikz}. \quad (16.30)$$

Let us write $\psi^{(1)} = e^{ikz} \cdot g$, with g a slowly varying function. For g we get at large k

$$2ik \frac{\partial g}{\partial z} \simeq \frac{2m}{\hbar^2} V,$$

i.e.

$$g \simeq -\frac{im}{k\hbar^2} \int^z V dz \sim \frac{i m |V| d}{k \hbar^2}.$$

In this case the correction is small if

$$\frac{m |V| d}{k \hbar^2} \ll 1, \quad (16.31)$$

a weaker condition than eqn (16.29). We note that this condition is exactly the opposite of eqn (16.8) (the semi-classical condition for scattering).

Remarks

Some qualitative aspects of the Born approximation deserve some comments.

- (i) For low energy $k \ll 1/d$, we can approximate $\exp i(\mathbf{k} - \mathbf{k}') \rightarrow 1$, and then $f(\theta)$, and the cross section, becomes independent of θ . The scattering is dominated by the S-wave, as anticipated in eqn (16.19) (see also Section 16.6).
- (ii) In the high energy limit, $k \gg 1/d$, the exponential factor determines the amplitude. Due to its rapid oscillations the amplitude is mostly in a narrow forward direction, as follows from $|\mathbf{k} - \mathbf{k}'| = 2k \sin(\theta/2)$. In this regime an improvement on the Born approximation is available; see Section 16.5.

16.5 The eikonal approximation

At higher energies a (partial) resummation of the Born corrections gives a substantial improvement with respect to first-order perturbation theory.

This approximation is essentially a solution of eqn (16.30) and is strictly related to the semi-classical approximation. At high energy the classical trajectory differs slightly from a straight line parallel to the z axis (the beam direction) with an impact parameter b (the distance of the line from the scattering center). The classical phase for a free particle traveling along this line is kz and in eqn (16.30) this is the main phase variation. Thus it is reasonable to build an approximation based on a leading term of the form

$$\psi(\mathbf{r}) \sim e^{iS(\mathbf{r})\hbar}, \quad (16.32)$$

where S is the classical action,

$$S = \int \mathbf{p} \cdot d\mathbf{x}. \quad (16.33)$$

Function (16.32) has to be substituted on the right-hand side of the Lippmann–Schwinger equation:

$$\psi^{(+)}(\mathbf{r}) = \psi_0(\mathbf{r}) + \int d^3\mathbf{r}' G^{(+)}(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi^{(+)}(\mathbf{r}'), \quad \psi_0(\mathbf{r}) = e^{ikz}.$$

As usual the semi-classical approximation will be valid for potentials slowly varying on distances of the order of the de Broglie wavelength $\lambda \sim 1/k$, this condition being better fulfilled as the energy grows.

At high energy the classical trajectory for the integral (16.33) can be approximated by a straight line with impact parameter b , and S is given by

$$\frac{S}{\hbar} \simeq \int_{-\infty}^z \sqrt{k^2 - \frac{2m}{\hbar^2} V(\sqrt{b^2 + z'^2})} dz' + \text{const.}$$

The constant will be fixed by the condition $S/\hbar \rightarrow k z$ as $V \rightarrow 0$. For large k

$$\frac{S}{\hbar} \simeq k z - \frac{m}{\hbar^2 k} \int_{-\infty}^z V(\sqrt{b^2 + z'^2}) dz'.$$

If \mathbf{b} is a vector in the plane perpendicular to the direction of the incident particle, $\hat{\mathbf{k}}$, a point \mathbf{r} can be written as $\mathbf{r} = \mathbf{b} + \hat{\mathbf{k}} z$ and the semi-classical wave function takes the form

$$\psi^{(+)}(\mathbf{r}) = \psi^{(+)}(\mathbf{b} + \hat{\mathbf{k}} z) = e^{ikz} \exp \left[-\frac{i m}{\hbar^2 k} \int_{-\infty}^z V(\sqrt{b^2 + z'^2}) dz' \right]. \quad (16.34)$$

Using eqn (16.26)

$$G^{(+)}(\mathbf{r}, \mathbf{r}') = -\frac{2m}{\hbar^2} \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{4\pi |\mathbf{r}-\mathbf{r}'|} \simeq -\frac{2m}{\hbar^2} \frac{e^{ikr-i\mathbf{k}'\cdot\mathbf{r}'}}{4\pi r},$$

we find that substitution of eqn (16.34) in the Lippmann–Schwinger equation gives immediately for the scattering amplitude

$$f(\mathbf{k}', \mathbf{k}) = -\frac{m}{2\pi\hbar^2} \int d^3 \mathbf{r}' e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}'} V(\sqrt{b^2 + z'^2}) \exp \left[-\frac{i m}{\hbar^2 k} \int_{-\infty}^{z'} V(\sqrt{b^2 + z''^2}) dz'' \right].$$

The exponential in this expression gives the correction to the first-order Born approximation. An instance of the obtained improvement is shown in Figure 16.2 (see Numerical analyses Problems 16.3 and 16.4).

For small angle scattering

$$\mathbf{k} = (0, 0, k), \quad \mathbf{k}' = (k \sin \theta, 0, k \cos \theta),$$

$$(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}' \simeq -\mathbf{k}' \cdot \mathbf{b} = -kb\theta \cos \phi_b,$$

where angular variables have been used for \mathbf{b} : $\mathbf{b} = (b \cos \phi_b \hat{x} + b \sin \phi_b \hat{y})$. The volume element can be written as $d^3 \mathbf{r}' = db b d\phi_b dz$ and the ϕ integration gives

$$\int_0^\infty db b \int_0^{2\pi} d\phi_b e^{-ikb\theta \cos \phi_b} = 2\pi \int_0^\infty db b J_0(kb\theta),$$

where J_0 is the Bessel function of order zero. The z integration is trivial:

$$\int_{-\infty}^\infty dz V(\sqrt{b^2 + z^2}) e^{-\frac{im}{\hbar^2 k} \int_{-\infty}^z V(\sqrt{b^2 + z'^2}) dz'} = \frac{ik\hbar^2}{m} (e^{2i\Delta(b)} - 1),$$

$$\Delta(b) \equiv -\frac{m}{2k\hbar^2} \int_{-\infty}^\infty V(\sqrt{b^2 + z'^2}) dz'.$$

Assembling together the two integrations we have for the amplitude

$$f(\mathbf{k}', \mathbf{k}) = -ik \int_0^\infty db b J_0(kb\theta) (e^{2i\Delta(b)} - 1).$$

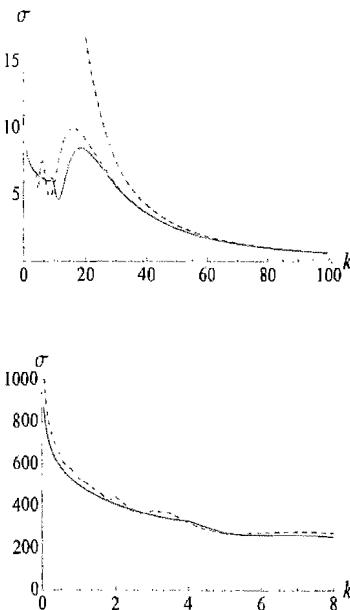


Fig. 16.2 σ as a function of k for a repulsive well of radius a . The continuous line is the numerical solution, the two dotted lines the eikonal approximation, and the Born approximation (the closest to numerical values is the eikonal). The second plot shows σ for a potential $V_0 r^2 e^{-r}$. In this case the Born approximation does not fit in the scale of the plot. The dotted line is the eikonal approximation.

The phase $\Delta(b)$ is usually known as *eikonal*, from the analogous approximation in optics, and gives the name to the approximation.

An important point is that this approximation satisfies the optical theorem [Joachain (1975).], i.e. from eqn (16.18):

$$\sigma = \frac{4\pi}{k} \operatorname{Im} f(0) = 8\pi \int_0^\infty \sin^2(\Delta(b)) b db .$$

16.6 Low-energy scattering

Let us consider now the opposite limit of low-energy scattering. We will suppose that the potential has a finite range d beyond which it can be neglected. Low energy in this context means that the de Broglie wavelength λ is much bigger than d or $k d \ll 1$. For $r > d$ the radial equation, eqn (16.10), reduces to the free one with general solution (16.11). The coefficients c_1, c_2 have to be fixed by solving the equation in the inner region, $r \leq d$, and connecting this solution with the outer solution. The detailed values for the c 's depend on the potential but the form of phase shifts can be obtained by general arguments. At small energy there will be an interval in r where both kinetic energy and potential can be neglected, $d \ll r \ll \frac{1}{k}$. In this interval the radial equation can be approximated by

$$\left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{\ell(\ell+1)}{r^2} \right] R_\ell(r) = 0,$$

with general solution

$$R_\ell(r) \simeq a_1 r^\ell + a_2 r^{-\ell-1}. \quad (16.35)$$

The coefficients $a_{1,2}$ are independent of k but depend on the potential. They can be found by connecting the solution (16.35) with the solution in the region $r \leq d$, and in this region as $k \simeq 0$

$$\left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{2m}{\hbar^2} V(r) - \frac{\ell(\ell+1)}{r^2} \right] R_\ell(r) = 0.$$

The connection formulas, and hence the coefficients, do not depend on k .

We know that the general form of the scattering solution is

$$2 k (c_1 j_\ell(kr) + c_2 n_\ell(kr)), \quad (16.36)$$

and this solution has to be connected to the solution in the intermediate region (16.35). For small k the connection involves the first Taylor coefficients of spherical Bessel functions, and from eqn (6.4)

$$j_\ell(x) \sim \frac{x^\ell}{(2\ell+1)!!}, \quad n_\ell \sim \frac{(2\ell-1)!!}{x^{\ell+1}}.$$

The r behavior correctly reproduces eqn (16.35) and the matching condition imposes the condition

$$\frac{c_1 k^\ell}{(2\ell+1)!!} / \frac{c_2 (2\ell-1)!!}{k^{\ell+1}} = \frac{a_1}{a_2} = \text{indep. of } k,$$

or

$$\frac{c_1}{c_2} \sim k^{-2\ell-1}.$$

The phase shifts are determined by the asymptotic behavior of the radial function, using

$$j_\ell(x) \sim \frac{1}{x} \cos \left(x - \frac{(\ell+1)\pi}{2} \right); \quad n_\ell(x) \sim \frac{1}{x} \sin \left(x - \frac{(\ell+1)\pi}{2} \right).$$

We then have

$$\chi_\ell(r) = r R_\ell(r) \sim \sin \left(k r - \frac{\ell\pi}{2} + \delta_\ell \right).$$

From eqn (16.36)

$$\tan \delta_\ell = \frac{c_2}{c_1} \sim k^{2\ell+1}; \quad \delta_\ell \sim k^{2\ell+1}. \quad (16.37)$$

This is the result anticipated above.

It is clear from eqn (16.37) that the s wave dominates at low energy and

$$\delta_0(k) \simeq -ka, \quad (16.38)$$

The constant a has the dimension of a length and it is named the *scattering length*. For the scattering amplitude it follows that

$$f(\theta) \simeq \frac{1}{2ki} (e^{2i\delta_0} - 1) = \frac{1}{k \cot \delta_0(k) - i k} \simeq \frac{1}{-\frac{1}{a} - i k},$$

$$\lim_{k \rightarrow 0} k \cot \delta_0(k) \equiv -\frac{1}{a},$$

while the cross section is¹

$$\sigma \simeq \frac{4\pi}{k^2} \sin^2 \delta_0(k) \simeq 4\pi a^2.$$

The scattering length depends on the potential and can be both positive or negative and its absolute value can be quite different from the effective range d . Its meaning will become clear by studying the behavior of the s -wave solution at low energy.

As $k \rightarrow 0$ the scattering solution is

$$\chi_0(r) = r R_0(r) \sim \sin k(r-a) \simeq k(r-a),$$

and then a is the value of the intercept with the r axis of the graph of $\chi_0(r)$. More formally if χ_0^{as} is the asymptotic solution of the reduced radial equation, then

$$-\frac{1}{a} = \lim_{k \rightarrow 0} k \cot \delta_0 = \lim_{k \rightarrow 0} \frac{\chi_0^{(as)\prime}(0)}{\chi_0^{(as)}(0)}. \quad (16.39)$$

¹For an impenetrable spherical well, $V(r) = \infty$ for $r > R$, one obtains $a = R$ and the cross section is $4\pi R^2$, four times the geometrical cross section.

Let us now consider the equation for the exact solution χ_0 and its asymptotic form

$$\chi_0'' + \left(k^2 - \frac{2m}{\hbar^2} V(r) \right) \chi_0 = 0, \quad \chi_0(0) = 0, \quad (16.40)$$

$$\chi_0^{(as)''} + k^2 \chi_0^{(as)} = 0, \quad \chi_0^{(as)} = \frac{\sin(kr + \delta_0)}{\sin \delta_0}. \quad (16.41)$$

For $r > d$

$$\chi_0(r) \simeq \chi_0^{(as)}(r).$$

The overall normalization has been fixed for convenience in eqn (16.41).

The overall sign is fixed by $\chi'(0) > 0$.

Some general conclusions can be drawn (see Figure 16.3) from eqns (16.40) and (16.41) and $k \sim 0$:

- (1) For a repulsive potential, $V > 0$, the curvature of the graph (r, χ) is positive, i.e. the wave function is “pushed away” from the interaction zone; it follows that $a > 0$.
- (2) For a weak attractive potential (without bound states) $a < 0$.
- (3) For an attractive potential with a bound state at energy $E = \epsilon_0 < 0$ the potential is strong enough to “bend” the wave function, and $a > 0$.

Let us consider in particular the case of a single bound state with a small binding energy. The eigenstate has the asymptotic form

$$\chi_0^{(as)} \sim e^{-\kappa r}, \quad \kappa = \frac{\sqrt{-2m\epsilon_0}}{\hbar}. \quad (16.42)$$

Schrödinger's equation depends on k in a very weak form for $r \leq d$, so then also the wave function must have a small variation with k in this region, i.e. the scattering solution for $k^2 > 0$ must be² similar to the bound state solution for small k . Substitution of eqn (16.42) in eqn (16.39) gives

$$a \simeq \frac{1}{\kappa}. \quad (16.43)$$

In this case the scattering length can be much larger than the potential range. The cross section behaves as

$$\sigma \simeq \frac{4\pi}{k^2 + \kappa^2} = \frac{2\pi\hbar^2}{m} \frac{1}{E + |\epsilon_0|}. \quad (16.44)$$

This “resonant” scattering can give rise to cross sections orders of magnitude greater than the geometrical cross section πd^2 .

An improvement of this approximation can be obtained by taking into account higher order terms in the low- k expansion of $\cot \delta_0(k)$. Using (16.40) and (16.41) one can show that

$$k \cot \delta_0(k) = -\frac{1}{a} + \frac{1}{2} r_0 k^2 + O(k^4).$$

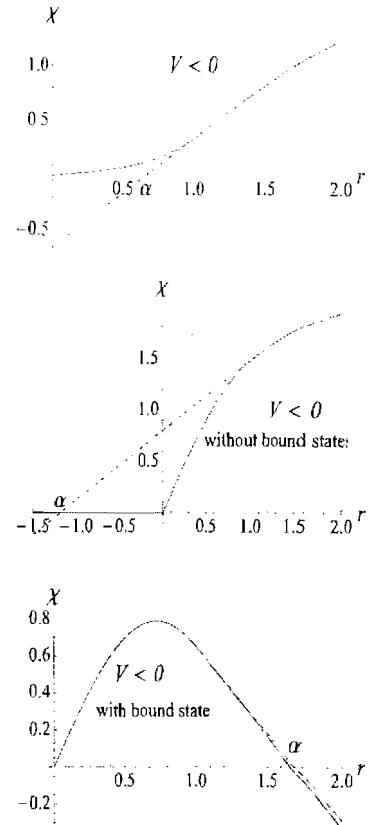


Fig. 16.3 The scattering length for a spherical well. In the plots is shown the reduced radial wave function and the extrapolation of the asymptotic solution. The intercept with the horizontal axis gives the scattering length.

²A similar question has been discussed in Section 3.3.2.

The constant r_0 is known as the *effective range*, and is of the order of the potential range. The two parameters a, r_0 give a complete description of low-energy scattering, no more details of the potential are involved.

A typical example is the proton-neutron scattering at low energy. In this case one has to distinguish between parallel spins ($S = 1$ scattering) and anti-parallel spins ($S = 0$). In the former case the system has a bound state, the deuteron, with binding energy $E = -2.23$ MeV. The scattering length and the effective range are $a^t = 5.415 \pm 0.012$ fm (1 fm = 10^{-13} cm), and $r_0^t = 1.704 \pm 0.028$ fm. The positive value for a^t is consistent with eqns (16.42) and (16.43); the resulting energy is $|\epsilon_0| = 2.23$ MeV. In the singlet case the experimental values are $a^s = -23.806 \pm 0.028$ fm, $r_0^s = 2.49 \pm 0.24$ fm.

16.7 Coulomb scattering: Rutherford's formula

The scattering of two charged particles, with charges e and e' , presents some peculiarities with respect to the general case. The interaction potential is

$$V(r) = \frac{ee'}{r}.$$

As it decreases slower than $1/r^2$ the total cross section is infinite: see Section 16.2.1. It turns out that even the single phase shifts are infinite, i.e. the scattering amplitude cannot be expanded in an analytic series of Legendre polynomials. To understand the origin of this behavior let us again consider Schrödinger's equation in a general central potential $U(r)$:

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi + U\psi = E\psi.$$

The partial wave expansion

$$\psi(r, \theta) = \sum_{\ell=0}^{\infty} \frac{\chi_{\ell}(r)}{r} P_{\ell}(\cos \theta)$$

requires the solution of the equation for reduced radial wave functions

$$\chi''_{\ell} + \left\{ k^2 - V(r) - \frac{\ell(\ell+1)}{r^2} \right\} \chi_{\ell} = 0.$$

To define phase shifts the solution must behave at large r as a superposition of spherical waves

$$\chi_{\ell}(r) \sim e^{\pm ikr}.$$

Let us put

$$\chi_{\ell}(r) = \text{const. } e^{\pm ikr} \exp \int_a^r dr' f_{\ell}(r'). \quad (16.45)$$

Substitution in the radial equation gives for f_ℓ

$$f'_\ell + f_\ell^2 \pm 2ikf_\ell = V(r) + \frac{\ell(\ell+1)}{r^2} \equiv W_\ell(r).$$

It is easily checked that

$$f_\ell(r) \sim r^{-s}, \quad \text{if } W_\ell(r) \sim r^{-s}, \quad (s > 0).$$

If $s > 1$

$$\exp \int_a^r dr' f_\ell(r') \rightarrow \text{const.}, \quad \chi_\ell(r) \rightarrow \text{const. } e^{\pm ikr},$$

and the general solution of the radial equation can be written in the usual form

$$\chi_\ell(r) \sim \sin \left(kr - \frac{\ell\pi}{2} + \delta_\ell \right).$$

If $s = 1$, instead, the phase of the asymptotic solution (16.45) diverges and it is not possible to define finite δ_ℓ . In physical terms the wave function in a Coulomb field does not approach a free particle wave function, even at very large r . Nevertheless the scattering problem can be exactly solved.

We shall use parabolic coordinates ξ, η, ϕ :

$$\xi \equiv r + z; \quad \eta \equiv r - z; \quad \phi = \tan^{-1} \frac{y}{x},$$

the inverse transformation to Cartesian coordinates being

$$x = \sqrt{\xi\eta} \cos \phi; \quad y = \sqrt{\xi\eta} \sin \phi; \quad z = \frac{\xi - \eta}{2}; \quad r = \frac{\xi + \eta}{2}.$$

In parabolic coordinates the Laplacian takes the form

$$\Delta = \frac{4}{\xi + \eta} \left[\frac{\partial}{\partial \xi} \xi \frac{\partial}{\partial \xi} + \frac{\partial}{\partial \eta} \eta \frac{\partial}{\partial \eta} \right] + \frac{1}{\xi \eta} \frac{\partial^2}{\partial \phi^2},$$

and Schrödinger's equation reads

$$\frac{4}{\xi + \eta} \left[\frac{\partial}{\partial \xi} \xi \frac{\partial}{\partial \xi} + \frac{\partial}{\partial \eta} \eta \frac{\partial}{\partial \eta} \right] \psi + \frac{1}{\xi \eta} \frac{\partial^2}{\partial \phi^2} \psi + \frac{2\mu}{\hbar^2} \left(E - \frac{2e e'}{\xi + \eta} \right) \psi = 0. \quad (16.46)$$

We look for solutions invariant under rotations around the z axis (the direction of the incident particle); then the derivative with respect ϕ vanishes. To simplify the formulas we will use the units

$$\mu = \hbar = 1.$$

These dimensional constants can be easily recovered in the final results by dimensional analysis.

Equation (16.46) can be solved by separation of the variables:

$$\psi(\xi, \eta) = f_1(\xi) f_2(\eta).$$

Substitution in eqn (16.46) gives a solution if the equations

$$\left(\frac{\partial}{\partial \xi} \xi \frac{\partial}{\partial \xi} + \frac{k^2}{4} \xi - \beta_1 \right) f_1(\xi) = 0, \quad (16.47a)$$

$$\left(\frac{\partial}{\partial \eta} \eta \frac{\partial}{\partial \eta} + \frac{k^2}{4} \eta - \beta_2 \right) f_2(\eta) = 0 \quad (16.47b)$$

are satisfied, with the constraint

$$\beta_1 + \beta_2 = ee',$$

Let us first consider the repulsive case, $ee' > 0$.

We can choose a third³ unit by

$$ee' = 1. \quad (16.48)$$

We must supply eqn (16.46) with a boundary condition to describe the scattering process. The correct one is

$$\psi \sim e^{ikz}, \quad z < 0, r \rightarrow \infty.$$

The reader can easily convince him-/or herself of this position by considering a wave packet impinging on the scattering center from $z \rightarrow -\infty$.

In parabolic coordinates the boundary condition takes the form

$$\psi \sim e^{ik(\xi-\eta)/2}, \quad \eta \rightarrow \infty, \forall \xi.$$

This behavior must be valid for all ξ , so

$$f_1(\xi) = e^{ik\xi/2}, \quad \forall \xi, \quad (16.49)$$

while

$$f_2(\eta) \rightarrow e^{-ik\eta/2}, \quad \eta \rightarrow \infty. \quad (16.50)$$

It is easily seen that eqn (16.47a) holds with f_1 given by eqn (16.49) if

$$\beta_1 = \frac{ik}{2}. \quad (16.51)$$

For f_2 it follows, with $\beta_2 = 1 - \beta_1 = 1 - ik/2$, that

$$\left(\frac{\partial}{\partial \eta} \eta \frac{\partial}{\partial \eta} + \frac{k^2}{4} \eta - 1 + \frac{ik}{2} \right) f_2(\eta) = 0.$$

Using asymptotic behavior (16.50) we put

$$f_2(\eta) = e^{-ik\eta/2} w(\eta);$$

the resulting equation for w is

$$\eta w'' + (1 - ik\eta)w' - w = 0.$$

It is convenient to change variables to

$$\eta_1 \equiv ik\eta, \quad \dot{w} \equiv \frac{d}{d\eta_1} w, \quad \text{etc.}$$

The equation in the new variable is

$$\eta_1 \ddot{w} + (1 - \eta_1) \dot{w} + \frac{i}{k} w = 0. \quad (16.52)$$

This equation is the equation for confluent hypergeometric functions, and is usually written in the form

$$z \frac{d^2 \Phi}{dz^2} + (\gamma - z) \frac{d\Phi}{dz} - \alpha \Phi = 0.$$

The regular solution is (see for example [Gradshteyn and Ryzhik (1965)])

$$\Phi(\alpha, \gamma; z).$$

Its explicit form in term of a series is

$$\Phi^{(reg)}(\alpha, \gamma; z) = \sum_{\ell=0}^{\infty} \frac{\Gamma(\alpha + \ell) \Gamma(\gamma)}{\Gamma(\alpha) \Gamma(\gamma + \ell) \ell!} z^\ell.$$

The reader can easily verify by substitution that this is indeed a solution of eqn (16.52). The solution w can then be written as

$$w(\eta_1) = w(ik\eta) = \Phi^{(reg)}(-i/k, 1; ik\eta),$$

while the complete solution is

$$\psi = f_1(\xi) f_2(\eta) = e^{ik(\xi-\eta)/2} \Phi(-i/k, 1; ik\eta).$$

The asymptotic behavior of ψ can be obtained from the known asymptotic form of Φ ; the result is

$$\begin{aligned} \psi &\sim e^{ik\frac{\xi-\eta}{2}} \left[\frac{(-ik\eta)^{\frac{i}{k}}}{\Gamma\left(1 + \frac{i}{k}\right)} \left(1 + \frac{1}{ik^3\eta} + \dots\right) + \frac{e^{ik\eta}(ik\eta)^{-\frac{i}{k}-1}}{\Gamma\left(-\frac{i}{k}\right)} \right] \\ &= e^{ik\frac{\xi-\eta}{2}} \left[\{1 + O(1/\eta)\} e^{\frac{i}{k} \log |k\eta|} - \frac{i}{k} \frac{\Gamma\left(1 + \frac{i}{k}\right)}{\Gamma\left(1 - \frac{i}{k}\right)} \frac{e^{-\frac{i}{k} \log k\eta}}{ik\eta} \cdot e^{ik\eta} \right]. \end{aligned}$$

In the last expression a constant $c = e^{\pi/2k}/\Gamma(1 + i/k)$ has been deleted, by changing the overall normalization of ψ (in scattering problems we will be interested in the ratio of scattered and incoming currents).

In terms of the usual r, z coordinates the asymptotic form of ψ is

$$\psi \simeq e^{ikz + (i/k) \log kz} + \frac{f(\theta)}{r} e^{ikr - (i/k) \log 2kr}, \quad (16.53)$$

where

$$f(\theta) = -\frac{1}{2k^2 \sin^2(\theta/2)} e^{-(2i/k) \log \sin(\theta/2)} \frac{\Gamma(1 + i/k)}{\Gamma(1 - i/k)}.$$

As anticipated the asymptotic wave function does not have the usual behavior (16.2), due to the infinite range of the Coulomb interaction. Nevertheless there is no problem in identifying the first term in eqn (16.53) as a distorted incident wave, while the second is the scattered wave, also with a phase distorted by the logarithmic term.

The elastic differential cross section is

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 = \frac{1}{4k^4 \sin^4(\theta/2)} = \frac{\mu^2 e^2 e'^2}{4k^4 \hbar^4 \sin^4(\theta/2)}. \quad (16.54)$$

In the last expression we have reintroduced the dimensional constants. This formula coincides with the classical Rutherford formula (and with the first order Born approximation). This is a peculiar property of Coulomb scattering of course.

The result for the attractive potential ($ee' < 0$) can be easily obtained from the previous one, it is just sufficient to change our conventions and write in place of eqn (16.48)

$$ee' = -1, \quad (\beta_1 + \beta_2 = -1).$$

The equation for w in the attractive case is the conjugate of the equation for the repulsive case, apart from the substitution $\eta \rightarrow -\eta$. The solution is then

$$w_{attr}(\eta) = w_{repul}^*(-\eta),$$

and the scattering amplitude

$$f_{attr}(\theta) = -f_{repul}(\theta)^* = \frac{e^{(2i/k) \log \sin(\theta/2)}}{2k^2 \sin^2(\theta/2)} \frac{\Gamma(1-i/k)}{\Gamma(1+i/k)}.$$

The scattering cross section is identical to the repulsive case and coincides with Rutherford's result

$$\frac{d\sigma}{d\Omega} = |f(\theta)_{attr}|^2 = \frac{\mu^2 e^2 e'^2}{4k^4 \hbar^4 \sin^4(\theta/2)}.$$

We note that the scattering amplitude in the attractive case has simple⁴ poles at

$$1 - \frac{i}{k} = -m, \quad m = 0, 1, 2, \dots, \Rightarrow k = \frac{i}{1+m}.$$

These poles (for $\text{Im}[k] > 0$) correspond to the bound state of the problem

$$E = \frac{k^2}{2} = -\frac{1}{2(m+1)^2}, \quad m = 0, 1, 2, \dots,$$

the well-known Bohr levels of hydrogen.

It is easily checked that the analytic continuation of the scattering solution has an asymptotic behavior

$$\psi \sim r^m e^{ikr} \sim r^m e^{-r/(m+1)},$$

in agreement with the known solution.

The reader can check that in the repulsive case the poles are in the unphysical sheet $\text{Im}[k] < 0$ (see Section 13.1.1) and do not correspond to normalizable solutions (i.e. bound states).

⁴ See an analogous discussion in Sections 11.4 and 13.1.1

16.7.1 Scattering of identical particles

Scattering of identical particles requires suitable symmetrization of the wave function. Let us first consider the case of the scattering of two spinless particles. The wave function must be symmetric for the exchange of their coordinates; in the center of mass of the system this amounts to symmetry under $\mathbf{r} \leftrightarrow -\mathbf{r}$. The asymptotic form of the wave function will be

$$\psi \simeq e^{ikz} + e^{-ikz} + \frac{e^{ikr}}{r} (f(\theta) + f(\pi - \theta)),$$

and the corresponding cross section

$$\frac{d\sigma}{d\Omega} = |f(\theta) + f(\pi - \theta)|^2. \quad (16.55)$$

In this formula $f(\theta)$ is the scattering amplitude computed for different particles. The interference terms appearing in eqn (16.55) are a typical example of a quantum effect, absent in classical mechanics. In particular the cross section at $\theta = \pi/2$ is

$$\left. \frac{d\sigma^{ident}}{d\Omega} \right|_{\theta=\pi/2} = 4|f(\pi/2)|^2 = 4 \left. \frac{d\sigma^{diff}}{d\Omega} \right|_{\theta=\pi/2},$$

i.e. four times the cross section for different particles (all other parameters kept fixed). In classical mechanics the measured cross section would be

$$\left. \frac{d\sigma^{ident}}{d\Omega} \right|_{\theta=\pi/2} = 2 \left. \frac{d\sigma^{diff}}{d\Omega} \right|_{\theta=\pi/2},$$

the factor 2 being due to the (classical) identity of particles, i.e. a detector placed at an angle θ counts as scattered both particle 1 and particle 2.

In the particular case of Coulomb scattering, as an instance a scattering of α particles, we have

$$\frac{d\sigma}{d\Omega} = \left(\frac{e^2}{mv^2} \right) \left[\frac{1}{\sin^4(\theta/2)} + \frac{1}{\cos^4(\theta/2)} + \frac{2 \cos \left(\frac{e^2}{\hbar v} \log \tan^2(\theta/2) \right)}{\sin^2(\theta/2) \cos^2(\theta/2)} \right].$$

For fermions if the interaction is spin independent we can classify states with total spin, which can be $S = 0, 1$. Fermi-Dirac statistics imply that singlet states must be symmetric in their orbital variables while triplet states must be antisymmetric:

$$\begin{aligned} S_{tot} = 1 &\rightarrow \chi_{spin} = \text{symm.} & \rightarrow \psi^{orb}(-\mathbf{r}) = -\psi^{orb}(\mathbf{r}); \\ S_{tot} = 0 &\rightarrow \chi_{spin} = \text{antisymm.} & \rightarrow \psi^{orb}(-\mathbf{r}) = +\psi^{orb}(\mathbf{r}). \end{aligned}$$

The corresponding amplitudes are

$$f_S = f(\theta) + f(\pi - \theta); \quad f_T = f(\theta) - f(\pi - \theta).$$

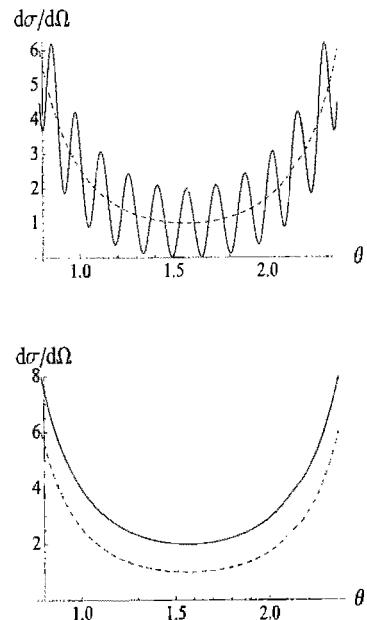


Fig. 16.4 Coulomb scattering for identical particles at low (upper graph) and high (lower graph) energies. The dashed line is the classic contribution, i.e. without interference terms.

Let us consider the scattering of a beam of unpolarized electrons. Each particle has an equal probability of being in the state $|\uparrow\rangle$ or $|\downarrow\rangle$.

The total spin takes the value 1 or 0 with probability 3/4 and 1/4, and then the cross section is

$$\frac{d\sigma}{d\Omega} = \frac{1}{4} |f(\theta) + f(\pi - \theta)|^2 + \frac{3}{4} |f(\theta) - f(\pi - \theta)|^2,$$

In particular for Coulomb scattering (the Mott cross section)

$$\frac{d\sigma}{d\Omega} = \left(\frac{e^2}{mv^2} \right) \left(\frac{1}{\sin^4(\theta/2)} + \frac{1}{\cos^4(\theta/2)} - \frac{\cos\left(\frac{e^2}{\hbar v} \log \tan^2(\theta/2)\right)}{\sin^2(\theta/2) \cos^2(\theta/2)} \right). \quad (16.56)$$

Note that in this case the cross section at $\theta = \pi/2$ is

$$\frac{d\sigma^{ident}}{d\Omega} \Big|_{\theta=\pi/2} = \frac{1}{2} \frac{d\sigma^{diff}}{d\Omega} \Big|_{\theta=\pi/2},$$

i.e. $\frac{1}{2}$ with respect to the cross section for distinct particles. This suppression was measured in the early days of quantum mechanics, [Williams (1930)].

The Born approximation is accurate for $\hbar v \gg e^2$, as is apparent from eqn (16.56); see also eqn (16.31). For $\hbar v \ll e^2$ the semi-classical approximation is valid: see eqn (16.8). We expect that the interference term must oscillate around zero in this region. Figure 16.4 shows how the classical result gives the average over the quantum oscillations at low energies. A similar phenomenon has been noted on several occasions in Chapter 11.

Further reading

A systematic exposition of scattering theory can be found in [Berestetskii, Lifshitz, and Pitaevskii (1980)] and [Goldberger and Watson (1964)]. The reader is also referred to Section 11.4 for a simple account on resonant scattering.

Guide to the Supplements

In Section 22.10 we complete our exposition on the semi-classical approximation to the scattering amplitude and give a simplified version of rainbow scattering. Some particular examples are exposed in the problems and in the numerical problems. In particular the analogue of the Kirchhoff approximation for scattering on an impenetrable sphere is found in Problem 16.3 and in Numerical analyses Problem 16.2. The rainbow is considered for a

simple potential in Numerical analyses Problem 16.3. The resonance scattering is exemplified in Numerical analyses Problem 16.4. To give a feeling of possible results we present in Figures 16.5 and 16.6 the shadow formation behind a scattering sphere and the trapping of a particle at resonant energy, from Numerical analyses Problems 16.2 and 16.4.

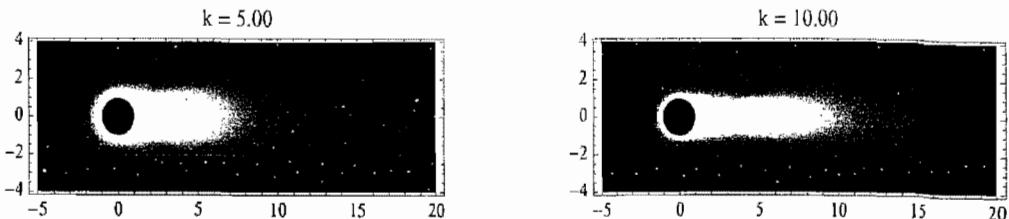


Fig. 16.5 Shadow formation behind an impenetrable sphere, from numerical problem 16.2

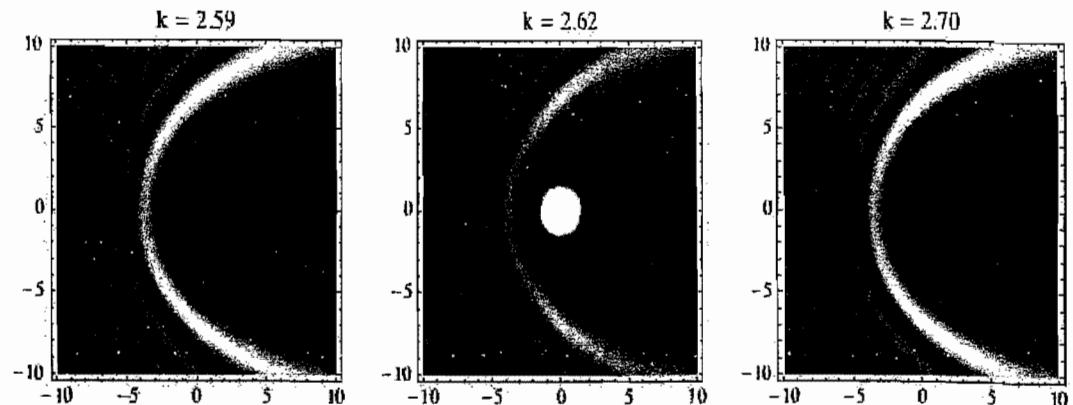


Fig. 16.6 Trapping of the wave function at a resonance, from the numerical problem 16.4

Problems

- (16.1) Write in the Born approximation the amplitude for two identical particles, subject to a spin-independent interaction. Consider in particular the Coulomb interaction.
- (16.2) Derive the eikonal approximation from the asymptotic form of Legendre polynomials (for large L and small θ):
- $$P_\ell(\cos(\theta)) \simeq J_0(\ell\theta).$$
- (16.3) Compute the scattering amplitude for an impenetrable sphere of radius R in the Kirchhoff approximation.

Numerical analyses

- (16.1) Check in **Mathematica** the asymptotic form of the scattering solutions.
- (16.2) Solve numerically the scattering problem for an infinite spherical potential well of radius a .
- (16.3) Solve numerically the scattering problem for a spherical potential well of radius a . Study the cross section and the possible rainbow.
- (16.4) Solve numerically the scattering problem for a spherical potential
- $$V(r) = V_0 r^2 \exp(-r).$$
- In particular make a density plot for the wave function for resonant scattering. Verify the eikonal approximation.

Atomic nuclei and elementary particles

17

A few salient features of atomic nuclei and elementary particles are discussed in this chapter. The need for relativistic quantum field theories for describing fundamental interactions among the elementary particles in Nature is explained. Locality, the existence of anti-particles, causality, and the spin–statistics connection, some of which are part of the constituent principles of ordinary (non-relativistic) quantum mechanics, are all deeply rooted in the relativistic quantum field theories of elementary particles.

17.1 Atomic nuclei	477
17.2 Elementary particles: the need for relativistic quantum field theories	485
Further reading	496

17.1 Atomic nuclei

17.1.1 General features

Atomic nuclei (referred to as *nuclei* below) are composite states made of protons and neutrons. The proton and neutron, together called the *nucleon*, have masses

$$m_p \simeq 1.673 \times 10^{-24} \text{ g} \simeq 938.3 \text{ MeV}; \quad (17.1)$$

$$m_n \simeq 1.675 \times 10^{-24} \text{ g} \simeq 939.6 \text{ MeV}; \quad (17.2)$$

to be compared with that of the electron,

$$m_e \simeq 9.109 \times 10^{-28} \text{ g} \simeq 0.511 \text{ MeV}.$$

The proton has charge $+|e|$ (identical, apart from the sign, with that of the electron); the neutron has no net charge.

Apart from the difference in the charge, and in their masses, the two particles have very similar properties with respect to the nuclear interactions (“strong interactions” in modern terminology, see the next section).

A generic nucleus is composed of Z protons and N neutrons. Z is the atomic number, equal to the number of the electrons in the normal, neutral atom. The sum of the numbers $A = Z + N$ is the mass number, and represents approximately the mass of the nucleus in the unit of the proton mass. A nucleus is represented by a symbol such as

$$_Z^A(\text{Name}),$$

for instance,

$${}_{\frac{1}{8}}^{16}O, {}_{\frac{28}{28}}^{58}Ni, {}_{\frac{79}{79}}^{197}Au, {}_{\frac{92}{92}}^{238}U,$$

respectively, for the nuclei of oxygen, nickel, gold, and uranium. Today roughly 300 stable and about 1700 metastable nuclei are known to exist in Nature. As the nucleon (proton or neutron) has spin $\frac{1}{2}$, a nucleus with an even mass number is a boson; one with an odd number of nucleons is a fermion.

The binding energy of a nucleus is given by

$$B = Zm_p + Nm_n - M_{nuc},$$

where M_{nuc} is the mass of the nucleus. Empirically there is an approximate relation

$$B/A \sim \text{const.} \simeq 8 \text{ MeV} : \quad (17.3)$$

governing the binding energy of a nucleus and its mass number: that is the binding energy *per nucleon* is approximately constant. This property is known as the *saturation* of the nuclear binding energy. Compare eqn (17.3) with the typical atomic binding energy, $me^4/2\hbar^2 \simeq 14 \text{ eV}$ (the Rydberg energy): a nucleus is a far more strongly bound system than an atom. One needs roughly $\sim 10^5$ times bombarding energy to disintegrate a nucleus as compared to what is needed to split an atom apart.

The linear size of nuclei can be determined, for instance, through an electron scattering by various nuclei. Empirically, their size is given by

$$R \simeq \text{const. } A^{1/3} \equiv r_0 A^{1/3} :$$

$$r_0 \simeq 1.1 \text{ fm}; \quad 1 \text{ fm} \equiv 10^{-13} \text{ cm}.$$

Nuclei are thus 10^5 times smaller than a typical atom (cf. $r_B \simeq 5 \times 10^{-9} \text{ cm}$). For this reason the nuclei can be taken to be point-like in a first approximation, in the consideration of atomic properties.

17.1.2 Isospin

The “similarity” between the proton and neutron mentioned above actually goes much deeper than the near equality of their masses or of their nuclear interactions. As far as nuclear (strong) interactions are concerned, the proton and neutron can be regarded as two different internal quantum states—isospin or isotopic spin states—of the same particle, called the *nucleon*. In other words, the nucleon is an isospin $t = \frac{1}{2}$ particle, whose components are

$$|p\rangle = |\frac{1}{2}, \frac{1}{2}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad |n\rangle = |\frac{1}{2}, \frac{-1}{2}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

in a notation similar to the one used for spin. The isospin operators act as

$$\hat{T}^2|t, t_3\rangle = t(t+1)|t, t_3\rangle; \quad \hat{T}_3|t, t_3\rangle = t_3|T, T_3\rangle,$$

formally exactly as angular momentum (or spin) operators, T_1, T_2, T_3 being the analogues of J_x, J_y, J_z .

Just as in the case of spin, all strongly interacting particles in Nature (they are called *hadrons*) belong to definite isospin multiplets. The nucleons form an isospin doublet, as already mentioned; the three pions (π^+ , π^- of mass 139.6 MeV and π^0 of mass 135.0 MeV) form an iso-triplet, that is, $t = 1$; the kaons form two doublets (K^+, K^0) and (\bar{K}^0, K^-); the so-called Σ particles form a triplet; and so on. The composition-decomposition rule for isospin is formally identical to the case of angular momentum, discussed in Section 4.7. The relations between direct-product states and states with definite total isospins are then provided by the same Clebsch-Gordan coefficients (see Subsection 4.7.1 and the table at the end of the book). Thus a two-nucleon state can be either in one of the isospin triplet states

$$|1, 1\rangle = |p\rangle|p\rangle, \quad |1, 0\rangle = \frac{1}{\sqrt{2}}(|p\rangle|n\rangle + |n\rangle|p\rangle), \quad |1, -1\rangle = |n\rangle|n\rangle,$$

or in the isospin singlet state,

$$|0, 0\rangle = \frac{1}{\sqrt{2}}(|p\rangle|n\rangle - |n\rangle|p\rangle),$$

whereas a pion-nucleon state may be in an isospin-quartet state ($t = \frac{3}{2}$) or an isospin-doublet ($t = \frac{1}{2}$). The Wigner-Eckart theorem (see Subsection 5.2.5) then gives us a set of relations among the decay or scattering amplitudes, in terms of the “reduced matrix elements”. The latter correspond to the amplitudes connecting the initial and final states which are definite total-isospin eigenstates.¹

The Hamiltonian describing the interactions of two nucleons, for instance, is invariant under rotations in the internal (isospin) space,

$$\begin{pmatrix} |p\rangle \\ |n\rangle \end{pmatrix} \rightarrow U \begin{pmatrix} |p\rangle \\ |n\rangle \end{pmatrix},$$

where U is an $SU(2)$ transformation,

$$U = \begin{pmatrix} \alpha & \beta \\ -\beta^* & \alpha^* \end{pmatrix}, \quad |\alpha|^2 + |\beta|^2 = 1.$$

Isospin-invariant two-nucleon interactions have forms such as $V(r)$, $\tau_1 \cdot \tau_2 V(r)$, and so on. A more general form of the two-nucleon interaction Hamiltonian will be given below (see eqn (17.12)).

Historically, the isospin symmetry group has played an important role in the development of elementary particle physics as the latter grew out of nuclear physics. As the particles carrying the “strangeness”—such as kaons or Λ baryons—were gradually discovered in high-energy (e.g.,) proton-proton scattering processes, the $SU(2)$ isospin group was generalized to the $SU(3)$ “unitary” symmetry group. These ideas eventually led to the quark model through the work of Nishijima, Gell-Mann, Ne'eman, Zweig, and others, and subsequently, to the dynamical theory of strong interactions, known as quantum chromodynamics. These developments are briefly reviewed in Supplement Subsection 20.6.4. See also the comments at the end of this chapter, Subsection 17.2.6.

¹ Exercise. A prominent peak observed in the pion-nucleon scattering cross sections shows the existence of an excited state of the nucleon, the so-called Δ resonance, of mass about 1232 MeV/c². Experimentally the various decay branching ratios satisfy

$$\frac{P(\Delta^+ \rightarrow \pi^+ n)}{P(\Delta^+ \rightarrow \pi^0 p)} \simeq \frac{1}{2},$$

$$\frac{P(\Delta^0 \rightarrow \pi^0 n)}{P(\Delta^0 \rightarrow \pi^- p)} \simeq 2$$

where + and 0 indicate two of the charge components of Δ . Determine the isospin of Δ . Tell what one can say about the ratio

$$\frac{P(\Delta^+ \rightarrow \pi^+ n)}{P(\Delta^0 \rightarrow \pi^0 n)}.$$

Isospin breaking

Isospin symmetry is an approximate symmetry of Nature. There are at least two known sources of $SU(2)$ isospin symmetry *breaking*. First, the isospin is broken by the mass differences between the u and d quarks—see the Table 24.8 at the end of the book—which are believed to be mainly responsible for the observed small mass differences between members of isospin multiplets, such as in eqns (17.1), (17.2). Put in a more formal way, the observed isospin breaking pattern can be empirically expressed by the presence of an isospin breaking operator,

$$O = cT^3,$$

which is proportional to the third component of the isospin. Such a term, treated as a perturbation to the main, $SU(2)$ -invariant Hamiltonian, leads to various calculable consequences of isospin breaking, e.g., via the Wigner-Eckart theorem. Analysis of this sort, which turns out to be extremely informative, goes under the name of the theory of broken symmetries.

Another important source of isospin breaking is electromagnetic interactions. They clearly distinguish the proton (with charge, $|e|$) from the neutron (with no net charge). Again, one should be able to treat the effect of weak gauge interactions (in this case, the electromagnetic interactions) as a perturbation; however, the fact that the hadrons are relativistic bound states, bound by strong interaction dynamics, often makes the problem of evaluating the corrections quantitatively rather difficult.

17.1.3 Nuclear forces, pion exchange, and the Yukawa potential

The characteristics which distinguish nuclei from atoms as composite (bound) systems principally derive from the very different nature of the nuclear forces themselves, as compared to the Coulomb forces in the case of atoms. Nuclear forces are short-ranged, with a more or less well-defined interaction range of the order of a fermi, 1×10^{-13} cm, in contrast to the Coulomb force, which has an infinite range.

Although today we know that the origin of the nuclear forces is in the strong interactions (the so-called color $SU(3)$ gauge interactions) among the quarks and gluons, in a first approximation the nuclear forces can be regarded as arising from the “exchange” of the lightest of the hadrons, the pions. The potential between two nucleons, caused by a pion exchange, takes the form of the Yukawa potential

$$V_Y(r) = -g^2 \frac{e^{-r/r_\pi}}{r}, \quad (17.4)$$

where

$$r_\pi \equiv \frac{\hbar}{m_\pi c}$$

is the Compton length of the pion. From the known mass of the pion ~ 140 MeV, we can deduce the range of the force to be of the order of $r_\pi \simeq 1.4$ fm, in agreement with the typical size of a nucleus. The asymptotic behavior of the Yukawa potential (17.4) reflects the mass of the particles (pions) that “mediate” the nuclear interactions. To see this fact, recall that the Coulomb potential

$$V(r) = -\frac{e^2}{r}$$

can be obtained as a solution of Poisson’s equation,

$$\Delta\phi = \nabla^2\phi = -4\pi\rho, \quad \rho = e\delta^3(\mathbf{r}),$$

which is Maxwell’s equation (with $\mathbf{E} = -\nabla\phi$) in the presence of a static, point-like charge.

In the case of nuclear forces, the relevant equation is the equation for the pion field: it is the so-called Klein–Gordon equation (with a static source),

$$\left(\Delta - \frac{m_\pi^2 c^2}{\hbar^2} \right) \phi_\pi(\mathbf{r}) = -4\pi g \delta^3(\mathbf{r}). \quad (17.5)$$

The Yukawa potential follows as a regular solution of this equation.²

The difference between the Coulomb force and the nuclear forces lies not only in the range of the action: the coupling constant also differ considerably. If we compare the dimensionless combinations, we find for the nuclear potential

$$\frac{g^2}{\hbar c} \simeq 0.28,$$

to be compared with the fine-structure constant,

$$\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137} \simeq 0.0073.$$

Yukawa’s meson theory contained several revolutionary concepts. The first was that the nuclear forces were due to the *exchange* of some physical particles. According to such an idea, the range of the interactions is given by the Compton wavelength of the mediating particle, which is inversely proportional to the mass. Yukawa was able to predict, by using the range of nuclear forces known at that time, of the order of a few fm (1 “fermi” = 10^{-13} cm), the existence of a new particle whose mass is of the order of 200 MeV/c². The predicted particles, the pions, with mass 140 MeV/c², were subsequently discovered among cosmic rays, after an initial misidentification with another particle, the μ (muon), with $m \sim 106$ MeV/c², which turned out not to be the particle predicted by Yukawa, but rather one of its decay products. In comparison, electromagnetic interactions have an infinite range, due to the massless nature of the photon, the particle mediating electromagnetic interactions. Also, the fact that nuclear forces are always attractive while electromagnetic interactions can be either attractive or repulsive, can be attributed to the scalar nature of the pion, as compared to the vector nature of the

²Exercise. Find the Yukawa potential by solving eqn (17.5). Hint: consider the Fourier transform of both sides of the equation, find the Fourier transform of ϕ_π , and transform it back by the inverse Fourier transformation.

photon. Finally, the *relation between an elementary particle and the field associated with it* has been clearly recognized, and this has since become one of the basic concepts of elementary particle physics, described by a quantum field theory.

17.1.4 Radioactivity

Many nuclei are unstable and spontaneously decay, via emission of various particles: α particles (α decay), electrons (β decay), or photons (γ decay). Some of them also decay by fission. The nature of these phenomena varies considerably.

- α decay occurs through a tunnel effect; to a good approximation an alpha particle, a tightly bound system of two protons and two neutrons, moves in an effective potential due to other nucleons, and penetrates through the Coulomb barrier and emerges as a free particle. See Subsection 11.3.2 for an elementary discussion on α decay.
- β decay is a consequence of the elementary weak-interaction process,

$$n \rightarrow p + e^- + \bar{\nu}_e ; \quad p \rightarrow n + e^+ + \nu_e , \quad (17.6)$$

where ν_e is the (electron-) neutrino. This process has been discussed briefly in Section 9.4. Neutrinos interact only weakly, having no electric or strong-interaction (i.e., color) charges, and their existence was predicted by Pauli in 1931, precisely because the electron coming from the nuclear decay process of the type

$$(Z, A) \rightarrow (Z + 1, A) + e^- + \bar{\nu}_e \quad (17.7)$$

had a continuous energy spectrum, apparently violating energy conservation. In β decay parity is violated [Lee and Yang (1956)]. The neutrino masses are as yet unknown. Recently (1998), however, the non-vanishing mass differences (more precisely, the differences in the mass squared) of neutrinos of different kinds, of the order of $O(10^{-3})$ eV², have been observed in the Kamiokande experiment. Understanding their masses remains one of the most important tasks of experimental high-energy physics, not to mention the theoretical task of understanding the masses of the neutrinos as well as of other elementary particles. See Table 24.11 for the complete list of the presently known elementary particles, and their properties.

- γ decay is the result of an electromagnetic transition between nuclear levels, by a spontaneous emission of a photon. Photons emitted from nuclear transitions are in general of much higher energy than those involved in atomic transitions. Light with frequency higher than 10^{20} (corresponding to a photon energy of 1 MeV or higher) is known as gamma rays — see Table 17.1.

Name	wavelength (cm)	ν (1/s)	E (eV)
Gamma rays	$< 10^{-10}$	$> 10^{20}$	$> 10^6$ (=1 MeV)
X rays	$10^{-8}-10^{-9}$	$10^{18}-10^{19}$	10^4-10^5
UV light	$10^{-6}-10^{-7}$	$10^{16}-10^{17}$	10^2-10^3
Visible light	$4000-8000 \text{ \AA}$	10^{15}	10^1
IR light	$10^{-2}-10^{-4}$	$10^{12}-10^{14}$	$10^{-2}-1$
Microwave	$10^{-1}-10^1$	10^9-10^{11}	$10^{-5}-10^{-3}$
Radio wave	10^2-10^5	10^5-10^8	$10^{-9}-10^{-6}$

Table 17.1

17.1.5 The deuteron and two-nucleon forces

The deuteron is the simplest of the nuclei: it is made of a proton and a neutron. It is the nucleus of deuterium, the component of heavy water. Its mass is given by

$$1875.6 \text{ MeV}/c^2$$

and its binding energy is about 2.3 MeV. The deuteron has a magnetic moment,

$$\mu_D \simeq 0.86 \mu_N, \quad \mu_N = \frac{e\hbar}{2m_p},$$

where μ_N is the *nuclear magneton*. Comparison with the magnetic moments of the nucleons,

$$\mu_p \simeq 2.79 \mu_N; \quad \mu_n \simeq -1.91 \mu_N$$

suggests that the spins of the two nucleons are parallel :

$$S_{tot} = 1.$$

If we assume furthermore that the two nucleons are in the S ($\ell = 0$) state of the orbital motion, as is reasonable to assume for the ground state of the relative motion, we would be led to the conclusion that the deuteron is in a 3S_1 . This is not quite correct, as will be seen below.

The orbital wave function is symmetric (even) under parity $\mathbf{r} \rightarrow -\mathbf{r}$, and the spin wave function is also symmetric under the exchange of the two spins, being in a triplet state. If the proton and neutron are to be regarded as the same particle (nucleon), one might wonder whether such a state is consistent with Fermi-Dirac statistics. The way out consists in the consideration of the isospin. The proton and neutron are “isospin up” and “isospin down” states of the nucleon. Fermi-Dirac statistics requires that the deuteron is an isospin singlet state,

$$\psi_{isospin} = \frac{1}{\sqrt{2}}(|p\rangle|n\rangle - |n\rangle|p\rangle),$$

antisymmetric under the exchange of the two nucleons. The total wave function

$$|\psi^{(orb)}\rangle|\psi^{(spin)}\rangle|\psi_{isospin}\rangle$$

is antisymmetric. The empirical fact that there are no other deuteron states with charge 2 or 0 in Nature is in agreement with the above assignment.

Another important property of the deuteron is the electric quadrupole moment

$$Q \simeq 0.002738 \times 10^{-24} \text{ cm}^2. \quad (17.8)$$

We recall that the electric quadrupole operator is defined by

$$Q_{ij} = e \left(r_i r_j - \frac{1}{3} \delta_{ij} r^2 \right)$$

(with $Q \equiv \langle Q_{33} \rangle$). Q is a spherical tensor of rank 2. The experimental fact (17.8) implies by the Wigner–Eckart theorem that the ground state cannot be a pure S state, but it must contain a D wave component³ ($\ell = 2$),

$$\psi = c_0 \psi_S + c_2 \psi_D; \quad c_2 \neq 0. \quad (17.9)$$

In turn this implies that the potential responsible for the deuteron binding cannot have a simple form,

$$V = V_W(r) + V_B(r) \frac{1 + \sigma_1 \cdot \sigma_2}{2} \quad (17.10)$$

(the first and the second terms are called respectively Wigner and Bartlett forces). The potential (17.10) indeed commutes with the orbital angular momentum operator \mathbf{L} : the ground state, if unique, would have to be an eigenstate of \mathbf{L}^2 , which is not. It means that the two-nucleon forces contain terms which are not spherically symmetric. A simple such interaction term which is nonetheless invariant under three-dimensional rotations, that is, which commutes with the total angular momentum,

$$\mathbf{J} = \mathbf{L} + \mathbf{s}_1 + \mathbf{s}_2,$$

³Exercise. Show that the Hamiltonian

$$H = -\frac{\hbar^2 \nabla^2}{2\mu} + V + V_{\text{tensor}}$$

commutes with the total angular momentum J_z .

is

$$V_{\text{tensor}} = V_T(r) \cdot \left\{ \frac{3(\sigma_1 \cdot \mathbf{r})(\sigma_2 \cdot \mathbf{r})}{r^2} - \sigma_1 \cdot \sigma_2 \right\}, \quad (17.11)$$

known as the *tensor* force.⁴

Indeed, empirically it is known that the two-nucleon forces contain, besides the Wigner, Bartlett, and tensor forces, terms involving nontrivial isospin-flipping interactions:

$$\begin{aligned} V' &= V_H(r) \frac{1 + \tau_1 \cdot \tau_2}{2} + V_M(r) \frac{1 + \tau_1 \cdot \tau_2}{2} \cdot \frac{1 + \sigma_1 \cdot \sigma_2}{2} + \\ &\quad V'_T(r) \left\{ \frac{3(\sigma_1 \cdot \mathbf{r})(\sigma_2 \cdot \mathbf{r})}{r^2} - \sigma_1 \cdot \sigma_2 \right\} \frac{1 + \tau_1 \cdot \tau_2}{2}, \end{aligned} \quad (17.12)$$

where τ_1, τ_2 are the isospin operators of the two nucleons. The first two terms containing the isospin dependence are known as the Heisenberg and Majorana forces, respectively. The total Hamiltonian

$$H = -\frac{\hbar^2 \nabla^2}{2\mu} + V + V_{tensor} + V'$$

commutes with the total angular momentum as well as the total isospin operator,

$$\hat{T}_{tot} = \frac{1}{2}(\hat{\tau}_1 + \hat{\tau}_2) :$$

H is invariant under rotations in the internal (isospin or charge) space, as well as in three-dimensional physical space.

17.2 Elementary particles: the need for relativistic quantum field theories

The smallest entities of matter in Nature are called elementary particles. Their definition, however, changes with time. At the time of Yukawa's meson theory only a few elementary particles were known, but in the sixties the list of "elementary" particles became embarrassingly large. Today we know that the hadrons (strongly interacting particles such as the proton, neutron, pions, kaons, and hundreds of other particles) are all composite particles made of quarks and gluons. The set of "elementary particles" known today include leptons (particles which do not interact strongly: the electron, the muon, the tau lepton and associated neutrinos), quarks (six types of quarks are known today: up, down, strange, charm, bottom and top quarks) and particles mediating various interactions (photons, gluons, W and Z bosons, and perhaps, gravitons). See Table 24.10.

A quantum mechanical description of elementary particles requires a markedly different approach as compared to the treatment of atoms, molecules, or nuclei. For this reason, the passage from atomic or nuclear physics to elementary particle physics is often seen as a somewhat mysterious or rather complicated step by a student. Although some such a feelings are purely psychological, there are indeed several concrete issues involved.

First of all, elementary particles are typically studied with velocities comparable to that of light and consequently the effects of special relativity cannot in general be neglected. This implies that a relativistic treatment is needed from the beginning: the non-relativistic Schrödinger equations so far used are no longer a good approximation. Their relativistic counterparts such as the Klein-Gordon equation (for spinless particles) or the Dirac equation (for spin- $\frac{1}{2}$ particles) must be used instead.

There is a serious problem, however: relativistic equations such as these, as it turns out, necessarily possess solutions with negative energies (a little analogous to non-relativistic systems with a potential unbounded

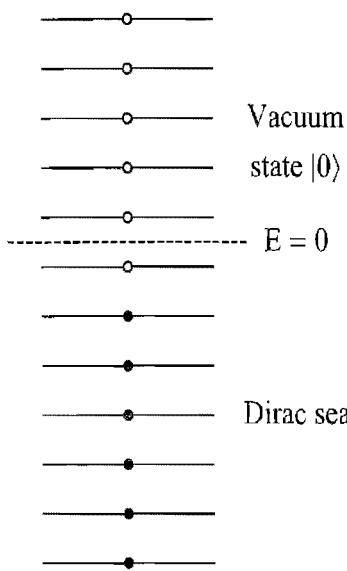


Fig. 17.1

below). To overcome this difficulty, Dirac proposed that the ground state of the system of a free spin- $\frac{1}{2}$ particle with mass m , for instance, is the one in which all negative energy levels are occupied (the *Dirac sea*) while all positive energy levels are empty. Because of Pauli's principle, a fermion with positive energy cannot fall to a negative-energy level emitting light, so such a state is indeed stable, a little like a closed-shell state of an atom is.

A state in which a negative energy level is empty, in such a picture, would have the property of a state with a particle (i.e., with positive energy) having exactly the same mass but opposite charge as the original particle. Dirac was thus led to predict the existence of an *anti-particle* for each elementary particle, a prediction soon confirmed by the experimental discovery of the positron (anti-electron) and anti-proton.

Another closely related property of these relativistic systems is the fact that *the particle number is no longer conserved*. Particles can be annihilated and created during interaction processes; only the total relativistic energy, including both the kinetic energies and rest masses of the particles, is conserved. We need a formalism which naturally describes such processes.

The required formalism is the so-called "second quantization", a formalism in terms of creation and annihilation operators (which is illustrated in the context of non-relativistic quantum mechanics in Supplement 20.11). As the interaction vertex (point) where particles can be annihilated or created can be anywhere in space and time, the annihilation and creation operators become functions of the spacetime point, or equivalently, of the momentum, as well as of the particle species, spin, etc. In other words, the theory becomes a quantum theory of *fields*, a theory of *infinite degrees of freedom*, and no longer a one-particle or few-body problem. In the second quantization formalism, the particles and anti-particles are treated in a symmetric fashion: a somewhat artificial Dirac sea need not be introduced.

In short, a proper description of elementary particles requires *relativistic quantum field theories*.

A necessary price to pay in working with relativistic quantum field theories seems to be the occurrence of ultraviolet divergences in the quantum corrections, and the necessity of *renormalization*. The constants appearing in the theory, such as masses and coupling constants (and wave functions) all suffer from divergent quantum corrections. Physical quantities must be expressed systematically in terms of certain set of reference (physical) quantities, and not in terms of the "bare" quantities. For instance the electric charge e is to be defined as the value of the three-point function

$$\langle \bar{\psi} \gamma^\mu A_\mu \psi \rangle$$

at the zero-momentum photon and at the "on-mass-shell" value of the electron momenta (i.e. p_1 and p_2 such that $p_1^2 = p_2^2 = m^2$). The predictions of the theory are calculated in terms of these physically defined (finite) constants, while the bare coupling constant, mass, etc. can be infinite. When the amplitudes calculated and expressed in terms of

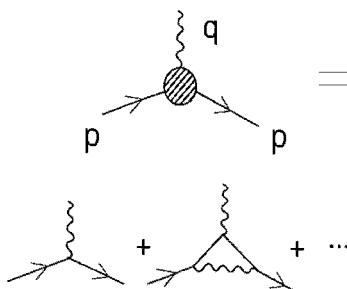


Fig. 17.2 The photon-electron-electron three-point function, including the bare coupling constant, e_0 , the first term, and all possible quantum corrections up to the given order, evaluated at a given reference set of momenta, is identified with the observed electric coupling constant e , $e^2/\hbar c \approx 1/137$. The wavy line is the photon propagator, the straight line is the electron propagator.

these physical quantities defined at some conveniently chosen physical criterion—they are called the renormalized coupling constant, renormalized mass, etc.—are all finite functions of momenta, spin, and particle species, one has a well-defined prediction. When this systematic renormalization procedure works (i.e., all the ultraviolet divergences get eliminated, leaving a finite answer) order by order in perturbation theory, the theory is said to be *renormalizable*. A renormalizable theory is predictable as physical quantities can be *computed* in terms of a finite number of physical parameters (whose values must be fixed experimentally), and compared against experiments.

Another aspect of the theories of fundamental interactions deserves mention. One of the first elementary particles which entered quantum physics is the photon. As an elementary particle the photon is of a special kind: it is one of the *gauge particles*, i.e., particles mediating so-called gauge interactions. Photons mediate electromagnetic interactions. Analogously, W bosons and Z bosons, together with photons, mediate electroweak interactions. Gluons mediate the strong interactions. The theory describing the electron and photon is quantum electrodynamics, an Abelian gauge field theory. The electroweak theory and quantum chromodynamics are all gauge theories. In a sense, the symmetry requirement of local gauge invariance is so strong that the form of the interactions is basically fixed by it (the *gauge principle*). Yang and Mills further generalized the gauge principle to the cases of multi-component wave functions [Yang and Mills (1954)], thus introducing the concept of *non-Abelian gauge theories* or *Yang–Mills theories*, where the local reparametrization freedom involves non-Abelian groups, such as $SU(2)$ and $SU(3)$.

It is an extraordinary empirical fact that all of the known fundamental interactions in Nature are described by this kind of theories—renormalizable, Yang–Mills gauge theories. In this sense, there seems to be a deep unification underlying the theory of fundamental interactions.⁵

Finally, let us note that the relation between the statistics (Fermi–Dirac or Bose–Einstein) and spin, which is an empirical law in the context of non-relativistic quantum mechanics, follows theoretically from the consistency of the principles of relativistic quantum mechanics (and positive-energy requirement): see Subsection 17.2.3 below.

Below we shall just touch a few of these issues, trying to give the reader a flavor of the ideas involved in elementary particle physics (the physics of fundamental interactions).⁶

17.2.1 The Klein–Gordon and Dirac equations

The first example of a relativistic Schrödinger equation is the so-called Klein–Gordon equation, describing a free, spinless scalar particle with mass m :⁶

$$\left(\frac{\partial^2}{\partial t^2} - \nabla^2 + m^2 \right) \phi = 0.$$

⁵To be scrupulous, the part of the Glashow–Salam–Weinberg model involving the so-called Higgs particles is *not* determined by any gauge principle. Indeed this happens to be the part least understood both theoretically and experimentally.

⁶Historically, it was Schrödinger who studied it first, but he himself discarded it, as it did not give very precise results about the hydrogen atom, when coupled to the Coulomb potential. Schrödinger subsequently considered its non-relativistic limit and arrived at what is known today as Schrödinger's equation. See [Weinberg (1989)].

Here and below, as is customary in the elementary particle physics literature, the so-called natural unit, $c \equiv 1$, $\hbar \equiv 1$, is adopted. Such an equation can be obtained by applying the quantization rule

$$E \rightarrow i \frac{\partial}{\partial t}, \quad p_i \rightarrow -i \frac{\partial}{\partial x^i},$$

or simply

$$p_\mu \rightarrow i \frac{\partial}{\partial x^\mu}, \quad \mu = 0, 1, 2, 3,$$

to the relativistic energy-momentum relation (called the dispersion relation),

$$E^2 = \mathbf{p}^2 c^2 + m^2 c^4 = \mathbf{p}^2 + m^2.$$

Clearly, given the momentum \mathbf{p} , there are two solutions for the energy

$$E = \pm \sqrt{\mathbf{p}^2 + m^2} : \quad (17.13)$$

a positive and a negative energy solution. In the plane wave basis, they are just

$$\psi_+ = e^{-ip \cdot x}, \quad \psi_- = e^{ip \cdot x},$$

$$p^2 = m^2, \quad p^0 = E = \sqrt{\mathbf{p}^2 + m^2} > 0.$$

In search of a possible way out of such negative-energy solutions, Dirac attempted to construct an equation which is in a sense a “square root” of the Klein-Gordon equation. The idea is that by having a first-order derivative in $\partial/\partial t$, perhaps the problem of the negative-energy solution would have been obviated. He found that it was not possible to get a linearized (in the time derivative) equation if one worked with a simple function $\psi(x)$, but that it was possible to do so if a multi-component function, $\psi_\alpha(x)$, with the minimum number of components equal to four, was used. The equation for the free case takes the form (the Dirac equation)

$$[i\gamma^\mu \partial_\mu - m] \psi(x) = 0, \quad (17.14)$$

where the matrices γ^μ , called *Dirac gamma matrices*, satisfy the algebra

$$\{\gamma^\mu, \gamma^\nu\} \equiv \gamma^\mu \gamma^\nu + \gamma^\nu \gamma^\mu = 2g^{\mu\nu}, \quad (17.15)$$

where $\text{diag } g^{\mu\nu} = (1, -1, -1, -1)$ is the metric of Minkowski space, and

$$\partial_0 = \frac{\partial}{\partial t}, \quad \partial_i = \frac{\partial}{\partial x^i}.$$

The representation for the gamma matrices is not unique, but a convenient basis is the one (the so-called chiral representation) in which

$$\gamma^\mu = \begin{pmatrix} 0 & \sigma^\mu \\ \bar{\sigma}^\mu & 0 \end{pmatrix},$$

and

$$\sigma^\mu = (\mathbf{1}, \sigma_i), \quad \bar{\sigma}^\mu = (\mathbf{1}, -\sigma_i),$$

where σ_i are the usual Pauli matrices. An advantage of such a representation is that the physical meaning of the two upper components and two lower components of the Dirac spinor becomes quite clear. They are eigenstates of the so-called chirality operators $(1 \pm \gamma_5)/2$, where

$$\gamma_5 = i \gamma_0 \gamma_1 \gamma_2 \gamma_3 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}.$$

They are called ψ_L (left-handed) and ψ_R (right-handed) components, respectively. At high energies they correspond to the eigenstates of the helicity operators $p \cdot \sigma$, as can be verified easily by using eqn (17.16) below.

The positive-energy solutions can be taken to be plane waves ($\alpha = 1, 2$):

$$\psi_\alpha(x) = u_\alpha(p) e^{-ip \cdot x}, \quad p \cdot x \equiv p^\mu x_\mu; \quad p^2 = m^2, \quad p^0 > 0;$$

where $u(p)$, for p directed along the third axis, is given by

$$u_\alpha(p) = \begin{pmatrix} \begin{pmatrix} \sqrt{E-p_3} & 0 \\ 0 & \sqrt{E+p_3} \end{pmatrix} \xi_\alpha \\ \begin{pmatrix} \sqrt{E+p_3} & 0 \\ 0 & \sqrt{E-p_3} \end{pmatrix} \xi_\alpha \end{pmatrix}, \quad \xi_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \xi_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (17.16)$$

Analogously, the negative-energy solutions are given by

$$\psi_\alpha(x) = v_\alpha(p) e^{+ip \cdot x}, \quad p \cdot x \equiv p^\mu x_\mu; \quad p^2 = m^2, \quad p^0 > 0;$$

where $v(p)$ is:

$$v_\alpha(p) = \begin{pmatrix} \begin{pmatrix} \sqrt{E-p_3} & 0 \\ 0 & \sqrt{E+p_3} \end{pmatrix} \eta_\alpha \\ -\begin{pmatrix} \sqrt{E+p_3} & 0 \\ 0 & \sqrt{E-p_3} \end{pmatrix} \eta_\alpha \end{pmatrix}, \quad \eta_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \eta_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (17.17)$$

These free Dirac spinors are normalized as

$$u_\alpha(p)^\dagger u_\beta(p) = 2 E_p \delta_{\alpha\beta}; \quad v_\alpha(p)^\dagger v_\beta(p) = 2 E_p \delta_{\alpha\beta}.$$

Remarks

- After all, Dirac's equation does have negative-energy solutions, just as the Klein-Gordon equation does: it is an unavoidable consequence of a relativistic equation (which can be traced back to the relativistic energy-momentum relation, eqn (17.13)). They cannot just be disposed of, as the completeness requires all four solutions, (17.16), (17.17).
- To make sense of the negative-energy solutions, Dirac proposed that the vacuum state is the one in which all negative-energy states are occupied, while those of positive energies are empty (Figure 17.1).

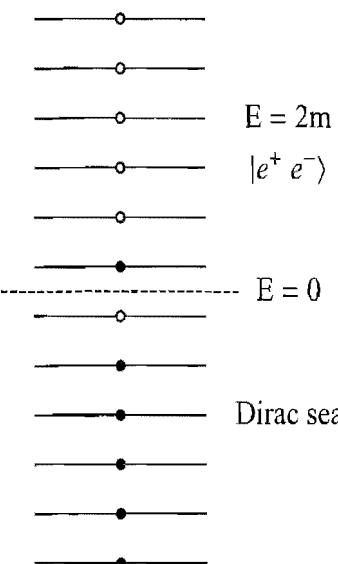


Fig. 17.3

- An excited state, e.g., a state with an electron–positron pair, corresponds to the state in which one negative level is empty and one positive energy level is occupied (Figure 17.3.)
The prediction of the existence of anti-particles for each elementary particle is one of the most important predictions of relativistic quantum mechanics.
- Dirac's equation, as it turned out, describes a relativistic spin- $\frac{1}{2}$ particle, such as the electron and proton, and as such, constitutes a fundamental building block of quantum electrodynamics as well as the standard model (the Glashow–Weinberg–Salam theory and quantum chromodynamics.)
- When the coupling to the external electromagnetic fields are appropriately taken into account by the minimal coupling, Dirac's equation (17.14) is modified to

$$[i\gamma^\mu (\partial_\mu - i\frac{e}{c}A_\mu) - m] \psi(x) = 0. \quad (17.18)$$

By systematically studying the $1/c$ expansion of this equation [Berestetskii, Lifshitz, and Pitaevskii (1980)] one ends up with the non-relativistic equation (Pauli's equation) for a two-component wave function $\psi^{(n.\text{rel})}$

$$i\frac{\partial}{\partial t}\psi^{(n.\text{rel})} = \left[\frac{(\mathbf{p} - \frac{e}{c}\mathbf{A})^2}{2m} + e\phi - \frac{e}{2mc}\sigma \cdot \mathbf{B} \right] \psi^{(n.\text{rel})}, \quad (17.19)$$

showing that the electron carries a gyromagnetic ratio $g = 2$ (it is twice what is classically expected from an orbital motion, but by taking into account the fact that the electron spin is $s = \frac{1}{2}$, we are back to the Bohr magneton). See Subsection 14.1.4, eqns (14.22), (14.23) and the side notes in that page for more discussions.

17.2.2 Quantization of the free Klein–Gordon fields

In the case of free electromagnetic fields, their quantization has already been considered in eqns (22.75) and (22.77) of Section 22.6. The corresponding step for the free Klein–Gordon and Dirac fields give the following. The action $S = \int dt L$ for the free Klein–Gordon field is

$$S = \frac{1}{2} \int d^4x [\partial_\mu \phi(x) \partial^\mu \phi(x) - m^2 \phi^2(x)], \quad (17.20)$$

where the quantized Klein–Gordon field (the analogue of the quantized electromagnetic field (22.75)) has the form

$$\phi(\mathbf{x}, t) = \int \frac{d^3\mathbf{p}}{(2\pi)^3} \frac{1}{\sqrt{2E}} [a_{\mathbf{p}} e^{-ip \cdot x} + a_{\mathbf{p}}^\dagger e^{ip \cdot x}], \quad p \cdot x \equiv p^0 t - \mathbf{p} \cdot \mathbf{x}, \quad (17.21)$$

where $p^0 = E \equiv \sqrt{\mathbf{p}^2 + m^2}$. The conjugate field momentum operator is

$$\pi(\mathbf{x}, t) = \frac{\delta L}{\delta \dot{\phi}(x)} = \frac{\partial \phi}{\partial t}.$$

The canonical commutation relation among the creation and annihilation operators

$$[a_{\mathbf{p}}, a_{\mathbf{p}'}^\dagger] = (2\pi)^3 \delta^3(\mathbf{p} - \mathbf{p}') \quad (17.22)$$

leads to the fundamental equal-time commutation relation for the field operators

$$[\phi(\mathbf{x}, t), \pi(\mathbf{x}', t)] = i \delta^3(\mathbf{x} - \mathbf{x}').$$

The Hamiltonian is given by

$$H = \int \frac{d^3 p}{(2\pi)^3} E_{\mathbf{p}} a_{\mathbf{p}}^\dagger a_{\mathbf{p}},$$

which is just the sum over independent harmonic oscillators. This is perfectly analogous to eqn (22.77) for the free electromagnetic fields.

17.2.3 Quantization of the free Dirac fields and the spin-statistics connection

In the case of the free Dirac field, the action is

$$S = \int d^4 x [\bar{\psi}(x)(i\gamma^\mu \partial_\mu - m)\psi(x)],$$

where $\bar{\psi} \equiv \psi^\dagger \gamma^0$ is the Dirac conjugate. The quantized free Dirac field takes the form

$$\psi(x) = \int \frac{d^3 \mathbf{p}}{(2\pi)^3 \sqrt{2E}} \sum_{\alpha=1,2} [a_{\mathbf{p}}^\alpha u_\alpha(\mathbf{p}) e^{-ip \cdot x} + b_{\mathbf{p}}^{\alpha\dagger} v_\alpha(\mathbf{p}) e^{ip \cdot x}],$$

where $u_\alpha(\mathbf{p})$, $v_\alpha(\mathbf{p})$ are the free Dirac spinors, eqns (17.16), (17.17); $a_{\mathbf{p}}$ is the annihilation operator of the electron; $b_{\mathbf{p}}$ is that of the positron. Note that the field operator $\psi(x)$ annihilates an electron and creates a positron, as these two operations change the quantum numbers of the state in the same way. Vice versa, the operator $\bar{\psi}(x) \equiv \psi^\dagger(x) \gamma_0$ creates an electron or destroys a positron. The creation and annihilation operators are required to satisfy the canonical *anti-commutation* relations

$$\left\{ a_{\mathbf{p}}^\alpha, (a_{\mathbf{p}'}^\beta)^\dagger \right\} = \left\{ b_{\mathbf{p}}^\alpha, (b_{\mathbf{p}'}^\beta)^\dagger \right\} = (2\pi)^3 \delta^3(\mathbf{p} - \mathbf{p}') \delta^{\alpha\beta}, \quad (17.23)$$

and

$$\left\{ a_{\mathbf{p}}^\alpha, a_{\mathbf{p}'}^\beta \right\} = \left\{ a_{\mathbf{p}}^\alpha, b_{\mathbf{p}'}^\beta \right\} = \left\{ b_{\mathbf{p}}^\alpha, b_{\mathbf{p}'}^\beta \right\} = 0,$$

and similarly for a^\dagger 's and b^\dagger 's. The vacuum state is defined by

$$a_{\mathbf{p}}^\alpha |0\rangle = b_{\mathbf{p}}^\alpha |0\rangle = 0, \quad \forall \alpha, \quad \forall \mathbf{p} :$$

the operators $a_{\mathbf{p}}^\alpha$ and $b_{\mathbf{p}}^\alpha$ annihilate the electron and the positron of the spin state (α), respectively, and $a_{\mathbf{p}}^{\alpha\dagger}$ and $b_{\mathbf{p}}^{\alpha\dagger}$ create them. Note that these particles are treated symmetrically: the Dirac sea is no longer required. The Hamiltonian is

$$H = \int \frac{d^3 p}{(2\pi)^3} E_{\mathbf{p}} \sum_{\alpha=1,2} [(a_{\mathbf{p}}^\alpha)^\dagger a_{\mathbf{p}}^\alpha + (b_{\mathbf{p}}^\alpha)^\dagger b_{\mathbf{p}}^\alpha],$$

where some infinite constant has been subtracted away so that the vacuum state has zero energy. All other states with non-vanishing number of electrons or positrons have positive energy.

A crucial point of this discussion is the introduction of the anti-commutation relations (17.23). They imply that an N -electron state

$$(a_{\mathbf{p}_1}^{\alpha_1})^\dagger (a_{\mathbf{p}_2}^{\alpha_2})^\dagger \dots (a_{\mathbf{p}_N}^{\alpha_N})^\dagger |0\rangle$$

is totally antisymmetric under exchanges of a pair of particles, as is required by Fermi–Dirac statistics. As $[(a_{\mathbf{p}_1}^{\alpha_1})^\dagger]^2 = 0$, no pairs of electrons can have the same quantum numbers (Pauli’s exclusion principle).

On the other hand, if a *commutation relation*

$$\left[a_{\mathbf{p}}^\alpha, (a_{\mathbf{p}'}^\beta)^\dagger \right] = \left[b_{\mathbf{p}}^\alpha, (b_{\mathbf{p}'}^\beta)^\dagger \right] = (2\pi)^3 \delta^3(\mathbf{p} - \mathbf{p}') \delta^{\alpha\beta}$$

were assumed, instead of the anti-commutation relations (17.23), to quantize the Dirac field, we would have ended up with a Hamiltonian,

$$H = \int \frac{d^3 p}{(2\pi)^3} E_{\mathbf{p}} \sum_{\alpha=1,2} [(a_{\mathbf{p}}^\alpha)^\dagger a_{\mathbf{p}}^\alpha - (b_{\mathbf{p}}^\alpha)^\dagger b_{\mathbf{p}}^\alpha],$$

⁷Vice versa, spin-integer particles are shown to obey Bose–Einstein statistics. The *spin-statistics connection* was derived by W. Pauli [Pauli (1940)].

which would have implied that the more we produce the particles, the less energy such a state would have. In other words the operator $b_{\mathbf{p}}^{\alpha\dagger} b_{\mathbf{p}}^\alpha$ could not have been interpretable as a number operator for the positron.

Thus Lorentz invariance and positivity of the energy of the physical states requires spin- $\frac{1}{2}$ particles to obey Fermi–Dirac statistics.⁷

17.2.4 Causality and locality

A fundamental principle which can only be appropriately formulated in the context of relativistic quantum field theory is *causality*. Use of the relativistic version of one-particle quantum mechanical equations, such as the Klein–Gordon or Dirac equations, does not in itself correctly introduce causality in quantum mechanics. Quite the contrary. In fact, consider the correlation function⁸

$$D(x - y) = \langle 0 | \phi(\mathbf{x}, t) \phi(\mathbf{x}', t') | 0 \rangle,$$

where $|0\rangle$ is the vacuum state. It can be easily seen to be equal to

$$\int \frac{d^3 p}{(2\pi)^3} \frac{1}{2E_{\mathbf{p}}} e^{-ip \cdot (x-y)}, \quad p \cdot x \equiv p^0 t - \mathbf{p} \cdot \mathbf{x}.$$

This function does not vanish when the two spacetime points x and y are separated by a spacelike distances, i.e.,

$$(x - y)^2 \equiv (t_1 - t_2)^2 - (\mathbf{x} - \mathbf{y})^2 < 0.$$

(In order to see this, it suffices to compute this at $t_1 = t_2$.) So it would appear that the particle created at the spacetime point y from

⁸This discussion closely follows that given in [Peskin and Schröder (1995)]

the vacuum is able to travel to another point x which is at a space-like separation!

Actually, in order to discuss causality, what matters is whether various events influence each other and under what conditions. We therefore study the commutator between the field operators

$$[\phi(x), \phi(y)] = \int \frac{d^3 p}{(2\pi)^3} \frac{1}{2E_p} \left[e^{-ip \cdot (x-y)} - e^{ip \cdot (x-y)} \right],$$

where eqns (17.21) and (17.22) have been used. Note that the commutator is a c-number. The exponent $\pm p \cdot (x-y)$ has a Lorentz-invariant form, and the integration measure $d^3 p / 2E_p$ is invariant under Lorentz transformations. Thus if $x-y$ is spacelike, i.e.,

$$(x-y)^2 \equiv (x_0 - y_0)^2 - (\mathbf{x} - \mathbf{y})^2 < 0,$$

it is always possible to make a Lorentz transformation to the frame where $x_0 - y_0 = 0$ and at the same time make an appropriate change of variables p having the form of the associated Lorentz transformation. In such a frame,

$$[\phi(x), \phi(y)] = \int \frac{d^3 p}{(2\pi)^3} \frac{1}{2E_p} \left[e^{ip \cdot (x-y)} - e^{-ip \cdot (x-y)} \right] = 0, \quad (17.24)$$

where in the last step we have made use of the (anti-)symmetry of the integrand under $\mathbf{p} \rightarrow -\mathbf{p}$. It turns out that the commutator vanishes for any spacelike separation,

$$[\phi(x), \phi(y)] = 0, \quad (x-y)^2 < 0;$$

it means that *the two events are causally unrelated*, if separated by a space-like distance. Vice versa, for time-like separations $x-y$ the above procedure is not available and we find that

$$[\phi(x), \phi(y)] \neq 0, \quad (x-y)^2 > 0.$$

When the discussion is generalized to the case of a charged scalar (with a complex scalar field) or a Dirac field, the same conclusion still holds, but it becomes manifest that the cancellation occurring for the spacelike separation (like the cancellation between the two terms of eqn (17.24)) is due to the cancellation between the contributions of the particle and the anti-particle. Thus the fact that in relativistic quantum field theory each particle is accompanied by an anti-particle with identical mass (but with opposite charges), discovered by Dirac and experimentally confirmed, is deeply related to causality.

Causality can also be seen from the fact that the physical amplitudes can be calculated by using Feynman's rules, such as the one mentioned in the next subsection for the case of simple self-interacting scalar particles, in which the particle propagations are expressed in terms of the causal (Feynman's) propagators which let the positive-energy states propagate in the forward time direction only.

On the other hand, the *locality* of the theory requires that all interaction Hamiltonians be local functions of space-time, i.e., field equations must contain only a finite number of derivatives with respect to x^μ . Such a requirement is indeed met by all presently known fundamental interactions in Nature: they are all described by a local interaction Lagrangian, $L_I(x)$, among point-like particles.

17.2.5 Self-interacting scalar fields

The quantized fields such as those introduced above must now be used in a nontrivial Lagrangian, containing interaction terms. The electron-positron field coupled minimally to the electromagnetic fields lead to quantum electrodynamics [Berestetskii, Lifshitz, and Pitaevskii (1980)], [Bjorken and Drell (1965)], a discussion of which would take us far beyond our scope here. Instead we shall illustrate the idea of interacting quantum fields by considering a self-interacting real scalar field, ϕ . The action is given by a slight generalization of eqn (17.20):

$$S = \int d^4x [\mathcal{L}_0 + \mathcal{L}_I],$$

where

$$\mathcal{L}_0 = \frac{1}{2} \partial_\mu \phi(x) \partial^\mu \phi(x) - \frac{1}{2} m^2 \phi^2(x); \quad \mathcal{L}_I = -\frac{g}{4!} \phi^4(x),$$

which is an analogue of the quartic anharmonic oscillator. We shall treat the $g\phi^4$ term as a perturbation.

A standard way to study the consequences of the theory is the canonical quantization procedure, starting with the construction of quantized fields as in the preceding subsection, and constructing the rules for perturbatively taking into account the interaction Hamiltonian and, by using Wick's theorem (see [Peskin and Schröder (1995), Weinberg (1989), Bjorken and Drell (1965)]) to construct n -point amplitudes.

Here we shall take an alternative route: Feynman's path integral quantization. Formally it is a natural generalization of the path integral method introduced in Chapter 8 for quantum mechanics. We first generalize the construction to the case of many particles $q(t) \rightarrow q_i(t)$, and then make a formal replacement

$$i \rightarrow \mathbf{x}; \quad q_i(t) \rightarrow \phi(\mathbf{x}, t), \quad \sum_i \rightarrow \int d^3x.$$

One ends up with the path integral (functional integral) for the generating functional

$$W[J] = \int \mathcal{D}\phi e^{i \int d^4x [\mathcal{L}_0 + \mathcal{L}_I + J\phi]},$$

where we have introduced the source $J(x)$, as in eqn (8.19). General n -point functions are given by the functional derivatives with respect to

the source

$$\begin{aligned} G(x_1, x_2, \dots, x_n) &= \langle 0 | T\{\phi(x_1)\phi(x_2)\dots\phi(x_n)\} | 0 \rangle \\ &= (-i)^n \left. \frac{\delta^n W}{\delta J(x_1) \dots \delta J(x_n)} \right|_{J=0}. \end{aligned}$$

Actually the procedure (8.17)–(8.19) can be straightforwardly generalized to the case of the ϕ^4 theory under consideration. The generating functional can be rewritten as

$$W[J] = e^{i \int d^4x \mathcal{L}_I \left(\frac{1}{i} \frac{\delta}{\delta J(x)} \right)} W_0[J],$$

but the free generating function is

$$\begin{aligned} W_0[J] &= \int \mathcal{D}\phi e^{i \int d^4x [\mathcal{L}_0 + J \phi]} = \int d\phi e^{i \phi \cdot K \cdot \phi + J \cdot \phi} \\ &= e^{\frac{i}{2} J \cdot K^{-1} \cdot J} \equiv e^{\frac{i}{2} \int d^4x d^4y J(x) K^{-1}(x,y) J(y)}. \end{aligned}$$

The two-point function⁹

$$D_F(x-y) = i K^{-1}(x,y) = \int \frac{d^4p}{(2\pi)^4} \frac{i}{p^2 - m^2 + i\epsilon} e^{-ip \cdot x} \quad (17.25)$$

is the (causal or Feynman) propagator.

Nontrivial amplitudes are calculated by using the functional derivatives $\frac{\delta}{\delta J(x)}$ and setting $J \equiv 0$ after that. We shall skip the derivation entirely; the result of analysis is summarized in *Feynman's rules* for computing the graphs.

- (i) Each vertex (Figure 17.4) gives a factor $i g$.
- (ii) Each propagator gives $D_F(x_1 - x_2)$ (Figure 17.5).
- (iii) For a given number of vertices (to a given order in g) draw all graphs combining vertices and propagators.
- (iv) Integrate over all x 's (interaction spacetime point).
- (v) Multiply by a factor $1/n!$ if there are n identical vertices.
- (vi) Count how many times a given graph arises.

⁹The reason why the path integrals defined with the particular (ϵ) prescription in the propagator gives rise to causal (or Feynman) Green functions, is the same as that already explained in Chapter 8 for quantum mechanics. See Subsection 8.2.4 in particular.

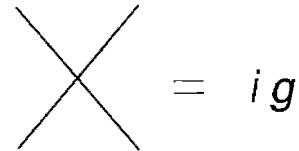


Fig. 17.4

$$\overline{x_1} \qquad x_2 = D(x_1 - x_2)$$

Fig. 17.5

17.2.6 Non-Abelian gauge theories: the Standard Model

Dirac fields (for spin- $\frac{1}{2}$ particles), scalar fields (spinless particles), and vector (gauge) fields are the building blocks of the standard model of fundamental interactions. Two more ingredients were however needed: the idea of non-Abelian gauge symmetry (the Yang–Mills theory) and spontaneously broken gauge symmetry (the so-called Higgs mechanism). Only the appropriate understanding of these theoretical ingredients, matured before 1970, allowed theoretical physicists to construct what is today known as the standard model of fundamental interactions. The Glashow–Weinberg–Salam electroweak theory [Weinberg (1967), Salam

(1968), Glashow, Iliopoulos and Maiani (1970)] is a gauge theory of quarks and leptons, based on the gauge group

$$SU_L(2) \times U(1) ,$$

under which quarks and leptons are charged in definite ways (see the tables in Chapter 24). It contains within it quantum electrodynamics, constructed earlier, and generalizes it. Strong (nuclear) interactions bind quarks (and gluons) and anti-quarks into nucleons, pions, and other hadrons. For instance,

$$|P\rangle \sim |uud\rangle, \quad |N\rangle \sim |udd\rangle. \quad |\pi^+\rangle \sim |u\bar{d}\rangle, \quad |\pi^-\rangle \sim |\bar{u}d\rangle,$$

where u, d are the up and down quarks, \bar{d} the anti- d -quark, and so on. Strong interactions are described by a gauge theory with the gauge group $SU(3)$ (color) group—known as quantum chromodynamics [Fritzsch, Gell-Mann, and Leutwyler (1973)]. The strong interactions are mediated by the $SU(3)$ -octet gluons, which are non-Abelian analogues of the photon. Analogously W, Z bosons, together with the photon, mediate the electroweak forces. We shall refrain here even from writing down the Lagrangean density for the $SU(3)_{\text{color}} \times SU_L(2) \times U(1)$ theory: any tiny step to derive their consequences and predictions would require an unreasonable amount of space, and at the same time would bring us far beyond the scope of this book. A nice introduction to the ideas of the standard model is a book [Taylor (1976)] and a review article [Abers and Lee (1973)].

Further reading

The limitation of space did not allow us to go into the discussion of general nuclear structure at all. See the books [Bohr and Mottelson (1969)], [Bohr and Mottelson (1975)].

In the second half of this chapter, we tried to give a flavor of what is needed in the description of elementary particles: the necessary framework (relativistic quantum field theory) is so different from what is used in atomic, molecular or nuclear physics.

On the other hand, being a system of infinite degrees of freedom, a remarkable set of theoretical ideas and techniques, common to elementary particle physics and quantum condensed matter physics (critical phenomena, superconductivity and superfluidity, the quantum Hall effect, Bose–Einstein condensation) have emerged and been developed since around 1970. Some of the main ideas involved are scale invariance, the renormalization group,

quantum solitons and topological excitations. The work by K. Wilson played a pioneering role [Wilson (1974)]. The book [Zinn-Justin (1989)] is indeed about both research fields. For earlier standard introductions to relativistic quantum field theory, see [Berestetskii, Lifshitz, and Pitaevskii (1980)], [Bjorken and Drell (1965)], [Bogoliubov and Shirkov (1959)]. For a more modern introduction to quantum field theory and to the standard model, the reader is referred to the books [Itzykson and Zuber (1980)], [Weinberg (1989)], [Peskin and Schröder (1995)] (earlier references and books can be found there). See also [Maggiore (2005)] for a more compact introduction. Extraordinary series of lectures on the non-Abelian gauge theories can be found in [t’Hooft and Veltman (1977), t’Hooft (1980)].

A recent development in certain two-dimensional crystals shows an unexpected area of application of the *rel-*

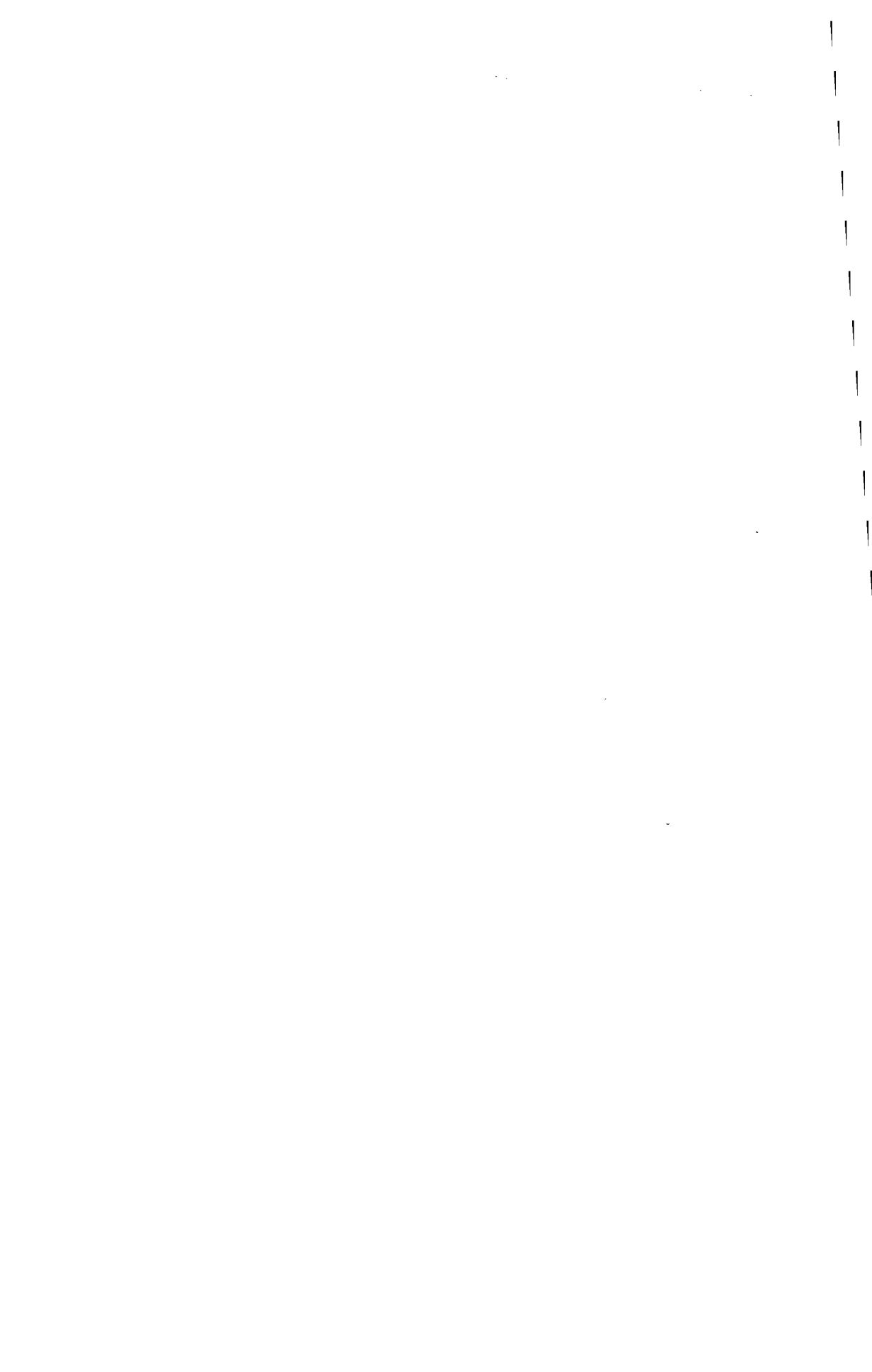
ativistic Dirac equation and related concepts. The so-called graphene, atom-thick carbon two-dimensional crystal, discovered in 2004, is getting considerable attention both from theoretical points of view and for possible applications for their remarkable properties. In a sense they are the same “building sheet” for the zero-dimensional buckminster fullerene (bucky balls) and one-dimensional

carbon nano tubes. The electrons near the particular edges of the Brillouin zones of the graphenes turn out effectively to be described by a three-dimensional (two space and one-time) relativistic massless Dirac equation [Semenoff (1984), Fradkin (1986), Geim and Novoselov (2007), Geim and MacDonald (2007)!]. See also the book [Ezawa (2008)].



Part IV

Entanglement and Measurement



There are two issues which are ubiquitous and indeed fundamental in most applications of quantum mechanics: *quantum entanglement* and *measurement* (probabilistic interpretation). Even though these two aspects of quantum mechanics are logically independent of each other, they are (too?) often discussed in a mixed manner in the analysis of one and the same problem. The fact is, quantum entanglement often looks very surprising, sometimes even paradoxical because of the probabilistic aspect of quantum mechanical prediction. Vice versa, in the physical process of measurement, entanglement between the micro-system which is the subject of the observation and the macroscopic system—apparatus—is the first step. Nevertheless, it is helpful in clarifying the matter, to try to separate as much as possible the first, which is one of the most elegant and important consequences of quantum mechanics, from the second, which involves deep but basically unsolved problems of the interpretation of quantum mechanics.

18

Quantum entanglement

Two or more particles which have interacted in the past, may in general maintain nontrivial quantum mechanical correlations, described by non-factorized wave functions. These correlations, under optimal conditions, can manifest themselves no matter how far they travel away from each other and even when the separate parts cannot dynamically influence each other, leading to apparently paradoxical situations. These correlations are known as *quantum entanglement*. However counter-intuitive and surprising it may sometimes look, it is rather one of the more beautiful and experimentally well established predictions of quantum mechanics.

18.1 The EPRB <i>Gedankenexperiment</i> and quantum entanglement	503
18.2 Aspect's experiment	508
18.3 Entanglement with more than two particles	511
18.4 Factorization versus entanglement	512
18.5 A measure of entanglement: entropy	514
Further reading	516

18.1 The EPRB *Gedankenexperiment* and quantum entanglement

The fact that a composite quantum mechanical system in general necessarily exhibits a characteristic correlation of experimental outcomes relating the separate parts was known from the early days of quantum mechanics. This aspect, however, was forcefully brought into question by Einstein and others [Einstein, Podolsky, and Rosen (1935)], as something implying that quantum mechanics, as it was, was an incomplete theory. Although their conclusion was a little too hasty, their argumentation (which is often referred to as the EPR “paradox”) nicely focuses on the two essential aspects of quantum mechanics: entanglement¹ and the probabilistic nature of quantum mechanical predictions.

Consider a system composed of two subsystems A and B , described by a wave function

$$\Psi(x, q) = \sum_n \psi_n(x) \tilde{\phi}_n(q), \quad (18.1)$$

where x and q are respectively the variables in subsystems A and B . ψ_n are (normalized) eigenstates of some observable F of A , with eigenvalues f_n . As $\Psi(x, q)$ considered as a function of x can always be expanded in terms of the complete set $\{\psi_n\}$ of F , eqn (18.1) generally holds, $\tilde{\phi}_n(q)$ being just the expansion coefficients. It is, however, possible, even though not necessary, that $\tilde{\phi}_n(q)$ also happens to be eigenstates of an observable G of the system B , with eigenvalues g_{α_n} . Let us assume that this is indeed the case (that this is possible will be shown below), and

¹The term *entanglement* was coined by Schrödinger in his reply [Schrödinger (1935)] to the EPR paper.

rewrite the above as

$$\Psi(x, q) = \sum_n c_n \psi_n(x) \phi_{\alpha_n}(q), \quad (18.2)$$

where $\phi_{\alpha_n}(q)$ are the normalized eigenfunctions of G , and $\tilde{\phi}_n(q) = c_n \phi_{\alpha_n}(q)$. For simplicity, let us assume that these eigenvalues are discrete and non-degenerate.

When an experiment is done at A to measure F , it will register one of its eigenvalues, for instance, f_n . The state would then be reduced to

$$|\psi_n\rangle |\phi_{\alpha_n}\rangle,$$

and as a consequence, the measurement of G at B , made *immediately after* the measurement at A , is predicted to give *with certainty* the result g_{α_n} . Note that this occurs however distant the two sites A and B may be, and more precisely, even if the two measurement events occur at a *spacelike* separation so that the two experiments cannot causally influence each other.

This does appear to contradict the statistical nature of quantum mechanical prediction for the observer at B ! In most books on the subject one embarks at this point on an elaborate discussion about where the contradiction may lie, how the “problem” might be solved by the introduction of some auxiliary variables (so-called hidden variables) complementing the wave function description of standard quantum mechanics, and how this does not really work, and so on. Let us, however, leave aside for the moment the uneasy feeling each of us might no doubt experience (to various degrees) thinking about this kind of process. We shall come back to these questions in the next chapter (Section 19.3.1).

Let us, for now, only note that there are actually no contradictions, neither with the locality of fundamental interactions nor with the principle of causality, at this stage. Just as the experiment done at A cannot dynamically influence another, distant experiment at B , neither can the *information* about the result at A reach site B before the experiment is done there. What quantum mechanics tells us is simply that if the two sequences of the experimental outputs, event by event, are recorded at both sides and collected, and brought together sometime later to a common site and compared, they are predicted to obey a precise *correlation*, such as in Table 18.1. These correlations can be verified experimentally *a posteriori*. Note that the precise chronological ordering of the two measurements (which is a delicate matter in special relativity; also, there is no way of knowing which was the first, anyway, for the experimentalists at the moments of their measurements) is immaterial. Of course, the experimental timing control (coincidence check) must be good enough to ensure that each pair of the outcomes refer to one and the same event.

Let us come back to our hypothesis in eqn (18.2) that both of the state vectors appearing in the expansion are eigenvectors of some operators, F (of A) and G (of B). In an example discussed in the EPR paper, the system is composed of two particles “at distance x_0 ”, described by the

sites \ experiments	1	2	...	n	...
A	f_2	f_5	...	f_3	...
B	g_{α_2}	g_{α_5}	...	g_{α_3}	...

Table 18.1

wave function

$$\Psi(x, q) = \int dp e^{ip(x-q+x_0)/\hbar} = 2\pi\hbar \delta(x - q + x_0). \quad (18.3)$$

If the experimentalist at A measured the momentum, with a result $p = P$, then it implies that the experimentalist at B would find the system in a momentum eigenstate with eigenvalue $-P$ (and vice versa!). If, on the other hand, the position was measured at A with the result $x = X_A$, then the system at B would also be found in a position eigenstate, $\psi_B \sim \delta(q - X_A - x_0)$, i.e., with particle 2 certainly² at $q = X_A + x_0$.

A pair of entangled spin- $\frac{1}{2}$ particles

In a more commonly discussed example of an EPR-like experiment considered by Bohm (hence the name EPRB), which has since become the prototype process for the discussion of quantum entanglement, the system is composed of two spin- $\frac{1}{2}$ particles forming the total-spin-singlet state

$$|\Psi_0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2), \quad (18.4)$$

where $|\uparrow\rangle_1$ is the eigenstate of the first spin with $s_{1z} = +\frac{1}{2}$, etc. Such a situation can clearly be realized as a real experiment, by studying a two-body decay of a spinless parent particle (nucleus, atom, etc.). (Analogous experiments can be made with two photons in the final state; see below.) Suppose that the two particles are far away, or flying away from each other, so that the experiment at A cannot dynamically influence the one at B . The components of the two spins are going to be measured by two Stern-Gerlach setups, at sites A and B .

If the magnets are aligned parallel (e.g., both in the z direction), the experimental outputs at the two sites will be exactly and oppositely correlated, as in Table 18.2. Even though, as in the EPR case, one may argue that there is something mysterious or fishy in the (purportedly) instantaneous implication of one result on the other, the precise correlation event by event as in the table is a straightforward prediction of quantum mechanics, confirmed by experiments. The details of the chronological order of the two “simultaneous” experiments are immaterial, as long as the two measurements refer to the same elementary event, and do not erroneously pair up results from two different decay events.

²There is nothing mysterious about these results in themselves: the state (18.3) is an eigenstate of the relative position operator (with eigenvalue, x_0) as well as of the total momentum operator P_{tot} (with eigenvalue 0). The two operators commute.

sites \ measurements	1	2	3	4	...	n	...
Magnet A in \hat{z}	\uparrow	\uparrow	\downarrow	\uparrow	...	\downarrow	...
Magnet B in \hat{z}	\downarrow	\downarrow	\uparrow	\downarrow	...	\uparrow	...

Table 18.2

sites \ measurements	1	2	3	4	...	n	...
Magnet A in \mathbf{a}	\uparrow	\uparrow	\downarrow	\downarrow	...	\uparrow	...
Magnet B in \mathbf{b}	\downarrow	\uparrow	\uparrow	\uparrow	...	\uparrow	...

Table 18.3

Note that if one of the observers (say, at B) were never to be aware of the experiments done at the far site (A), the system would present itself to her (or him) as a mixed state³, described by a density matrix⁴

$$\rho = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},$$

and she would observe half of the time spin-up, the other half of the time spin-down, in perfect agreement with the quantum mechanical prediction.

Entanglement looks subtler if the two distant magnets are aligned in arbitrary directions, \mathbf{a} and \mathbf{b} , where $\mathbf{a}^2 = \mathbf{b}^2 = 1$. In this case, the registration of the measurements of the spin components may look like the one in Table 18.3 with no obvious correlation between the two sequences. In preparation for the discussion in the next section, let us denote the individual outcomes of the measurement of $2\mathbf{s}_1 \cdot \mathbf{a}$, $2\mathbf{s}_2 \cdot \mathbf{b}$ at the two sites, as $R(\mathbf{a})$, $R(\mathbf{b})$, which take values ± 1 . In spite of the apparent randomness of the sequences in Table 18.3, quantum mechanics makes a precise prediction that the average (over many repeated experiments)

$$F(\mathbf{a}, \mathbf{b}) = \overline{R(\mathbf{a})R(\mathbf{b})}$$

be given by the expectation value of the corresponding operator product:

$$F^{(QM)}(\mathbf{a}, \mathbf{b}) = \langle \Psi_0 | (\sigma^{(1)} \cdot \mathbf{a}) (\sigma^{(2)} \cdot \mathbf{b}) | \Psi_0 \rangle = -\cos \theta_{\mathbf{a}, \mathbf{b}}, \quad (18.5)$$

where $\mathbf{s}_1 = \frac{1}{2}\sigma^{(1)}$, $\mathbf{s}_2 = \frac{1}{2}\sigma^{(2)}$ and θ is the angle between the two unit vectors: $\cos \theta_{\mathbf{a}, \mathbf{b}} = \mathbf{a} \cdot \mathbf{b}$.⁵ Thus the sum of the product of signs plus (for \uparrow) and minus (for \downarrow) of the two sites, in the experimental sequences such as in Table 18.3, must average out to give $-\mathbf{a} \cdot \mathbf{b}$. Again, this prediction of

³In Schrödinger's original phrasing, *Maximal knowledge of a total system does not necessarily include total knowledge of all its parts, not even when these are fully separated from each other and at the moment are not influencing each other at all* [Schrödinger (1935)].

⁴Exercise. Show this.

⁵Exercise. Prove this.

quantum mechanics has been repeatedly confirmed experimentally (see below).

A pair of photons with entangled polarizations

Entanglement can be studied in an entirely analogous fashion by using a pair of photons in the final state. Consider an atom in an excited state with $J = 0$, which decays through two successive electric dipole transitions,

$$|J=0\rangle \rightarrow |J=1\rangle \rightarrow |J=0\rangle,$$

known as an atomic SPS cascade. If the two photons are observed in opposite directions, they will have the same polarization. Indeed, as both the initial and final atomic states are rotationally invariant, so must be the state of the two photons. If

$$|x\rangle|x\rangle, \quad |x\rangle|y\rangle, \quad |y\rangle|x\rangle, \quad |y\rangle|y\rangle,$$

are the four possible polarization states of the pair, only two of them

$$\psi_+ = \frac{|x\rangle|x\rangle + |y\rangle|y\rangle}{\sqrt{2}}, \quad \psi_- = \frac{|x\rangle|y\rangle - |y\rangle|x\rangle}{\sqrt{2}},$$

are invariant under rotations around the z axis (the direction of the photon momenta). Taking into account the parity invariance of the electromagnetic interactions also, we are left with only the first state,

$$\psi_+ = \frac{|x\rangle \otimes |x\rangle + |y\rangle \otimes |y\rangle}{\sqrt{2}} \quad (18.6)$$

describing the final state of the photons.

The polarization measurement and its possible outcomes are described by the projection operators

$$P_1 = |x\rangle\langle x| = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad (18.7)$$

which refers to the linear polarization in the x direction, with the possible result 1 or 0 (see eqn (7.71)) and

$$P_2 = |y\rangle\langle y| = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}, \quad (18.8)$$

which gives the yes–no answer for the linear polarization in the y direction. Alternatively, one may use a more general projection operator

$$P_\theta = (|x\rangle \cos \theta + |y\rangle \sin \theta)(\langle x| \cos \theta + \langle y| \sin \theta) = \begin{pmatrix} \cos^2 \theta & \cos \theta \sin \theta \\ \cos \theta \sin \theta & \sin^2 \theta \end{pmatrix}, \quad (18.9)$$

corresponding to linear polarization in the direction $\mathbf{a} = (\cos \theta, \sin \theta, 0)$. Experimentally the “yes” answer means that the photon passes, and the “no” answer corresponds to the photon which does not pass (recall Section 2.1.2). Thus the counting of the photons arriving at the counter

per total number of photons is to be compared with the expectation value of the operator P .

In order to have a formal analogy to the spin- $\frac{1}{2}$ cases, we furthermore introduce associated operators

$$\Sigma_\theta \equiv 2P_\theta - 1 = \begin{pmatrix} \cos 2\theta & \sin 2\theta \\ \sin 2\theta & -\cos 2\theta \end{pmatrix},$$

which have eigenvalues, ± 1 : these are analogues of the operator $\sigma \cdot \mathbf{a}$ in the spin- $\frac{1}{2}$ case.

Again, if the two (distant) observers measured the same polarization, e.g., Σ_1 , the two registrations would show a perfect correlation, e.g.,

$$A : (+ - - + - + \dots) \quad \text{vs} \quad B : (+ - - + - + \dots).$$

The same would hold if the two polarization measurements referred to the same but generic direction $\mathbf{a} = (\cos \theta, \sin \theta, 0)$. If, instead, the two experimentalists measure the polarization in two generic directions,

$$A : \mathbf{a} = (\cos \theta, \sin \theta, 0) \quad B : \mathbf{b} = (\cos \theta', \sin \theta', 0),$$

then the recordings at the two sites will show two sequences which may not exhibit any obvious correlation. Consider in particular, as in the spin- $\frac{1}{2}$ EPRB experiment, the correlation function

$$F(\theta, \theta') \equiv F_{\mathbf{a}, \mathbf{b}} = \overline{R(\Sigma_\theta)R(\Sigma_{\theta'})}, \quad (18.10)$$

where $R(\Sigma_\theta) = \pm$ stands for the measurement output for each photon. The prediction of quantum mechanics for this quantity is

$$F^{(QM)}(\theta, \theta') = F_{\mathbf{a}, \mathbf{b}}^{(QM)} = \langle \psi_+ | \Sigma_\theta \otimes \Sigma_{\theta'} | \psi_+ \rangle = \cos 2(\theta - \theta'), \quad (18.11)$$

as can easily be found by computing the expectation value of the operator $\Sigma_\theta \otimes \Sigma_{\theta'}$ in state (18.6).⁶

⁶Exercise. Show eqn (18.11)).

18.2 Aspect's experiment

A beautiful experiment verifying quantum entanglement, eqns (18.5), (18.11), has been performed by Aspect and others [Aspect, Dalibard, and Roger (1981)].

The setup of their experiment is schematically illustrated in Figure 18.1. Two photons, of wavelengths $\lambda = 422.7$ nm and $\lambda = 551.3$ nm from an SPS cascade of calcium atoms are sent to two distant polarizers (PM1 and PM2), ~ 12 m apart. For each photon pair PM1 and PM2 simultaneously measure the linear polarization in two different directions. The measured average value of $R(\Sigma_\theta)R(\Sigma_{\theta'})$ (Figure 18.2) shows the predicted cosine dependence (18.11) clearly.

The most extraordinary feature of the experimental setup of [Aspect, Dalibard, and Roger (1981)], however, is the following. At the end of

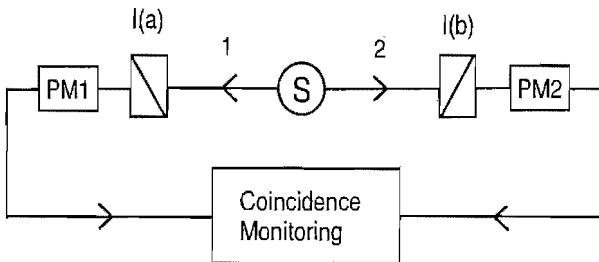


Fig. 18.1

each arm there are two polarizers, in the directions a, a' on the one side and b, b' , on the other. Now optical-acoustic switches set just before the polarizers randomly direct the photons to each side, to one of the polarizers. As the time scale of the alternations of the switch (about 10 ns), as well as the internal time during the SPS cascade (about 5 ns), are both much shorter than the time of flight between the atom and the polarizers (40 ns), it can be reasonably argued that at the time of "birth" of the photon pair, the direction of the linear polarizers is not even yet decided.⁷ Thus the polarization measurements truly occur "simultaneously" at a spacelike separation, the experimental "apparatus setup" having no possibility of influencing the quantum state to be measured. The correlation between the photon polarization at the far ends, indeed has a non-local character.

Such a precaution might appear not to be strictly indispensable, if the experiment is considered just one of the tests of quantum mechanics. Nevertheless, such care was regarded as crucial if this experiment were conceived (as was indeed the case) as a test discriminating quantum mechanics from so-called local hidden-variable theories, in which *each* single experimental output is uniquely predetermined by specifying some statistical, classical variable (even if unknown to us). As will be discussed more extensively in the next chapter, such alternative theories with dispersion-free states lead to a wide class of relations, the most celebrated among them being Bell's inequalities [Bell (2004)]. In the context of the present two-photon experiment, a particular combination of $F_{a,b}$ of eqn (18.10)

$$S \equiv \frac{1}{4} (F_{a,b} - F_{a,b'} + F_{a',b} + F_{a',b'} - 2)$$

satisfies an inequality, known as the CHSH (Clauser–Horne–Shimony–Holt) inequality [Clauser, et. al. (1969)] in hidden-variable theories (for the proof, see eqn (19.22) in the next chapter),

$$-1 \leq S^{(\text{hidd.var.})} \leq 0, \quad (18.12)$$

⁷This way of setting up the experiments has become known as a "delayed-choice experiment".

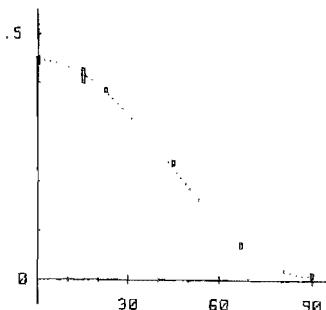


Fig. 18.2 Experimental verification of the quantum mechanical prediction, eqn (18.11), from [Aspect, Dalibard, and Roger (1981)]. The curve is not a fit but the prediction of quantum mechanics, with experimental corrections for the polarimeter efficiency taken into account. Analogous experimental confirmation of eqn (18.11) in their first experiment was actually of much better quality, being based on higher statistics, even though no "delayed-choice" setting was made. See [Aspect, Grangier, and Roger (1981)].

while quantum mechanics predicts (see eqn (18.11)):

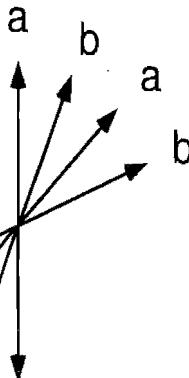


Fig. 18.3

$$S^{QM} = \frac{1}{4} [\cos 2(\theta_a - \theta_b) - \cos 2(\theta_a - \theta_{b'}) + \cos 2(\theta_{a'} - \theta_b) + \cos 2(\theta_{a'} - \theta_{b'}) - 2].$$

With their polarization angles chosen to maximize the quantum mechanical prediction (so that the discrimination is as high as possible), with 22.5° between the vectors (see Figure 18.3), their experimental result is

$$S^{(exp)} = 0.101 \pm 0.020,$$

to be compared with the quantum mechanical prediction (taking into account the experimental solid-angle and polarizer efficiencies)

$$S^{QM} = 0.112$$

and with the CHSH inequality (18.12). The experiment clearly confirms the validity of quantum mechanics, and rules out hidden-variable theories.

Energy-entangled photon pairs

In a series of elegant experiments Chiao and others [Chiao, et.al. (1995), Chiao (1993)] used energy-entangled photon pairs,

$$|2\text{ photons}\rangle = \int dE_1 \int dE_2 A(E_1, E_2) \delta(E_0 - E_1 - E_2) |E_1\rangle |E_2\rangle,$$

arising from a so-called parametric down-conversion of a parent photon through a non-linear crystal (a process in which the parent photon is effectively “split” into two photons, via a non-linear response of the crystalline polarization). If the energy (the color) of one of the photons is measured, with energy $E = h\nu$, the energy of the other photon is instantaneously deduced to be equal to $E_0 - E$, just as in the EPR *Gedankenexperiment* (but this is a true experiment, not hypothetical). In close analogy to the original EPR example of the entangled state (18.3), here in the two-photon state the total energy as well as the relative time of emission have well-defined values.

In one (the so-called Franson-type) experiment, two such correlated photons are sent to two distant, separate Mach-Zehnder interferometers. The differences in the two path lengths (long and short) in each Mach-Zehnder interferometer are much larger than the coherence length of the light, and thus no single photon interference is observed. Instead, two-photon interference has been measured, confirming the quantum mechanical prediction for the coincident two photon detection,

$$P = |1 \cdot 1 - e^{i\phi_1} e^{i\phi_2}|^2 = 2(1 - \cos(\phi_1 + \phi_2)),$$

where ϕ_1 (ϕ_2) is the phase difference between the photon which has traveled the long and short paths in arm 1 (arm 2). Again, by combining

four different experimental settings (four different choices of $\phi_1 + \phi_2$) one can study the CHSH inequality (which would be valid in a hidden-variable theory). For carefully chosen experimental settings, the latter is shown to be violated in quantum mechanics, and indeed, also by the experimental data [Chiao, et.al. (1995)].

18.3 Entanglement with more than two particles

Analogous considerations and experiments can be made by using a system with more than two particles. An interesting example is the one considered by Mermin, to illustrate more sharply the mysterious (apparently paradoxical) feature of quantum mechanical entanglement. It describes three spin- $\frac{1}{2}$ particles in the state

$$|\Psi_M\rangle = \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \frac{1}{\sqrt{2}}(|\uparrow\rangle|\uparrow\rangle|\uparrow\rangle - |\downarrow\rangle|\downarrow\rangle|\downarrow\rangle), \quad (18.13)$$

where again the space part of the wave function might describe the three particles receding from each other (such could be the case if the three particles are the decay product of some parent particle) each pair being separated by a spacelike distance. Let us consider four product operators,

$$M_1 = \sigma_{1x} \sigma_{2y} \sigma_{3y}, \quad M_2 = \sigma_{1y} \sigma_{2x} \sigma_{3y}, \quad M_3 = \sigma_{1y} \sigma_{2y} \sigma_{3x},$$

and

$$M_4 = \sigma_{1x} \sigma_{2x} \sigma_{3x}.$$

The operators M_1, \dots, M_4 commute with each other.⁸ A remarkable property of state (18.13) is that it is a simultaneous eigenstate of all four operators M_i :

$$M_1 |\Psi_M\rangle = M_2 |\Psi_M\rangle = M_3 |\Psi_M\rangle = |\Psi_M\rangle, \quad (18.14)$$

while

$$M_4 |\Psi_M\rangle = -|\Psi_M\rangle, \quad (18.15)$$

as can be easily seen from the fact that σ_x or σ_y flips one of the spins.⁹ Now consider performing simultaneous measurements of commuting operators σ_{1x} , σ_{2y} and σ_{3y} . Each of the measurements will yield ± 1 as a result: let us call them m_{1x} , m_{2y} , m_{3y} , respectively. But because of relation (18.14), the triplet of the outcomes must satisfy

$$m_{1x} m_{2y} m_{3y} = 1. \quad (18.16)$$

Thus if for instance m_{1x} and m_{2y} turn out to be -1 , this would imply, instantaneously, that the third experiment will give the result $+1$ with certainty! Again, this would appear to violate either the quantum mechanical (statistical) prediction, or some principles such as locality or

⁸Exercise. Show this.

⁹Exercise. Show eqns (18.14), (18.15)).

causality—let us, however, leave this apparent paradox to the discussion in the next chapter.

Similarly, other triple experiments,

$$[\sigma_{1y} \sigma_{2x} \sigma_{3y}], \quad [\sigma_{1y} \sigma_{2y} \sigma_{3x}], \quad [\sigma_{1x} \sigma_{2x} \sigma_{3x}],$$

will give results such that

$$m_{1y} m_{2x} m_{3y} = 1, \quad (18.17a)$$

$$m_{1y} m_{2y} m_{3x} = 1, \quad (18.17b)$$

$$m_{1x} m_{2x} m_{3x} = -1. \quad (18.17c)$$

As each of the m 's take only values ± 1 , and because of the crucial minus sign in eqn (18.17c), relations (18.16)–(18.17) are mutually incompatible! Is quantum mechanics inconsistent?

Actually, we have been a little too hasty in jumping to a wrong conclusion. We incorrectly regarded m_{3y} appearing in eqn (18.16) and in eqn (18.17a) as the same and identical number, but this is not at all guaranteed. The point is that the triple measurement 1 (which gives m 's satisfying eqn (18.16)) and a triple experiment 2 (which gives m 's satisfying eqn (18.17a)), for instance, cannot be performed at the same time, *in spite of* the fact that the operators M_1 and M_2 commute. As $[\sigma_{1x}, \sigma_{1y}] \neq 0$, the experimentalist at site 1 cannot measure them simultaneously¹⁰.

In other words, relations (18.16)–(18.17c) refer to four different events. There is no inconsistency whatsoever among them, and quantum mechanics correctly predicts eqns (18.16)–(18.17c), for the outcome of *each* triple measurement.

The discussion can be straightforwardly generalized to the case of more than three entangled particles, for instance, to the case of N spin- $\frac{1}{2}$ particles in the state [Mermin (1990), Peres (1995)],

$$|\Psi_N\rangle = \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \frac{1}{\sqrt{2}}(|\uparrow\rangle|\uparrow\rangle\dots|\uparrow\rangle - |\downarrow\rangle|\downarrow\rangle\dots|\downarrow\rangle). \quad (18.18)$$

18.4 Factorization versus entanglement

Entanglement is a very general feature of quantum mechanics, as all subsystems in the universe do interact or have interacted with each other in the past, to various degrees. If a part has never interacted with the rest of the universe and will never interact with it, then such a part for all purposes stays outside our universe, and it is of purely philosophical interest to talk about them: no theory or prediction about them could be tested against experimental tests, which will necessarily involve significant entanglement between the system observed and those parts of the world.

It is thus quite extraordinary that the assumption of *factorization* works so well in general, and that many systems can be rather precisely described by using a few-body Hamiltonian, such as the one for the

¹⁰Indeed, all operators M_1, \dots, M_4 of eqns (18.16)–(18.17c) commute with each other. Nevertheless, observation of such composite variables, each of which requires more than one “simultaneous” measurement taking place in different sites, cannot be simultaneously performed, in contrast to the standard lore of quantum mechanics (i.e., commuting operators correspond to compatible observables). This state of affair lies in the heart of the generalization of the measurement concept from projection-operator-valued measurements (*PVM*) to positive-operator-valued-measurements (*POVM*), as will be discussed in the next chapter.

hydrogen atom, neglecting the rest of the world. For example, due to Fermi-Dirac statistics the wave function of more than one identical fermion must be totally antisymmetric under exchange of the particles—electrons—and thus a factorized wave function such as

$$\Psi = \psi_{100,\uparrow}^{(\text{hydrogen})} \cdot \Xi_{\text{the rest}}(\xi_1, \xi_2, \dots)$$

can never be, strictly speaking, correct. In the case of two electrons, for instance, the wave function must be totally antisymmetric under the exchange of the two particles. However, if the electrons are far apart (one in the laboratory (L), the other on the moon (M), for instance) their interactions are so weak that the system may be described by a separable Hamiltonian, $H = H_1 + H_2$, and the states may be approximated by an (anti-symmetrized) product of wave functions of the form

$$|\Psi\rangle = |p_1\rangle^{(1)}|p_2\rangle^{(2)} - |p_2\rangle^{(1)}|p_1\rangle^{(2)}$$

where p_1 and p_2 are single-particle states of the two electrons. For instance $p_1 = (L, \uparrow)$, $p_2 = (M, \downarrow)$, where L and M stand for the spatial wave functions with support in the laboratory and in some region on the moon, respectively. In the coordinate-spin representation, the wave function is

$$\Psi = \frac{1}{\sqrt{2}} [\psi_L(\mathbf{r}_1)|\uparrow\rangle \otimes \psi_M(\mathbf{r}_2)|\downarrow\rangle - \psi_M(\mathbf{r}_1)|\downarrow\rangle \otimes \psi_L(\mathbf{r}_2)|\uparrow\rangle]. \quad (18.19)$$

It is clear then that in studying the first electron (\mathbf{r}_1) in the laboratory, one finds that the second term of eqn (18.19) is utterly negligible and the wave function has an approximately factorized form,

$$\Psi \simeq \psi_L(\mathbf{r}_1)|\uparrow\rangle \otimes \psi_M(\mathbf{r}_2)|\downarrow\rangle,$$

where the irrelevant normalization constant has been dropped. For all purposes, one can work with the wave function

$$\tilde{\Psi} \simeq \psi_L(\mathbf{r}_1)|\uparrow\rangle,$$

as long as our study is restricted to a small region in the laboratory (Figure 18.4).

The situation is entirely different when the two spin- $\frac{1}{2}$ particles arise as S -wave decay products of a spinless parent system at rest ($\mathbf{J} = 0$). Such a pair is described by a wave function of the form

$$\Psi = \psi_0(\mathbf{r}) (|\uparrow\rangle \otimes |\downarrow\rangle - |\downarrow\rangle \otimes |\uparrow\rangle), \quad (18.20)$$

where $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ is the relative position of the pair, and $\psi_0(\mathbf{r})$ is an expanding wave, for instance,

$$\psi_0(r) \sim \frac{e^{ikr}}{r}, \quad r \rightarrow \infty,$$

or more realistically, by a wave packet (linear combination of these spherical waves of slightly different momenta). Note the qualitative difference

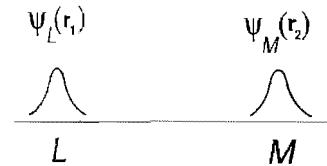


Fig. 18.4 Two unentangled electrons. Because $\psi_M(\mathbf{r}_1) \simeq \psi_L(\mathbf{r}_2) \simeq 0$ if $\mathbf{r}_1 \in L, \mathbf{r}_2 \in M$ the system is effectively factorized.

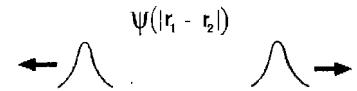


Fig. 18.5 A spherical wave packet parts of it receding from each other, seen along one direction. Compare this with the previous figure.

between the entangled state (18.20) and the unentangled one (18.19), that is, between Figure 18.4 and Figure 18.5. In an entangled state such as (18.20), kept carefully isolated from the rest of the world, the pair of particles remain forever entangled, no matter how far they travel away from each other.

18.5 A measure of entanglement: entropy

Not all systems are described by a wave function in quantum mechanics. Any kind of lack of information leads to a mixed state, described by a density matrix, as is well known. In the above we discussed the manifestation of quantum entanglement, in the pure case, but entanglement can manifest itself even when the state is not pure.

Let us again consider the simple case of a system composed of two spin- $\frac{1}{2}$ particles, described by a wave function

$$|\Psi(\alpha)\rangle = \cos \alpha |\uparrow\rangle \otimes |\downarrow\rangle + \sin \alpha |\downarrow\rangle \otimes |\uparrow\rangle,$$

where we have arbitrarily chosen the relative phase so as to make the coefficients real. Let us assume that the spatial wave function is such that the experimentalist at A is able to make observations only on particle 1. For then subsystem A is effectively described by a density matrix (called the reduced density matrix)

$$\rho_A = \begin{pmatrix} \cos^2 \alpha & 0 \\ 0 & \sin^2 \alpha \end{pmatrix}. \quad (18.21)$$

A mixed state is a state in which a complete knowledge of the state (in the sense of a definite wave function) is lacking for one reason or another. In the present case our ignorance clearly is due to the inaccessibility to the rest of the system (subsystem B). Now, can we quantify our ignorance? A possibly useful concept (which becomes important in quantum information theory) is the so-called von Neumann entropy,

$$E = -\text{Tr } \rho \log \rho.$$

This is a quantum mechanical version of the concept of entropy,

$$E^{(Shannon)} = - \sum_i p_i \log p_i, \quad \sum_i p_i = 1,$$

where $p_i (\geq 0)$ is the probability for the i -th outcome for some distribution, introduced by Shannon in information theory (known as Shannon entropy), as something that quantitatively characterizes the degree of our ignorance. In fact, its maximum $E^{(Shannon)} = \log N$ occurs when our ignorance is total, i.e., $p_i = 1/N, \forall i$. Its minimum (0) corresponds to complete knowledge, e.g., $p_1 = 1, p_i = 0, i \neq 1$. Partial knowledge (or partial ignorance) would give rise to a value of $E^{(Shannon)}$ between 0 and $\log N$.

In quantum mechanics one could adopt a similar definition of entropy, by using a particular observable (or a set of them), p_i being the quantum mechanical probability for finding the i -th result. It turns out, however, that such an entropy depends on the dynamical variable chosen: a completely known pure state may look like a state in which things are poorly known, if an unfortunate choice of variable is made. On the other hands, the von Neumann entropy (18.21) does not depend on the particular choice of observable and it does measure an intrinsic property (whatever that may mean) of our (mixed or pure) state.

In the case of mixed state (18.21) the entropy is given by

$$E(\alpha) = -2 (\cos^2 \alpha \log \cos \alpha + \sin^2 \alpha \log \sin \alpha) .$$

Its derivative with respect to α gives

$$dE(\alpha)/d\alpha = -2 \sin 2\alpha \log \tan \alpha .$$

It is easily seen (Figure 18.6) that the entropy is minimum when α is a multiple of $\pi/2$:

$$E(0) = E(\pi) = E\left(\frac{\pi}{2}\right) = E\left(\frac{3\pi}{2}\right) = 0 ;$$

whereas it is maximum when the phase α differs by $\pi/4$ from these:

$$E\left(\pm\frac{\pi}{4}\right) = E\left(\pm\frac{3\pi}{4}\right) = \log 2 \simeq 0.693147 .$$

Now in the former cases the wave function reduces to the form

$$\Psi \sim |\uparrow\rangle \otimes |\downarrow\rangle , \quad \text{or} \quad |\downarrow\rangle \otimes |\uparrow\rangle ,$$

in which case it has a factorized form and the subsystem A has a wave function. Indeed it is a pure state even for the observer at A who has no access to subsystem B , as can also be seen from the reduced density matrix (18.21). Vice versa, in the latter cases (maximal ignorance) the state is

$$\Psi \sim |\uparrow\rangle \otimes |\downarrow\rangle \pm |\downarrow\rangle \otimes |\uparrow\rangle ,$$

and entanglement is maximal.

Thus the von Neumann entropy for the reduced density matrix for a subsystem such as eqn (18.21) is a *measure of the entanglement* between the observed subsystem and the rest of the system. For that reason it is now often called *entanglement entropy*. Such a concept is a very general one, and can be introduced in a system with more than two particles, and even in systems with infinite degrees of freedom, such as spin systems or quantum field theories. These are subject of intense study nowadays: for some recent results, see [Vidal, et. al. (2003), Cardy and Calabrese (2004)].

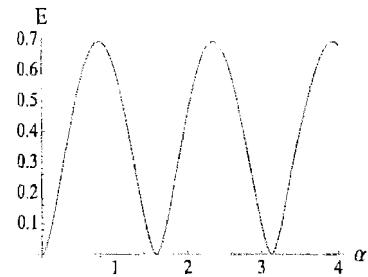


Fig. 18.6 Entanglement entropy for mixed state (18.21)

Further reading

J. S. Bell's book [Bell (2004)] is a collection of Bell's research and review papers on quantum entanglement and related issues, spanning twenty years of his thinking. It remains one of the deepest (and most enjoyable) books on the subject. The book by Peres [Peres (1995)] is a more modern and comprehensive introduction to the whole subject, from quantum entanglement and quantum measurement to quantum-information-theory-related subjects such as entropy, information gain by measurements, quantum erasure, etc. The book by Wheeler and Zurek [Wheeler and Zurek (1983)] is a collection of

original papers by the founding fathers of quantum mechanics (Bohr, Schrödinger, Einstein, ...) to more recent, experimental papers on the verification of quantum entanglement.

The subjects of quantum information theory, quantum cryptography, and quantum computing are not covered here at all. These are today rapidly developing fields of research and of technological applications. The interested reader can consult the lecture by J. Preskill [Preskill (2006)] or the book by Nielsen et al. [Nielsen and Chuang (2000)], for instance.

Probability and measurement

19

The probabilistic aspect of quantum mechanics, the fundamental postulate of quantum mechanics, eqn (2.14) of Section 2.3, in spite of innumerable experimental tests which establish its correctness beyond any doubt, still arouses some uneasy feelings in us. Can a microscopic, “complete” theory predict only a probability for the outcome of an individual experiment? At which exact moment should we stop using Schrödinger’s equation and switch to apply the statistical, Born rule for computing the probability for a certain outcome? Can quantum mechanics be applied to the entire universe, where there are no “external observers” to make measurements? Doesn’t macroscopic world actually evolve in time in a unique fashion (whether deterministic or not), and surely not into various possibilities?

In this chapter we shall discuss these and related questions. We shall summarize what is well established and what has been clarified in the last several decades concerning these issues, trying to distinguish as clearly as possible different issues which are all called the “measurement problem”, and in each case, making an effort to clarify as sharply as possible the nature of the problem.

19.1 The probabilistic nature of quantum mechanics

The fundamental postulate of quantum mechanics, eqn (2.14) of Section 2.3, states that if the state is given by a linear combination

$$|\psi\rangle = \sum_n c_n |n\rangle, \quad \sum_n |c_n|^2 = 1, \quad (19.1)$$

where $|n\rangle$ is the n -th normalized eigenvector of some operator \hat{F} with eigenvalue f_n , then the observation of the associated variable F gives one of the eigenvalues $\{f_n\}$, with a *probability* (or relative frequency of such outcomes in many, repeated experiments)

$$P_n = |c_n|^2.$$

To simplify the discussion, let us assume that the spectrum of the operator \hat{F} is purely discrete, and moreover that there is no degeneracy, so

19.1 The probabilistic nature of quantum mechanics	517
19.2 Measurement and state preparation: from PVM to POVM	519
19.3 Measurement “problems”	521
19.4 Hidden-variable theories	532
Further reading	539
Guide to the Supplements	539

¹We seem to have already stumbled upon an ill-defined term too often encountered in discussions about the measurement "problems" (see more about these later). In spite of its not-too-rigorous appearance, actually, here the term is used to mean "after a sufficiently short interval of time $\Delta t = t - t_0 \approx 0$ (assuming that the measurement is made at time t_0), so that the unitary time evolution operator of the system $U(t, t_0)$ can be reasonably well approximated by the unit operator. Such an assumption is quite an acceptable one because for any system $\lim_{t \rightarrow t_0} U(t, t_0) = 1$.

²For more specific, dynamical meanings of these words, see later. Here we use the term to simply mean eqn (19.2).

³The commutation of the operators is a sufficient condition for there being a state which is a simultaneous eigenstate, but it is not necessary. A well-known example is that of the angular momentum operators, $[L_i, L_j] = i\epsilon_{ijk}L_k$ which allow for a state $|L, L_z\rangle = |0, 0\rangle$ in which all of the operators L_i have definite values.

that the label n uniquely fixes the state of the system. Let us recall a few facts. The first is that the above postulate must be complemented by another, almost implicit hypothesis, that the state of the system, *immediately after*¹ the experiment has yielded one of the outcomes f_n , is given by

$$\mathcal{P}_n |\psi\rangle = c_n |n\rangle \sim |n\rangle : \quad (19.2)$$

namely, the state has been reduced to the associated eigenstate $|n\rangle$. This assumption, called "state vector reduction" or "wave function collapse"², apart from being confirmed experimentally, is actually a logically indispensable part of postulate (19.1) itself. For if this were not so, there would be no way to tell whether the theory (quantum mechanics) has successfully predicted experimental outcomes or not. In other words, the result of the measurement could not be used as the initial data for successive analysis of the system; in brief, the theory would not be much use at all. Another way to formulate this supplementary assumption is to say that the same measurement, repeated immediately after it has yielded f_n , gives the same result, f_n .

In more general systems it is not sufficient to measure just one dynamical variable to uniquely specify the state. There are in general a maximum set of ("compatible") observables, \hat{F}^I , which correspond to mutually commuting operators³

$$[\hat{F}^I, \hat{F}^J] = 0 ,$$

and hence which admit a simultaneous eigenstate, $|n_1, n_2, \dots\rangle$,

$$\hat{F}^I |n_1, n_2, \dots\rangle = f_{n_I}^I |n_1, n_2, \dots\rangle, \quad n_I = 1, 2, \dots$$

It is necessary (and sufficient) to perform simultaneous experimental determinations of all of f^I , $I = 1, 2, \dots$, in order to specify (or prepare) the quantum state uniquely.

On the other hand, in quantum mechanics one in general deals with incompatible observables, such as position and momentum, whose operators satisfy

$$[Q_i, P_j] = i\hbar\delta_{ij} .$$

For any such pair of self-adjoint operators K, L , obeying

$$[K, L] = i\hbar,$$

the standard argument shows that their determination in any state Ψ is constrained by Heisenberg's relation

$$\Delta K \cdot \Delta L \geq \frac{\hbar}{2} , \quad (19.3)$$

$$\Delta K \equiv \sqrt{\langle (K - \langle K \rangle)^2 \rangle}, \quad \Delta L \equiv \sqrt{\langle (L - \langle L \rangle)^2 \rangle} .$$

In other words, there cannot be any state in which both K and L have definite values (in the sense that if prepared in the same way, repeated experiments give always the same, definite answers for the two). For

instance, if K is experimentally determined to have a definite value, then *immediately after* that measurement the system is left in a state such that the observable L cannot have a definite value in it. For if this were not so either the uncertainty relation (19.3) is invalid, or the quantum system evolves in an uncontrolled manner in whatever small amount of time (which, as we argued above, would contradict the success of the fundamental postulate (19.1)).⁴

Photon polarization

The above consideration is about logical consistency of the quantum mechanical laws, but actually it is also a reflection of the properties of the physical world of particles. Recall the situation of linearly polarized photons sent to a polarizer (Section 2.1.2). A photon which has passed a polarizer with a given polarization axis, is linearly polarized in that direction. When this photon impinges upon another polarizer with a different, generic polarization axis, it has only two options: either it passes or it does not pass. The empirical fact that a photon cannot split into fractions is essential. The probabilistic quantum mechanical prediction would seem to be the only logical possibility of describing this kind of physical situation.

⁴This point, that Heisenberg's uncertainty relations necessarily imply a probabilistic nature of quantum mechanical predictions, was emphasized in [Schrödinger (1935)].

19.2 Measurement and state preparation: from PVM to POVM

Before going on, it is appropriate to recall that in order to prepare the state uniquely, in general, it is not sufficient to perform a measurement of just one observable. A system usually has more than one commuting (self-adjoint) operator, corresponding to a nontrivial set of compatible observables. It is necessary to make the simultaneous experimental determination of their values, sometimes called a “maximal test”, to determine the wave function completely. Even though the choice of the maximum set is not unique, given the system, one can choose any set $\{n\}$ and parametrize the state vectors as $|n\rangle$. The projection operator to a particular state is given by

$$P_n = |n\rangle\langle n|, \quad P_n P_m = \delta_{nm} P_n, \\ \sum_n P_n = \mathbb{1}. \quad (19.4)$$

In any pure state $|\psi\rangle$ the probability of finding the state $|n\rangle$ is given by

$$\langle\psi|P_n|\psi\rangle = \text{Tr}(P_n|\psi\rangle\langle\psi|), \quad (19.5)$$

the probability adding up to 1 due to eqn (19.4). Immediately after the measurement, and if the result is known to be n , then the system is left in the projected state

$$P_n|\psi\rangle \sim |n\rangle$$

(wave function reduction or wave function collapse).

But often the state preparation cannot be done in a complete fashion; for one reason or another the state of the system is only partially known. We talk about a mixed state in such a case: the properties of a mixed state are expressed by a density matrix ρ . The probability of finding the state $|n\rangle$ is then given by

$$\text{Prob}_n = \text{Tr}(P_n \rho), \quad \sum_n \text{Prob}_n = 1. \quad (19.6)$$

Note that formula (19.5) is a special case for a pure state.

Each of the projection operators is a positive operator⁵. They further add up to the identity operator. They are orthogonal to each other. This way of defining measurements (due to von Neumann) is also known as the projection-valued measurement (*PVM*).

It is now widely realized that this traditional definition of a measurement in quantum mechanics is far too restrictive. There are many other experimental questions (which have a yes–no answer, just like a *PVM* question) which cannot be formulated in terms of projection operators of the system under consideration. Simple examples of such yes–no questions are [Wallace (2007)]:

- Is the state (of a given system) an energy eigenstate?
- Is the state such that the energy expectation value in it is larger than 100 Joules?

Whole new classes of measurements can be formulated in terms of the so-called positive operator-valued measure (*POVM*). The basic idea is that the “standard” orthogonal projection operators and the associated maximum tests in a *composite* system made of subsystems A and B , do not necessarily imply an orthogonal-projection-valued measurement (*PVM*) in subsystem A , which is (say) the system of our main interest. Let us assume that system B is described by a density matrix, R , while system A is in the (mixed) state ρ . The combined system is thus in the state

$$\rho \otimes R.$$

Now consider a set of orthogonal projection operators P_N for the full system (a “partition of unity” or “resolution of identity”) such that

$$P_N P_M = \delta_{NM} P_M, \quad \sum_N P_N = 1. \quad (19.7)$$

The probability that a maximal test gives one of the results N in the state $\rho \otimes R$ is given by

$$\begin{aligned} \text{Prob}_N &= \text{Tr}(P_N \rho \otimes R) = \sum_{m,k,M,K} (P_N)_{mM;kK} \rho_{km} R_{KM} \\ &\equiv \text{tr}(E_N \rho), \end{aligned} \quad (19.8)$$

where

$$(E_N)_{mk} = \sum_{M,K} (P_N)_{mM;kK} R_{KM}$$

⁵An operator whose eigenvalues are all non-negative is called in the literature a “positive operator”, perhaps not very appropriately. In the case of a projection operator each has eigenvalues 1 or 0.

is a matrix defined in system A . It is a positive operator and satisfies

$$\sum_N (E_N)_{mk} = \mathbb{1} :$$

the set $\{E_N\}$ is a possible partition of unity. By using this it can be seen that

$$\sum_N \text{Prob}_N = 1,$$

so Prob_N defined in eqn (19.8) allows for its interpretation as the probability for the N -th outcome.

Note the formal similarity between eqns (19.6) and (19.8). In both cases $\{P_n\}$ or $\{E_N\}$ can be regarded as the sets of all possible alternative outcomes in a given state. However, there are important differences. The orthogonal projection operators in the standard PVM trivially commute, and if the dimension of the Hilbert space is given by D , the index n (the number of different P_n 's) runs from 1 to D . In the case of a POVM, the operators $\{E_N\}$ do not in general commute, and the number of different E_N can be greater than D .

Many interesting examples are discussed in [Peres (1995)]. For instance consider a spin- $\frac{1}{2}$ system. The four operators $(\mathbb{1} \pm \sigma_x)/4$ and $(\mathbb{1} \pm \sigma_z)/4$ together form a POVM, each with eigenvalues $(1, 0)$, and summing up to the identity operator $\mathbb{1}$. To construct another example, consider again a spin- $\frac{1}{2}$ system. The eigenvectors of the three operators

$$\sigma \cdot \mathbf{n}_i, \quad \mathbf{n}_1 + \mathbf{n}_2 + \mathbf{n}_3 = \mathbf{0}$$

with eigenvalue +1 are

$$|\mathbf{n}_i\rangle = \begin{pmatrix} e^{-i\phi_i/2} \cos \theta_i/2 \\ e^{i\phi_i/2} \sin \theta_i/2 \end{pmatrix},$$

where (θ, ϕ) are the standard spherical coordinates

$$\mathbf{n}_i = (\sin \theta_i \cos \phi_i, \sin \theta_i \sin \phi_i, \cos \theta_i).$$

It can be easily verified that the three operators

$$E_i = \frac{2}{3} |\mathbf{n}_i\rangle \langle \mathbf{n}_i|, \quad i = 1, 2, 3$$

form a POVM, each with eigenvalues 1, 0 and satisfying

$$\sum_{i=1}^3 E_i = \mathbb{1}.$$

19.3 Measurement "problems"

So all said, what is the problem? Often an apparent problem arises simply from an improper use of words. A good example is the word

“measurement” itself. As was pointed out by Bell, the word “measurement” implies the act of finding out something already there, with definite properties, this or that, and the sole scope of the act of “measurement” is to discover which of the properties was “there”. Indeed in classical physics this is precisely what is meant by a measurement. The effect of the action of the measuring process is assumed to be negligible compared to the property of the object being investigated. This way of conceiving measurement has been with us for hundreds of years. Even with the advent of modern experimental science, introduced by Galileo, there was no change in this respect.⁶

⁶Galileo's observation of the moon using his telescope involved certain light scattered off the surface of the moon and sent into the objective lens, and so on, but such a process certainly did not change the shape of the lunar surface being discovered, at least not to any significant extent.

In quantum mechanics the situation is entirely different. In quantum mechanical measurement where the object of the investigation typically involves atomic systems, the effects of the interactions involved in the measurement and the back reaction to the system being “measured” are in general not negligible, as was vividly illustrated in a series of Gedankenexperiments by Heisenberg [Heisenberg (1930)]. In more realistic situation, a typical quantum mechanical experiment involves an interaction between a (quantum mechanical) system and a classical apparatus (such as the Stern–Gerlach magnets and the photographic plate): the quantum mechanical property of the microscopic system is amplified and is somehow transferred (in a good experiment, faithfully) into classical properties of the apparatus which reads the results (the pointer position, the small region on the photographic plate where the ionization clouds are formed, etc.) The use of the word “measurement” in discussing quantum mechanical observation, with a (classical) preconception of what the word means, can certainly lead us astray.⁷.

There are many similar examples of the improper use of a word (or an inappropriate word) producing apparent paradoxes and difficulties, encountered in the discussion of quantum mechanics. Alongside these, however, there are more serious issues. It is therefore essential in the following that we distinguish the true problems from the apparent, and discuss the nature of each problem with as much clarity as possible.

19.3.1 The EPR “paradox”

The Einstein–Podolsky–Rosen “paradox” at first sight appears to be the most serious of the problems related to the foundation of quantum mechanics. Let us go back to the Gedankenexperiment considered in the original EPR paper, briefly discussed in the previous chapter. In that example, the system composed of two particles is, before the experiments, assumed to be in a state

$$\Psi^{(EPR)}(x, q) = \int dp e^{ip(x-q+x_0)/\hbar} = 2\pi\hbar\delta(x - q + x_0), \quad (19.9)$$

which is a simultaneous eigenstate of the total momentum operator P_{tot} (conjugate to $(x + q)/2$) with eigenvalue 0, and of the relative position operator, $x_{rel} = q - x$, with eigenvalue, x_0 . In the instant the position of particle 1 is measured, suppose that it yielded a result $x = X$; the distant

particle is predicted to be at $q = X + x_0$, with certainty. If instead the momentum of particle 1 is measured, with the result $p_1 = P$, this implies instantly that the other particle is also in a momentum eigenstate, with momentum $-P$.

Now EPR argues that if in a state the result of a measurement is known beforehand with 100% certainty (i.e., is an eigenstate of the operator associated with the variable in question), then there is an *element of physical reality* in such a state⁸. If one believes in the locality of interactions and in causality, the experiment at site 1 certainly cannot dynamically influence the experiment at the distant site 2, at least before the moment in which the second observer makes his (or her) experiment. Thus such an instant change of "physical reality" at the distant site 2 caused by the experiment at site 1 cannot be correct!—That is, unless things were actually predetermined from the beginning, and that the single or double experiments are just trying to find out "what was there". This is precisely the idea of the hidden variables, which will be discussed below, in Section 19.4. We shall find out that no theories of this sort can actually reproduce the full content of quantum mechanics.

This is another example of the introduction of words (*element of physical reality*), quite foreign to quantum mechanics, which has unfortunately made things more obscure, instead of clarifying them. In fact, the above reasoning does not hold. Precisely because the two experiments are made at a spacelike separation, and this means that one experiment cannot dynamically influence the outcome of the other, *and neither can the information about the first experiment reach the second experimental site in time*. Information transmission is a dynamical, physical process, and just as no dynamical effects can propagate faster than light, neither can any signal about them. The fact that the two processes (the possible dynamical influence of one on the other and the information transmission) are both limited by the timelike light-cone of one event with respect to the other is no coincidence.

The second observer, without access to the outcome of the first experiment, finds the system in a mixed state and has a probabilistic expectation, and indeed, sometimes one result and sometimes others. In the simpler example of Bohm's spin-singlet entangled state, eqn (18.4), the second observer would see the system effectively described by the density matrix

$$\rho = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

and half of the time would find spin-up and half of the time spin-down, independently of the magnet orientation, in perfect agreement with the quantum mechanical prediction.

Of course, if the data from the two Stern-Gerlach experiments were brought together and confronted, we would find *a posteriori* that the two data are correlated, precisely as quantum mechanics predicts: as in eqn (18.5), or in eqn (18.11) in the case of two-photon experiments. It is true that it looks as if one experiment on site 1 instantly (or even before!) influenced the other distant experiment, but the point is: it

⁸Verbatim it went as follows. "If, without in any way disturbing a system, we can predict with certainty (i.e., with probability equal to unity) the value of a physical quantity, then there exists an element of physical reality corresponding to this physical quantity."

remains *as if*.

Very often talk is made about the non-locality of quantum mechanics, referring to the “instantaneous” implication of one experimental result on another, distant experiment, in an entangled state. As we have already noted, even though such apparently non-local correlations are indeed one of the characteristic features of quantum mechanical systems, neither truly non-local interactions of any sort nor super-luminal transmission of information is ever involved in these experiments.

As far as we know today, all of the fundamental interactions are described by a local and causal theory of point-like particles. See the discussion in Section 17.2.4. The electromagnetic interactions are described to very high precision by quantum electrodynamics. The strong nuclear forces are described by quantum chromodynamics of quarks and gluons. The so-called weak interactions, responsible for beta decays, are now known to be part of the forces which unify electromagnetism and weak interactions and described by the electroweak theory of Glashow, Weinberg, and Salam. They are all local and causal quantum field theories of *point-like particles* (for the list of presently known elementary particles, see Table 24.6–24.11).

Gravitation is an exception. Even though it allows for a formulation as a gauge field theory like other theories of fundamental interactions, a way of correctly incorporating quantum mechanical principles together with the theory of gravity—general relativity—is not yet known. However, the gravitational interactions are rather tiny effects at the atomic level⁹. It would be quite unlikely that gravitation plays any significant role in most quantum-mechanical measurement processes.¹⁰

Barring the possibility that gravity is somehow responsible for heretofore unknown effects on quantum measurement, at the heart of entanglement is the fact that the distant “simultaneous” measurements (of spin, energy, position, etc.) all refer to a single, elementary local *event* in which these particles have been produced. The latter is described perfectly well by the local, causal quantum field theories of fundamental interactions. The outcome of each simultaneous measurement thus carries the common *event label*. In each event the property of the relevant quantum state (such as angular momentum conservation for the EPRB state (18.4)) must be rigorously respected. It is this constraint that brings in apparently non-local, non-causal correlations among the distant particles.

To conclude, the EPR “paradox” is, in spite of its appearance, neither a “problem” nor a paradox; rather it should be regarded as representing intriguing physical effects [Chiao, et.al. (1995)]. With its strong appeal to mysterious aspects of quantum mechanical entanglement, it in fact remains a constant source of inspiration for quantum information theoretic and related technological developments.

⁹The ratio between the gravitational and Coulomb forces between a proton and an electron (such as in the hydrogen atom) at the same distance—they obey the same Newton law—is equal to $G_N m_p m_e / e^2 \simeq 4.3 \times 10^{-40}$.

¹⁰Except that some people think that the effects related to quantum gravity, which becomes important at extremely short distances of the order of 10^{-32} cm, might somehow be responsible for the wave function collapse.

19.3.2 Measurement as a physical process: decoherence and the classical limit

The first real problem regarding quantum measurement is the understanding of measurement itself as a physical process. As such it should be described by Schrödinger’s equation. It involves the microscopic system, the main object of study, as well as the experimental apparatus, which is usually a classical (macroscopic) system carefully arranged to interact with the microscopic system, so as to read and amplify the quantum mechanical properties of the system and permanently record the result of the measurement. It is quite likely also that the external environment (e.g., the air surrounding the experimental apparatus) plays a subtle but crucial role: see below.

One of the severe problems we encounter immediately is the fact that the macroscopic, experimental apparatus must be treated as a quantum mechanical system, to be treated in a coupled Schrödinger equation. At the same time it must behave classically, pointing in a definite position or giving a definite number on the counter, etc. A proper understanding of this dual nature of the experimental apparatus¹¹ is one of the central unanswered questions today.

The first step of the measurement is the entanglement between the microscopic system described by the wave function (let us assume it to be in a pure state)

$$|\psi\rangle = \sum_n c_n |n\rangle \quad (19.10)$$

with the macroscopic apparatus system, in the state $|\Phi\rangle_0$, as follows

$$\begin{aligned} |\psi\rangle \otimes |\Phi\rangle_0 &= \sum_n c_n |n\rangle \otimes |\Phi\rangle_0 \\ \implies U(t)|\psi\rangle \otimes |\Phi\rangle_0 &= \sum_n c_n |n\rangle \otimes |\Phi_n\rangle, \end{aligned} \quad (19.11)$$

where $U(t)$ is a unitary evolution describing the system-apparatus interaction and the reading of the latter.¹²

As a toy model of the measurement process, let us consider a spin- $\frac{1}{2}$ particle of large mass going through an inhomogeneous Stern–Gerlach magnetic field directed towards \hat{z} . The Hamiltonian is [Bell (2004)]

$$H = g \sigma_z P_z + \frac{P_x^2}{2m}, \quad (19.12)$$

where P_x, P_z are the momentum operators of the massive atom.¹³ As the particle is heavy, motion in the x direction can be treated classically and therefore neglected in the following. Let the initial wave packet in the transverse direction (z) be given by

$$\psi(0) = \phi(z) \begin{pmatrix} a \\ b \end{pmatrix} \quad |a|^2 + |b|^2 = 1, \quad \int dz |\phi(z)|^2 = 1.$$

Schrödinger’s equation

$$i\hbar \frac{\partial}{\partial t} \psi = H \psi$$

¹¹This is termed the *ambivalence* of the experimental apparatus, in [Peres (1995)].

¹²The *real-life problems* of measurements, such as preparation of unbiased detectors, the full coverage of the final particles, the coincidence check, the fidelity and sufficient sensitivity of the counters, etc., are assumed here to be solvable with arbitrary perfection, at least in principle, thanks to the professional skills of the experimentalists and to the sophisticated technology available today.

¹³This is not a very realistic form of the interaction between the magnetic moment of the particle and inhomogeneous magnetic field, $-\mu \cdot \mathbf{B}$, but it is sufficient for the present purpose of illustrating certain aspects of the measurement process. Also, we shall neglect another perpendicular direction y .

is solved by

$$\psi(t) = \begin{pmatrix} a\phi(z - \frac{g}{\hbar}t) \\ b\phi(z + \frac{g}{\hbar}t) \end{pmatrix},$$

so that the wave packet is now split into two smaller wave packets, one going up and the other going down in the z direction as they travel uniformly in the x direction. If the atom is allowed to impinge on some photographic plate, the relative intensity of the two images will be proportional to $|a|^2/|b|^2$.

As the two wave packets get separated by a macroscopic distance in the z direction, the two terms in

$$\psi(t) = a\phi\left(z - \frac{g}{\hbar}t\right) |\uparrow\rangle + b\phi\left(z + \frac{g}{\hbar}t\right) |\downarrow\rangle$$

cease interfering in any significant way. If the relative phase between the two terms is never going to matter, the system is *for all practical purposes* equivalent to a mixed state described by the density matrix

$$\rho = \begin{pmatrix} |a|^2 & 0 \\ 0 & |b|^2 \end{pmatrix}.$$

In a sense this oversimplified model captures the basic features of (the first step of) a typical quantum measurement. The property of the spin (a macroscopic vertical separation of the wave packet positions).

This is, however, not quite the whole story. Even if a macroscopic separation of the two wave packets is a necessary condition for an unambiguous determination of the spin state, it does not necessarily mean that the measurement has been performed in fact. Actually, if the vertical position of the atom is *not* measured (no photographic plate is placed and no chain ionization process has been triggered), and by another set of magnets the beams are carefully re-focused, the interference between the two terms can again become observable.

Many experiments of this sort ("reviving quantum interferences") have been successfully performed¹⁴.

Thus the first step of the measurement is to bring the apparatus state

- to be entangled with the microscopic system so that it "reads" the quantum mechanical information of the system being studied;
- to be in macroscopically distinct states $|\Phi\rangle_n$ so that the relative phases between different terms in eqn (19.11) become practically unobservable,

which however, under carefully controlled situation, maintain the coherence among the different terms of the sum in eqn (19.11).

The final stage of the measurement process—a decisive recording of the result—involves the entanglement of the system-apparatus composite system with the rest of the world: the environment. The system-apparatus-environment wave function evolves further as¹⁵

$$\sum_n c_n |n\rangle \otimes |\Phi\rangle_n \otimes |Env\rangle \implies \sum_n c_n |n\rangle \otimes |\Phi\rangle_n \otimes |Env_n\rangle, \quad (19.13)$$

¹⁴Such a setup has been coined—somewhat paradoxically—as the *quantum eraser*.

¹⁵The question how this process might actually occur has been the subject of intense study recently. There are indications that decoherence actually occurs extremely rapidly. See [Joos, et al. (2002)].

where the environment state vector now describes (in a manner of speaking) unspecified and unspecifiable numbers of degrees of freedom¹⁶. The state $|Env_n\rangle$ also includes the state of the experimentalist who reads the result " n ". Clearly, once this stage is reached, the process is *irreversible* and the phase relations among the terms in eqn (19.13) get definitively lost: there is no way of keeping track of hugely different and uncontrolled phase relations among the terms. *Decoherence* has taken place, and the pure state $\sum_n c_n |n\rangle$ has been reduced to a mixed state

$$\rho = \begin{pmatrix} |c_1|^2 & 0 & 0 & 0 & 0 \\ 0 & |c_2|^2 & 0 & 0 & 0 \\ 0 & 0 & \ddots & 0 & 0 \\ 0 & 0 & 0 & |c_n|^2 & 0 \\ 0 & 0 & 0 & 0 & \ddots \end{pmatrix}. \quad (19.14)$$

19.3.3 Schrödinger's cat

Isn't this a satisfactory account of the quantum mechanical measurement process? If the coherence is irremediably lost and for all purposes one is left with a mixed state (19.14) in place of the original pure state (19.10), isn't this a good enough explanation of state reduction? Actually, this brings us to the very heart of the problem: *does not the macroscopic world as we know it evolve in a unique fashion, whether deterministic or not, and certainly not in a probabilistic superposition implied by eqn (19.13)?* The dilemma was famously illustrated by Schrödinger's cat [Schrödinger (1935)], which is kept in a delicate state between life and death, according to whether some radioactive decay has occurred or not. A sophisticated arrangement is assumed to be set up so that a spontaneous α decay of a nucleus would trigger a chain process leading to poisoning of the unfortunate cat. The state evolves as

$$|\Psi\rangle = |\text{Metastable nucleus}\rangle \otimes |\text{unaware cat}\rangle \Rightarrow \\ a(t) |\text{Undecayed nucleus}\rangle \otimes |\text{alive cat}\rangle \quad (19.15) \\ + b(t) |\text{Decayed nucleus}\rangle \otimes |\text{dead cat}\rangle,$$

the survival (of the unstable nucleus--hence of the cat) amplitude behaving as

$$|a(t)| \sim e^{-\Gamma t/2}$$

at large t . A superposition of alive and dead states of the same cat is indeed quite an unusual notion.

The apparent contradiction with our experience (we never see a cat half-alive and half-dead; we always see it *either* alive *or* dead), can actually easily be avoided. As the truly faithful description of the measurement process must include the environment (including us) as well, as noted in the previous subsection, the state (19.15) actually evolves as¹⁷

¹⁶These will include the air molecules, the electrons in the cables, the photons illuminating the computer screen, the experimentalist watching the screen, etc.

¹⁷Of course, the details of the evolution are more complicated. There will be instants when the nucleus has decayed but the cat is still alive, or the interval of time in which the cat has died but the observer has not yet realized it, and so on.

$$\begin{aligned}
 |\Psi(0)\rangle &= |\text{Undecayed nucleus}\rangle \otimes |\text{unaware cat}\rangle \otimes |\text{unaware us}\rangle \\
 \Rightarrow |\Psi(t)\rangle &= a(t) |\text{U nucleus}\rangle \otimes |\text{L cat}\rangle \otimes |\text{us seeing cat alive}\rangle \\
 &\quad + b(t) |\text{D nucleus}\rangle \otimes |\text{D cat}\rangle \otimes |\text{us seeing cat dead}\rangle,
 \end{aligned} \tag{19.16}$$

so indeed we see the cat *either* alive *or* dead!

Isn't this a good enough answer? Have not all the problems been solved? Actually, we are still stuck with the problem mentioned above. The point is that quantum mechanics tells us that equations such as eqn (19.16) should not be regarded as a real-time evolution of the system but describe the time evolution of the probability amplitude of *what might be observed* at each moment, if the experiment were made.

There are at least two difficulties in eqn (19.16). One is that quantum transitions of an excited nucleus to a lower state, as in transitions among atomic levels, occur in "quantum jumps", i.e., as space-time pointlike events. Although quantum mechanics is able to deal with the decay of metastable states reasonably well (see Chapter 13), the sudden jumps (which do occur, as in the α or β decays of radioactive nuclei, spontaneous emission of light from an excited atom, etc.) are not encoded literally in eqn (19.16).¹⁸

The second problem, closely related to it, is the fact that even though the apparatus and environment occur as state vectors in it, they (we) evolve in time classically and uniquely, that is, with a well-defined position and momentum at any instant (i.e., the problem of the *ambivalence* of the apparatus, mentioned already).

Is there any way out? There are three main attitudes taken by physicists today, disregarding fine nuances of varieties of philosophical points of view in each case¹⁹.

- (1) There are indeed all these terms in eqn (19.13) or eqn (19.16) present all the time: we just live in one branch of the evolution tree, unaware of other possible evolution branches (the *many-worlds interpretation* [Everett (1957)]). We shall discuss this briefly later, in Section 23.1.
- (2) There occur from time to time true quantum jumps, not only of atoms, but of everything, wave function reduction being a physical process, and each time, only one term in eqn (19.13) or eqn (19.16) survives (*dynamical wave function collapse*) [Ghirardi, Rimini and Weber (1986)]: this will also be discussed later, in Section 23.1; or
- (3) Or there are no real difficulties. There are no such things as dynamical wave function collapse or continuously branching worlds. Quantum mechanics gives us an extremely successful statistical rule for calculating the relative frequencies of an event occurrence or certain experimental results, *given* initial preparation of the system, i.e., atoms, electrons, etc., that is, *given* the results of some earlier, preparatory experiments.

From this last, rather pragmatic viewpoint [Ballantine (1998)], what is incorrect is to regard the state vector as a physical object (*physical reality?*—Sometimes philosophers talk about the *ontology* of wave

¹⁸For practical purposes, it turns out to be possible and useful to consider a mixed time evolution, a statistical—according to quantum mechanical probabilities—occurrence of quantum jumps from time to time, alongside a smooth Schrödinger evolution between them. A beautiful analysis of atom-laser coupled systems of this sort leads to a phenomenologically excellent description of the momentum distribution of laser-cooled atoms. See [Bardou et. al. (2002)].

¹⁹An up-to-date review of various thoughts can be found in [Wallace (2007)].

functions): the wave function is just a bookkeeping devise for the rules relating past events to future events. It is possible that all "problems" have been created by ourselves, who continue to think and talk classically, and not quantum mechanically enough. A future generation might accept this pragmatic attitude naturally.

19.3.4 The fundamental postulate versus Schrödinger's equation

Even if this could be the case, there is a final, and perhaps the true, problem of quantum mechanics today, independent of one's philosophical point of view:

Can Born's statistical rule, i.e. that the various possible events in eqn (19.13) or eqn (19.16) occur with probability (or relative frequency)

$$P_n = |c_n|^2$$

(the fundamental postulate of quantum mechanics) be derived from Schrödinger's equation? Or is this rule an independent axiom,²⁰ in addition to Schrödinger's equation? The problem certainly appears to be a formidable one, as the full Schrödinger evolution (19.13) in principle involves the entire world. A proper understanding of the quantum-classical behavior of objects made of a macroscopic number of molecules is needed. Perhaps we must learn how to consistently describe the coupled quantum mechanical-classical systems.

These are problems left for the future.

In this context, an intriguing theorem is the following.

Gleason's theorem

In the case of a mixed state, described by a density matrix ρ , the fundamental rule of quantum mechanics asserts that the expectation value of an operator A is given by

$$\bar{A} = \text{Tr } A \rho .$$

In particular, the probability of finding the system in a given state specified by the projection operator $P_n = |n\rangle\langle n|$, is given by

$$\text{Prob}_n = \text{Tr } P_n \rho . \quad (19.17)$$

According to Gleason [Gleason (1957)], this is a very general property of quantum systems with the following properties:

- (i) Elementary (yes-no) measurements are represented by projection operators (with eigenvalues 1, 0) in real or complex vector space.
- (ii) Compatible measurements (which can be performed simultaneously) correspond to mutually commuting projection operators.

²⁰This reminds us of the fifth Euclidean axiom...

- (iii) If P_1 and P_2 represent any pair of orthogonal projection operators (thus $[P_1, P_2] = 0$ trivially) then the expectation value of their sum $P_{12} = P_1 + P_2$, which is also a projection operator, is the sum of their expectation values:

$$\langle P_{12} \rangle = \langle P_1 \rangle + \langle P_2 \rangle.$$

Under these conditions, and if the dimension of the Hilbert space is larger than two, Gleason's theorem asserts that the expectation value of a projection operator P is in general given by

$$\langle P \rangle = \text{Tr } P \tilde{\rho} \quad \text{Tr } \tilde{\rho} = 1, \quad (19.18)$$

where $\tilde{\rho}$ is some positive operator depending on the state (but not on the particular operator considered). The probability is a linear function of P . In deriving the basic rule (19.17) the crucial assumption is (iii) above. For the proof, see [Gleason (1957)] and also [Peres (1995)].

Gleason's theorem²¹ looks almost like a proof of the *fundamental postulate* of quantum mechanics. However, all the dynamical aspects of the problem (how the system evolves according to the coupled Schrödinger equation, how exactly the information carried by the wave function ψ is transferred into the relative frequency, $|\psi|^2$, why the state vector is such a precise description of the atomic systems, etc.) remain unanswered by it.

²¹The scope of Gleason's work was to find a way to define a basis-independent, positive-definite measure for each closed subspace of a Hilbert space. Such a measure naturally admits a probabilistic interpretation, when appropriately normalized. His conclusion is that under conditions (i)–(iii) it necessarily has the form of eqn (19.18).

19.3.5 Is quantum mechanics exact?

In addition to these, there are more sober issues, which might be ultimately related to the ones discussed already. For instance: is the quantum mechanical, *homogeneous* evolution law exact? Can there be tiny non-linear corrections to Schrödinger's (or Heisenberg's) equation? Can they be detected experimentally by existing data? Some such non-linear generalization has been discussed in [Weinberg (1989)]. To the energy level of the ${}^9\text{Be}$ nucleus the upper limit of a possible correction is found to be $O(10^{-21})$. This is quite in line with the fact that the standard model of fundamental interactions (quantum chromodynamics, the Glashow–Weinberg–Salam electroweak theory) describes Nature with a very high precision, down to distances of the order of 10^{-16} cm. These theories are based on the relativistic quantum mechanics of pointlike particles.

More important, perhaps, is the effect of gravity. It is not yet known how to correctly incorporate gravity and general relativity in a quantum mechanical context. (Super-)string theory [Green, Schwartz and Witten (1987), Polchinski (1998)] is regarded by many theoretical physicists today as one of the most promising candidates to achieve this goal. It is a quantum theory, and it *does* imply the existence of the graviton—the tensor quantum of the gravitational field—naturally and necessarily. The essential difference in string theory, as compared to quantum field theory upon which the Standard Model of fundamental interactions is based on,

is the fact that the fundamental entity here is no longer pointlike particles but one-dimensional continuous degrees of freedom (strings). Due to their fluctuations, there is a minimal physical length in string theory, and consequently, Heisenberg’s uncertainty relation is generalized to something like (by setting $\hbar = 1$)

$$\Delta X \sim \frac{1}{\Delta P} + L^2 \Delta P ,$$

where L is the fundamental length scale of string theory, of the order of $O(10^{-30})$ cm; see [Amati, Ciafaloni, and Veneziano (1989), Konishi, Paffuti and Provero (1990), Maggiore (1993)].

A second fundamental issue is that, unlike in particle theories (quantum field theories), quantum string propagation is consistent only in particular space-time backgrounds. The consistency conditions are nothing but the classical Einstein equations and other field equations (with string-theoretic corrections). In other words, the consistency of the theory determines the world in which it is defined! It is not known today whether such a consideration will eventually lead to the explanation of the fact we apparently live in four-dimensional Minkowski space, of why our universe looks the way it looks today, and so on. From the formal point of view, however, it should be noted that at the very basic level, string theory as we know it today is constructed by using the same principles of standard quantum mechanics (canonical commutation relation between the position and momentum operators) applied to the two-dimensional string degrees of freedom. It is not clear what light string theory can shed on fundamental issues such as the one related to Schrödinger’s cat.

19.3.6 Cosmology and quantum mechanics

A problem closely related to the probabilistic interpretation and Schrödinger’s cat paradox—a coherent sum of terms in the amplitude of a microscopic system versus the unique evolution of a macroscopic body—is the wave function of the universe. Assume that the wave function of the universe

$$\Psi^{(\text{universe})}(\mathbf{r}_1, \mathbf{r}_2, \dots; t)$$

is known, evolving in time in a definite way, according to Schrödinger’s equation. Some toy models of this sort of “wave function of the universe”, satisfying the so-called De-Witt–Wheeler equation, have been studied. But then the problem is: how to use it? As there is nobody outside our universe, who is going to make the measurement, perhaps repeating the identical experiment many times (the evolution of our universe is a unique and single “experiment”—at least for us). The standard rule of interpreting $|\Psi^{(\text{universe})}|^2$ as the probability of finding a particular outcome, does not make much sense.

Cosmological considerations may also be crucial in some other sense. If, at the time of the Big Bang, the temperature was so high quantum-gravity effects so strong, and the space-time so curved that *time* itself

may no longer have been a homogeneous parameter as used in the formulation of quantum mechanics, this implies that quantum mechanical concepts must somehow be modified in such extreme conditions. Quantum mechanics in highly curved space-time is not yet understood. A related question is: is the arrow of time to be explained by the expansion of the universe [Penrose (1989)]?

Perhaps one of the deepest problems in physics today is whether or not the evolution of systems under gravitational effects respects unitarity, the fundamental building block of quantum mechanics. The problem goes under the name of the *information paradox*. Typically, the formation of a black hole due to gravitational collapse of a star, followed by evaporation through Hawking radiation, would appear to let the whole system lose its information. In fact, the knowledge, for example, of the baryon number and other details about the matter which has been absorbed into the black hole becomes quite inaccessible to the observer outside the event horizon: it would look as if a pure state had been transformed into a mixed state.

An extremely suggestive idea is that of black hole entropy [Bekenstein (1973)]. In particular, the Hawking radiation may not, after all, be strictly thermal and the entropy of the ingoing matter might be encoded in the quantum string states at the horizon. This concept is known as the holographic principle ('t Hooft, Susskind, Maldacena). A complete theory of this sort, however, is as yet to be constructed.

19.4 Hidden-variable theories

We have already seen that the EPR “paradox” does not present any inconsistency of quantum mechanics; it highlights, if anything, the very nontrivial correlations among distant subsystems, typical of quantum mechanics. Nevertheless, quite independently of quantum entanglement, it is perfectly legitimate to ask whether a “complete” theory of the atomic world should give only a probabilistic prediction on an individual experiment. Would it not be conceivable that there exists an even more complete theory where the outcome of single measurement is, in principle, predictable? The (unknown) set of parameters whose unknown distribution would give rise, hopefully, to statistical predictions for various outcomes, reproducing the quantum mechanical rules, are called “hidden variables”. These hypothetical theories are alternatively known as theories with dispersion-free states [von Neumann (1932)], *cryptodeterminism* [Peres (1995)], or sometimes, not entirely appropriately, “theories with local causality.”

19.4.1 Bell’s inequalities

The milestone in the discussion of hidden-variable theories was laid down by J. S. Bell in an article of 1964 [Bell (1964)].²² Bell showed that, independently of the nature or number of hidden variables, these hypothetical theories cannot reproduce *all* of quantum mechanics’ predictions.

²²The significance of the earlier considerations on the impossibility of hidden-variable theories, including von Neumann’s “proof”, have been critically examined by Bell, and will not be discussed here. See [Bell (2004)].

His result is expressed in the form of a set of inequalities (*Bell's inequalities*), satisfied necessarily by any hidden-variable model, but that can be violated by quantum mechanics. His work thus turned the controversy into a well-defined experimental question: which is right? As in Aspect's experiments, which we discussed in the previous chapter, all the experimental tests so far performed have confirmed the correctness of quantum mechanics, ruling out any kind of hidden-variable theories.

So why bother? The importance of Bell's work lies, above all, in the fact that these inequalities (and their many generalizations, including discussions which do not use inequalities, to be discussed below) show very sharply and in mathematical language the deviation from the classical behavior of quantum systems.²³ They force upon us the necessity of switching definitively from the classical way of thinking about the measurements.

Consider again Bohm's version of the EPR-entangled state, two spin- $\frac{1}{2}$ particles in a total spin-singlet state,

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle).$$

in which the two particles, flying apart from each other, enter the two distant Stern-Gerlach magnetic fields. Could the correlations between the results of the measurements at the two distant sites, such as in Table 18.2 or in Table 18.3, be simply due to the fact that things were actually predetermined, at the moment the particle pair was produced?

Suppose that $\{\lambda\}$ represent the unspecified set of these parameters (*hidden variables*) whose precise value would determine the outcome of whatever experiments are done at the two sites, A and B . Let us denote the outcomes of the measurement of $2\mathbf{s}_1 \cdot \mathbf{a}$ and $2\mathbf{s}_2 \cdot \mathbf{b}$ in each coincident event, in such a hypothetical theory, by $R(\mathbf{a}, \lambda)$ and $\tilde{R}(\mathbf{b}, \lambda)$, respectively. They must take only the values

$$R(\mathbf{a}, \lambda) = \pm 1, \quad \tilde{R}(\mathbf{b}, \lambda) = \pm 1,$$

depending on λ , no matter how the magnets are oriented at the two distant sites, if this theory is to reproduce the known results of quantum mechanics.

Now the average of the correlation is given by

$$F(\mathbf{a}, \mathbf{b}) = \overline{R(\mathbf{a}, \lambda)\tilde{R}(\mathbf{b}, \lambda)} = \int d\lambda \mathcal{P}(\lambda) R(\mathbf{a}, \lambda) \tilde{R}(\mathbf{b}, \lambda),$$

where $\mathcal{P}(\lambda)$ is some unknown distribution of the hidden parameters,

$$\mathcal{P}(\lambda) \geq 0, \quad \int d\lambda \mathcal{P}(\lambda) = 1.$$

One condition on the functions $R(\mathbf{a}, \lambda)$ and $\tilde{R}(\mathbf{b}, \lambda)$ follows from the fact that when the two magnets are oriented parallel, $\mathbf{a} = \mathbf{b}$, there must be a perfect (anti-)correlation exemplified in Table 18.2. In order for this to follow from the hidden-parameter theory, it must be the case that

$$\tilde{R}(\mathbf{a}, \lambda) = -R(\mathbf{a}, \lambda),$$

²³Of course, the *whole* of quantum mechanics is about such a deviation from the classical behavior of atomic systems. In this sense nothing new in principle is involved here. One can perhaps say, however, that in entangled systems such quantum mechanical features manifest themselves in a particularly striking fashion.

which is assumed below. The correlation now takes the form

$$F(\mathbf{a}, \mathbf{b}) = - \int d\lambda \mathcal{P}(\lambda) R(\mathbf{a}, \lambda) R(\mathbf{b}, \lambda).$$

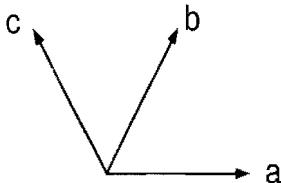
Consider now the combination

$$\begin{aligned} F(\mathbf{a}, \mathbf{b}) - F(\mathbf{a}, \mathbf{c}) &= - \int d\lambda \mathcal{P}(\lambda) [R(\mathbf{a}, \lambda) R(\mathbf{b}, \lambda) - R(\mathbf{a}, \lambda) R(\mathbf{c}, \lambda)] \\ &= \int d\lambda \mathcal{P}(\lambda) R(\mathbf{a}, \lambda) R(\mathbf{b}, \lambda) [R(\mathbf{b}, \lambda) R(\mathbf{c}, \lambda) - 1], \end{aligned}$$

and thus

$$|F(\mathbf{a}, \mathbf{b}) - F(\mathbf{a}, \mathbf{c})| \leq \int d\lambda \mathcal{P}(\lambda) (1 - R(\mathbf{b}, \lambda) R(\mathbf{c}, \lambda)) = 1 + F(\mathbf{b}, \mathbf{c}).$$

Therefore it follows that in any hypothetical hidden-variable theory, the spin-spin correlation satisfies (*Bell's inequality*)



$$|F(\mathbf{a}, \mathbf{b}) - F(\mathbf{a}, \mathbf{c})| \leq 1 + F(\mathbf{b}, \mathbf{c}). \quad (19.19)$$

It can be readily seen that such a relation cannot always be compatible with the quantum mechanical result,

$$F^{(QM)}(\mathbf{a}, \mathbf{b}) = -\cos \theta_{\mathbf{a}, \mathbf{b}}.$$

As $F^{(QM)}$ is a smooth function of the angle between the magnets, near $\mathbf{b} = \mathbf{c}$, the right-hand side of eqn (19.19) is $O(|\mathbf{b} - \mathbf{c}|^2)$ while the left-hand side is linear, $O(|\mathbf{b} - \mathbf{c}|)$, which is definitely larger. As a concrete example, if the unit vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are oriented with 60 degrees between them as in Figure 19.1, the left-hand side of (19.19) is equal to 1 while the right-hand side is $\frac{1}{2}$!

An analogous inequality can be constructed in the case of the polarization-entangled two-photon state of eqn (18.6),

$$\psi_+ = \frac{|x\rangle \otimes |x\rangle + |y\rangle \otimes |y\rangle}{\sqrt{2}},$$

arising from an SPS cascade decay of an atom. We define the operators

$$\Sigma_\theta \equiv 2P_\theta - 1, \quad \Sigma_{1,2} \equiv 2P_{1,2} - 1,$$

which have eigenvalues, ± 1 , the analogue of the operator $\sigma \cdot \mathbf{a}$ in the spin- $\frac{1}{2}$ systems, and where $P_{1,2}, P_\theta$ are the projection operators on the photon linearly polarized in the direction 1, 2 or the generic direction θ (eqns (18.7), (18.8), eqn (18.9)). If $R(\Sigma_\theta) = \pm$ denotes the measurement output for each photon, then the correlation function can be defined as

$$F(\theta, \theta') \equiv F_{\mathbf{a}, \mathbf{b}} = \overline{R(\Sigma_\theta) R(\Sigma_{\theta'})} \quad (19.20)$$

as in the case of the two spin- $\frac{1}{2}$ Bohm state.

In a hidden-variable theory, Bell's argument can be repeated for $F(\theta, \theta')$: it is given by

$$F(\theta, \theta') = \int d\lambda \mathcal{P}(\lambda) A(\theta, \lambda) A(\theta', \lambda), \quad A(\theta, \lambda) = \pm 1,$$

where $A(\theta, \lambda) = \pm 1$ is the outcome of each measurement of Σ_θ in such a theory; $\mathcal{P}(\lambda)$ is the unknown distribution of the hidden parameters. One easily finds Bell's inequality for the photon pairs,

$$|F(\theta, \theta') - F(\theta, \theta'')| \leq 1 - F(\theta'', \theta') \quad (19.21)$$

This inequality is violated by the quantum mechanical formula

$$F^{(QM)}(\theta, \theta') = \cos 2(\theta - \theta')$$

for some choice of the angles (e.g., for $\theta, \theta', \theta''$ making an angle $\pi/6$ between them).

Bell's inequality can be generalized in various ways. For instance, consider four sets of experiments and associated correlation functions. The combination

$$S^{(CHSH)} \equiv F(\theta_1, \theta_2) + F(\theta_3, \theta_2) + F(\theta_1, \theta_4) - F(\theta_3, \theta_4)$$

is given, in a hidden-variable theory, as

$$\int d\lambda \mathcal{P}(\lambda) [(A(\theta_1, \lambda) + A(\theta_3, \lambda))A(\theta_2, \lambda) + (A(\theta_1, \lambda) - A(\theta_3, \lambda))A(\theta_4, \lambda)].$$

But the expression in the square brackets above is always ± 2 , because if $A(\theta_1, \lambda) = A(\theta_3, \lambda)$ the first term is ± 2 , while if $A(\theta_1, \lambda) = -A(\theta_3, \lambda)$ the second term is ± 2 . It follows that

$$|F(\theta_1, \theta_2) + F(\theta_3, \theta_2) + F(\theta_1, \theta_4) - F(\theta_3, \theta_4)| \leq 2 \quad (19.22)$$

(known as the Clauser–Holt–Horne–Shimony, or simply the *CHSH*, inequality) [Clauser, et. al. (1969)]. Again quantum mechanics violates such an inequality in general, and as has been shown by Aspect [Aspect, Dalibard, and Roger (1981)], Chiao [Chiao, et.al. (1995)], [Chiao (1993)] and others, so does Nature.

19.4.2 The Kochen–Specker theorem

Bell's equality and its generalizations involve a statistical average over repeated experiments. Though the experiments done up to now have confirmed the validity of quantum mechanics (against hidden-variable alternatives) beyond any doubt, the conclusion would be sharper if the discrimination between them could be made by using a single experiment, rather than averaging over many similarly prepared experiments. Such was the motivation for Mermin's consideration of three or more entangled spin- $\frac{1}{2}$ particles [Mermin (1990)], discussed in Section 18.3.

More general consideration along this line of thought lead to a theorem due to Kochen and Specker [Kochen and Specker (1967)].

The theorem states that, in a Hilbert space of dimension three or more ($D \geq 3$), it is not possible to consistently assign a definite value ($a_n = 1$ or $a_n = 0$) simultaneously to *each* of *every* set of orthonormal (thus commuting) projection operators

$$P_n, \quad \sum P_n = 1,$$

so that their assigned values satisfy

$$\sum a_n = 1$$

also. The point is that if some of the projection operators $\{P_i\}$ are shared by more than one orthonormal set $\{P_n\}$ (it is here that the condition $D \geq 3$ is used), their assigned values a_i are assumed to be the same. It is not at all obvious that such a consistent assignment of a_n 's is possible. The proof that this is indeed impossible, is given by explicit construction (to prove something is *not* possible, it is sufficient to produce a single counter-example!).²⁴

Clearly the content of the Kochen–Specker theorem is a mathematical one about the property of vector spaces, a little analogous to the so-called coloring problem, and has in itself nothing to do with quantum mechanics. The interest in such a theorem in the context of quantum mechanics arises from the consideration of hidden-variable type theories, in which the result of each single experiment (whose outcome is $\{a_n\}$) could be in principle predictable. If in a hidden-variable theory, the choice of λ were to determine uniquely the result of all possible experiments on the system, and thus to determine all of the above a_n 's uniquely, then the Kochen–Specker theorem would tell us that such a theory is inconsistent, i.e., it cannot exist.

In an example using 33 rays in \mathbb{R}^3 illustrated in [Peres (1995)], a sequence of sets of orthonormal projection operators is constructed by using orthonormal sets of vectors,

$$\begin{aligned} \overline{(0,0,1)}, (1,0,0), (0,1,0) &\Rightarrow \{a_{(0,0,1)}, a_{(1,0,0)}, a_{(0,1,0)}\} = \{1, 0, 0\}; \\ \overline{(0,0,1)}, (1,1,0), (0,1,1) &\Rightarrow \{a_{(0,0,1)}, a_{(1,1,0)}, a_{(0,1,1)}\} = \{1, 0, 0\}; \\ \overline{(1,0,1)}, (-1,0,1), (0,1,0) &\Rightarrow \{a_{(1,0,1)}, a_{(-1,0,1)}, a_{(0,1,0)}\} = \{1, 0, 0\}; \end{aligned} \tag{19.23}$$

and so on. Only the direction (ray) matters here. The barred rays correspond to the projection operator to which the value 1 is assigned (the other two get assigned 0). Note that, so far, the projector $P_{(0,0,1)}$ has been consistently assigned the value 1, while $P_{(0,1,0)}$ has been consistently assigned the value 0, for instance. Continuing this way successively, however, one reaches at a certain point the conclusion that

$$a_{(1,0,0)} = a_{(0,\sqrt{2},1)} = a_{(0,-1,\sqrt{2})} = 0 :$$

but this is a contradiction because the vectors

$$(1, 0, 0), (0, \sqrt{2}, 1), (0, -1, \sqrt{2})$$

form an orthogonal basis.

The implication of the Kochen–Specker theorem for hidden-variable theories is actually subtler. The naïve conclusion that it implies an inconsistency in any hidden-variable theory is not correct. The reason why that argument is false is the same as in the case of Mermin’s four triple experiments M_1 – M_4 , discussed in Section 18.3. Those experiments, leading to an apparently contradictory set of results, eqns (18.16)–(18.17c), actually refer to four different events, hence, e.g., the $m_{1,x}$ appearing in eqns (18.16) and (18.17c) are not necessarily the same number. Therefore eqns (18.16)–(18.17c) do not imply either an inconsistency in quantum mechanics or the impossibility of hidden-parameter theories. Similarly, here the assignment of the numbers $(1, 0, 0)$ to each triplet of orthogonal projection operators must be done *event by event*. The $a_{(0,1,0)}$ appearing in the first of eqns (19.23) and the $a_{(0,1,0)}$ appearing in the last have no reasons to be the same number (though they might be).

There are two considerations to be made. The first is the fact that whenever one talks about a *simultaneous* measurement, e.g., of the three or more orthogonal projection operators, the two spin components at the far sites of an EPR–Bohm setting, or of the three operators $\sigma_{1x}, \sigma_{2y}, \sigma_{3y}$ in Mermin’s state (18.3), one does not really mean the contemporaneity of the separate measurements made at distant sites, but rather that the particles involved are produced by the same space-time event (a local interaction vertex). Such is the property of the electromagnetic and other fundamental interaction processes known today. This allows us to define the *contemporaneity of the measurements* unambiguously, in reasonably well-controlled experiments (i.e., with a good coincidence check). Thus, different sets of “simultaneous” measurements, such as eqns (18.16)–(18.17c) or the ones in eqns (19.23), correspond to different elementary processes (events), and the numbers (results) are assigned for each event separately.

Another point concerns the structure of quantum mechanics. Very generally, when the dimension of the Hilbert space is larger than two, the following situation can occur: three Hermitian operators A , B_1 and B_2 are such that²⁵

$$[A, B_1] = [A, B_2] = 0, \quad \text{but} \quad [B_1, B_2] \neq 0.$$

In such a situation A and B_1 can be measured simultaneously; similarly A and B_2 , but not all of A , B_1 , B_2 together. This means that the first measurement involving (A, B_1) and the second measurement for (A, B_2) necessarily refer to two different elementary processes, hence with no a priori relation between the results for A in the two cases. This state of affairs was termed the *contextuality* [Peres (1995)], in the sense that the result of a measurement of A depends on the context, on which other

²⁵A simple example is

$$A = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix};$$

$$B_1 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix};$$

$$B_2 = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

observable has been measured together (or has not been measured). It is actually quite a general feature of quantum mechanics.

To summarize, the Kochen–Specker theorem implies that for any hidden-variable theory to be compatible with quantum mechanics (and in fact, with Nature), the hidden variables $\{\lambda\}$ must carry information not only of the “state”, and which variable is measured, but also the complete information about its context, about which set of variables is measured together, about which precise event it ($\{\lambda\}$) refers to, etc.

As in an entangled system these data include non-local sets of data, and such a theory has a necessarily non-local character.

19.4.3 “Quantum non-locality” versus “locally causal theories” or “local realism”

It is quite unfortunate that words are sometimes used in a not entirely appropriate fashion in the discussion of quantum measurement and/or entanglement, causing possible misunderstanding or a sort of mystification. “Quantum non-locality” as often used in the literature must really be understood as meaning: “Aspects of quantum mechanics—entanglement—which, if they are to be exactly reproduced by the introduction of classical, hidden variables, require the latter to carry non-local and non-causal data.”²⁶ As is evident from the discussion of “delayed-choice” experiments such as the one by Aspect et al., the initial data carried by the relevant set of particles at the moment they are produced, would have to carry information about the experimental settings (e.g., orientation of the Stern–Gerlach magnets) which are not yet even decided! It is the (hypothetical) hidden variables which would have to possess non-local and non-causal properties, not quantum mechanics itself. Quite the contrary. Quantum mechanics is perfectly compatible with the local and causal nature of fundamental interactions (see the discussions of Subsection 17.2.4 and Subsection 19.3.1.) The success of quantum electrodynamics, and more generally, of the standard model of the fundamental interactions (the Glashow–Weinberg–Salam theory of the electroweak interactions and quantum chromodynamics of strong interactions) proves it.

In summary, the words “quantum non-locality” and “locally causal theories”, or “theory of local realism” (meaning hidden-variable theories) are used, in a way, in exactly opposite senses to those usually attributed to the words. Perhaps a healthier attitude would be to simply call them “quantum entanglement” and “hidden-variable theories”, respectively.

²⁶Of course, if “local causality” is defined by some other criteria [Bell (2004)], quantum mechanics could well violate it. But this is a matter of definition.

Further reading

This has become a vast subject of study in the last few decades and it is not easy to list a comprehensive list of references. As for the previous chapter the book [Peres (1995)] is a good introduction to the whole subject. A reprint collection [Wheeler and Zurek (1983)] contains many original papers, including the famous exchanges of views among Einstein, Bohr, Bohm, Schrödinger, and

many others. The book also contains more recent references up to the year 1983, and remains a useful guide to the whole subject. The book by Joos [Joos, et. al. (2002)] reviews many issues concerning the measurement problem in a series of readable lectures, especially about decoherence and the emergence of classical limits, and contains a vast list of references.

Guide to the Supplements

Supplement 23.1 briefly reviews various ideas which have been entertained concerning quantum measurement.

These comments should help to further sharpen various aspects of the measurement problems discussed here.

Part V

Supplements

Part V is a collection of supplements and appendices, which are useful aids for reading the main text and sometimes are a more-in-depth examination of some issues which could not be covered satisfactorily in the main text, for the lack of space. Each section is independent of the others; they can be read at pleasure in any order, even independently of the main text. More supplementary discussions are to be found in the Mathematica notebooks or in pdf files contained on the accompanying CD.

20

Supplements for Part I

20.1 Classical mechanics

Let us review a few salient features of classical mechanics, for completeness.

20.1.1 The Lagrangian formalism

Newton's equation for a particle moving under the influence of a force \mathbf{F} is

$$\frac{d\mathbf{p}}{dt} = \mathbf{F}, \quad (20.1)$$

where \mathbf{p} is momentum. If the force is of conserved type,

$$\mathbf{F} = -\nabla V, \quad (20.2)$$

V being the potential. From eqns (20.1) and (20.2) follow conservation of total energy

$$E = T + V; \quad T = \frac{\mathbf{p}^2}{2m} = \frac{1}{2} m \dot{\mathbf{r}}^2 \quad (\text{kinetic energy}).$$

Furthermore, if the potential is spherically symmetric

$$V(\mathbf{r}) = V(r),$$

angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ is also conserved.

In the Lagrangian formalism the fundamental quantity is

$$L = L(q_i, \dot{q}_i; t) = T - V$$

called the Lagrangian, which is considered as a functional of the generalized coordinates q_i , $i = 1, 2, \dots, s$, and of their time derivatives \dot{q}_i , as well as of time t .

Given the Lagrangian the equation of motion is:

$$\frac{\partial L}{\partial q_i} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} = 0, \quad i = 1, 2, \dots \quad (20.3)$$

(the Euler–Lagrange equation).

Euler–Lagrange equation follows from the *minimum action principle*. Action S is defined as

$$S \equiv \int_{t_1}^{t_2} L(q_i, \dot{q}_i; t) .$$

20.1 Classical mechanics	545
20.2 The Hamiltonian of the electromagnetic radiation fields in the vacuum	554
20.3 Orthogonality and completeness in a system with a one-dimensional delta-function potential	556
20.4 The S matrix; the wave-packet description of scattering	560
20.5 The Legendre polynomials	564
20.6 Groups and representations	566
20.7 Formulas for angular momentum	575
20.8 Young tableaux	581
20.9 N -particle matrix elements	584
20.10 The Fock representation	586
20.11 Second quantization	589
20.12 Supersymmetry in quantum mechanics	590
20.13 Two- and three-dimensional delta function potential	595
20.14 Superselection rules	601
20.15 Quantum representations	604
20.16 Gaussian integrals and Feynman graphs	611

Equations (20.3) follow from imposing the stationary condition for S with respect to an arbitrary variation of $q_i(t)$, with the constraint that their values at the initial and final time $q_i(t_1)$, $q_i(t_2)$, are kept fixed. In formulas

$$\delta S|_{\delta q(t_1)=\delta q(t_2)=0} = 0.$$

The proof of the preceding statement is left to the reader as an exercise. The fundamental tool is the following theorem

Theorem 20.1 If

$$\int_{t_1}^{t_2} dt \eta(t) F(t) = 0, \quad (20.4)$$

where $F(t)$ is a continuous function in the interval (t_1, t_2) ; $\eta(t)$ is any function continuous together with its first derivative in the same interval, such that $\eta(t_1) = \eta(t_2) = 0$, then

$$F(t) = 0, \quad t_1 \leq t \leq t_2.$$

Proof Suppose that there existed F satisfying eqn (20.4) but $F(t_0) > 0$, $t_1 < t_0 < t_2$. As the function F is continuous there must exist an interval $[\xi_1, \xi_2]$ ($\xi_1 < t_0 < \xi_2$) where $F(t) > 0$. Let us consider a function

$$\eta = \begin{cases} 0, & t_1 \leq t \leq \xi_1, \\ (t - \xi_1)^2(t - \xi_2)^2, & \xi_1 \leq t \leq \xi_2, \\ 0, & \xi_2 \leq t \leq t_2. \end{cases}$$

which satisfies the required conditions. For such η we find, however,

$$\int_{t_1}^{t_2} dt \eta(t) F(t) = \int_{\xi_1}^{\xi_2} (t - \xi_1)^2(t - \xi_2)^2 F(t) > 0,$$

which is a contradiction.

□

Remarks

- The Euler–Lagrange equation is invariant (in form) under arbitrary change of generalized coordinates, $q_i(t) \rightarrow Q_i(t) = Q_i(\{q_i(t)\}; t)$. These transformations are called *point transformations*.
- The Lagrangian formalism turned out to be very fruitful in subsequent developments in theoretical physics (relativistic quantum field theories, Feynman path integral formulation of quantum mechanics and field theory).
- The Lagrangian for a given system is not unique, but has an arbitrariness of the type,

$$L(q, p; t) \rightarrow L(q, p; t)' = L(q, p; t) + \frac{dF(q, t)}{dt}.$$

In fact, the action changes as

$$S \rightarrow S' = S + F(q_2, t_2) - F(q_1, t_1),$$

but then by virtue of the boundary conditions $\delta q_1 = \delta q_2 = 0$ we get

$$\delta S' = \delta S.$$

An important case is the system of a charged particle in an external electromagnetic field

$$L = \frac{m\dot{\mathbf{r}}^2}{2} + \frac{q}{c}\dot{\mathbf{r}} \cdot \mathbf{A} - q\phi(\mathbf{r}),$$

where

$$\mathbf{B} = \nabla \times \mathbf{A}, \quad \mathbf{E} = -\nabla\phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}.$$

The Euler–Lagrange equation following from it is¹

$$m\ddot{r}_i + \frac{q}{c}\dot{A}_i = -q\partial_i\phi + \frac{q}{c}\dot{r}_j\partial_iA_j.$$

Making the time derivative in the first term more explicit,

$$\frac{d}{dt}A_i = \frac{\partial}{\partial t}A_i + \dot{r}_j\partial_jA_i,$$

and collecting terms we find that

$$\begin{aligned} m\ddot{\mathbf{r}}_i &= -q\left(\partial_i\phi + \frac{1}{c}\frac{\partial}{\partial t}A_i\right) + \frac{q}{c}\dot{r}_j(\partial_iA_j - \partial_jA_i) = \\ &= -q\left(\partial_i\phi + \frac{1}{c}\frac{\partial}{\partial t}A_i\right) + \frac{q}{c}\dot{r}_j\epsilon_{ijk}B_k = q\mathbf{E}_i + \frac{q}{c}(\dot{\mathbf{r}} \times \mathbf{B})_i, \end{aligned} \quad (20.5)$$

which is Newton's equation, with terms representing Lorentz as well as electrostatic forces.

Vector and scalar potentials \mathbf{A} and ϕ are defined up to gauge transformation

$$\mathbf{A} \rightarrow \mathbf{A} + \nabla f; \quad \phi \rightarrow \phi - \frac{1}{c}\frac{\partial f}{\partial t} \quad (20.6)$$

under which \mathbf{E} , \mathbf{B} remain invariant, while the Lagrangian transforms as

$$\Delta L = \frac{q}{c}\frac{df(q(t), t)}{dt}.$$

As we have noted already, the variation of the action is such that Euler–Lagrange equation remains invariant.

20.1.2 The Hamiltonian (canonical) formalism

In the Lagrangian formalism independent variables are the generalized coordinates, q_i , $i = 1, 2, \dots, s$. There are s differential equations of second order. In Euler–Lagrange equation derivatives are taken as if q_i and \dot{q}_i were independent variables, but this is just a formal aspect.

¹Here and below Einstein's convention of taking the summation over repeated indices will be often used.

In fact, in the derivation of the Euler–Lagrange equation itself, the independent variations are δq_i , while the variation of $\dot{q}_i(t)$ is defined by $\delta\dot{q}_i(t) \equiv (d/dt)\delta q_i(t)$.

In the Hamiltonian formalism (also called the canonical formalism) the number of the independent variables is twice (2s) that in the Lagrangian formalism. Coordinates q_i and conjugate momenta p_i are both independent and appear symmetrically in the equations of motion. The Hamiltonian is defined by

$$H(q_i, p_i) \equiv \sum_i p_i \dot{q}_i - L(q_i, \dot{q}_i), \quad (20.7)$$

where

$$p_i \equiv \frac{\partial L}{\partial \dot{q}_i}. \quad (20.8)$$

Equation (20.7) is an example of a *Legendre transformation*. It is understood that eqn (20.8) is solved for \dot{q}_i , i.e., $\dot{q}_i = \dot{q}_i(p_j, q_j)$ and that dependence of H on q_i, p_i in the left-hand side of eqn (20.7) is understood thus. The equations of motion following from the Euler–Lagrange equations are:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad (i = 1, \dots, s), \quad (20.9)$$

known as *Hamilton equations or canonical equations*.

Remarks

- In a simple system such as $L = (\frac{1}{2})m\dot{\mathbf{r}}^2 - V$, the Hamiltonian takes the form

$$H = \frac{\mathbf{p}^2}{2m} + V,$$

Hamiltonian represents the energy of the system.

- The canonical equations are invariant under a large class of change of variables, known as *canonical transformations*, see below (Sub-section 20.1.4).
- Even if the number of equations (2s) is twice as compared to the Lagrangian formulation, they are now first-order equations, and as a consequence the number of boundary conditions (parameters of the solution) remains the same (2s).
- The state of the system is specified by a point in the 2s-dimensional hyperspace $\{q, p\}$ called *phase space*. The evolution of the system is given by a mouvement of the point in this space.

For a particle moving in an external electromagnetic fields the Hamiltonian is

$$H = \left[\mathbf{p} - \frac{q}{c} \mathbf{A}(\mathbf{r}, t) \right]^2 + q\phi(\mathbf{r}, t) + V(\mathbf{r}), \quad (20.10)$$

where $\phi(\mathbf{r})$, $\mathbf{A}(\mathbf{r})$ are the scalar and vector potentials, respectively. V indicates a possible mechanical potential. The electromagnetic fields are given in terms of the scalar and vector potentials as

$$\mathbf{E} = -\nabla\Phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}.$$

The gauge transformations

$$\mathbf{A} \rightarrow \mathbf{A}' = \mathbf{A} + \nabla\Lambda, \quad \Phi \rightarrow \Phi' = \Phi - \frac{1}{c} \frac{\partial\Lambda}{\partial t}$$

leave the electromagnetic fields invariant. The Hamiltonian changes its form, however a simple canonical transformation (see Section 14.1.1) brings equations of motion back to the original form. The equation of motion following from eqn (20.10) contains the term representing the Lorentz force (20.5). The interaction with electromagnetic fields are represented by the formal replacement, $\mathbf{p} \rightarrow \mathbf{p} - \frac{q}{c}\mathbf{A}(\mathbf{r}, t)$ in the kinetic term; this recipe to introduce interactions is known as the *minimal coupling*.

20.1.3 Poisson brackets

Time evolution of a generic variable in Hamiltonian formalism can be elegantly described by the so-called *Poisson's brackets*. The latter is defined by

$$\{f, g\} \equiv \sum_{i=1}^s \left(\frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q_i} \right) \quad (20.11)$$

for any pair of dynamical variables $f = f(q_i, p_i; t)$, $g = g(q_i, p_i; t)$. Time evolution of a variable f is given by

$$\begin{aligned} \frac{df}{dt} &= \frac{\partial f}{\partial t} + \sum_{i=1}^s \left(\frac{\partial f}{\partial q_i} \dot{q}_i + \frac{\partial f}{\partial p_i} \dot{p}_i \right) \\ &= \frac{\partial f}{\partial t} + \sum_{i=1}^s \left(\frac{\partial f}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = \frac{\partial f}{\partial t} + \{f, H\}. \end{aligned}$$

The equation of motion of a physical quantity is thus given by its Poisson bracket with the Hamiltonian, as well as by its explicit dependence on time.

From definition (20.11) the fundamental Poisson brackets follow:

$$\{q_i, p_j\} = \delta_{ij}, \quad \{q_i, q_j\} = 0, \quad \{p_i, p_j\} = 0. \quad (20.12)$$

Let us summarize the main properties of Poisson brackets, which can be easily verified:

$$\begin{aligned} \{f, g\} &= -\{g, f\}; & \{f, c\} &= 0 \quad (c = \text{const.}); \\ \{q_i, f\} &= \partial f / \partial p_i; & \{p_i, f\} &= -\partial f / \partial q_i; \\ \{f_1 + f_2, g\} &= \{f_1, g\} + \{f_2, g\}; & \{f_1 f_2, g\} &= f_1 \{f_2, g\} + f_2 \{f_1, g\}; \end{aligned}$$

$$\{\{f, g\}, h\} + \{\{g, h\}, f\} + \{\{h, f\}, g\} = 0 \quad (\text{Jacobi's identity}).$$

20.1.4 Canonical transformations

Canonical formalism allows a wide class of change of variables. The transformations

$$\{q_i, p_i\} \rightarrow \{Q_i(q, p; t), P_i(q, p; t)\}$$

which leave invariant the form of the canonical equations, i.e. such that

$$\dot{Q}_i = \frac{\partial \tilde{H}}{\partial P_i}; \quad \dot{P}_i = -\frac{\partial \tilde{H}}{\partial Q_i}, \quad (i = 1, \dots, s),$$

where \tilde{H} is the new Hamiltonian related in a certain way to the original Hamiltonian, are called *canonical transformations*.

To study which transformations have this property, and to see the relation between the old and new variables, we could start from the variational principle. The action can be rewritten as

$$S = \int L dt = \int \left(\sum p_i \dot{q}_i - H \right) dt$$

and the equation of motion follows from the principle of minimum action

$$\begin{aligned} 0 = \delta S &= \int \left[\sum_i \left(\delta p_i \dot{q}_i + p_i \frac{d}{dt} \delta q_i \right) - \sum_i \left(\frac{\partial H}{\partial q_i} \delta q_i + \frac{\partial H}{\partial p_i} \delta p_i \right) \right] dt \\ &= \int \left[\sum_i \left(\dot{q}_i - \frac{\partial H}{\partial p_i} \right) \delta p_i + \sum_i \left(-\dot{p}_i - \frac{\partial H}{\partial q_i} \right) \delta q_i \right] dt. \end{aligned} \quad (20.13)$$

As δq_i and δp_i are independent variations it follows that the equations of motion are precisely Hamilton's equations (20.9).

A canonical transformation must then be such that

$$S = \int dt \left(\sum p_i \dot{q}_i - H \right) = \int dt \left(\sum P_i \dot{Q}_i - \tilde{H} + \frac{dF}{dt} \right),$$

where F is some function of the generalized coordinates, conjugate momenta, and of t . Suppose that it is of the form $F = F_1(q, Q; t)$. As

$$\frac{dF_1}{dt} = \sum_i \left(\frac{\partial F_1}{\partial q_i} \dot{q}_i + \frac{\partial F_1}{\partial Q_i} \dot{Q}_i \right) + \frac{\partial F_1}{\partial t},$$

the relations between the new and old variables following from eqn (20.13) are:

$$p_i = \frac{\partial F_1(q, Q, t)}{\partial q_i}; \quad P_i = -\frac{\partial F_1(q, Q, t)}{\partial Q_i}; \quad (20.14)$$

$$\tilde{H}(Q, P) = H(q, p) + \frac{\partial F_1(q, Q, t)}{\partial t}. \quad (20.15)$$

Second equation of (20.14) must be solved for q_i , $q_i = q_i(Q, P; t)$. Substituting in the first relation one obtains $p_i = p_i(q, Q; t) = \tilde{p}_i(Q, P; t)$. Upon substitution of these expressions eqn (20.15) gives the new Hamiltonian.

In brief: given an arbitrary function $F_1(q, Q; t)$, the change of variables and of Hamiltonian defined by the set of relations (20.14) and (20.15) is a canonical transformation. The new equations of motion have the same canonical form in terms of the new variables and Hamiltonian. The function $F_1(q, Q)$ is called the *generating function* of the canonical transformation.

For example, take $F_1 = \sum_i q_i Q_i$. In this case one finds that $p_i = Q_i$; $P_i = -q_i$; $\frac{\partial F_1}{\partial t} = 0$ and $\tilde{H}(Q_i, P_i) = H(q_i, p_i) = H(-P_i, Q_i)$. Such a canonical transformation exchanges the role of coordinates and momenta.

There are other types of canonical transformations, classified according to the types of the generating function used

$$F_2(q, P; t), \quad F_3(p, Q; t), \quad F_4(p, P; t),$$

i.e., according to different kind of relations between the old and new variables. Canonical transformations of the second kind can be introduced from the first type considered above through

$$F_2(q, P; t) = F_1(q, Q; t) + \sum_i Q_i P_i; \quad \text{with: } P_i \equiv -\frac{\partial F_1}{\partial Q_i}.$$

The transformation in this case takes the form

$$p_i = \frac{\partial F_2(q, P, t)}{\partial q_i}, \quad Q_i = \frac{\partial F_2(q, P, t)}{\partial P_i}; \quad \tilde{H}(Q, P) = H(q, p) + \frac{\partial F_2(q, P, t)}{\partial t}.$$

Let us consider a few concrete examples:

- (a) $F_2 = \sum_i \Phi_i(q, t) P_i$. This corresponds to point transformations $Q_i = \Phi_i(q, t)$, familiar from the Lagrangian formalism.
- (b) $F_2 = \sum_i q_i P_i$. This corresponds to the *identity transformation* $Q_i = q_i$; $p_i = P_i$; $\tilde{H} = H$.
- (c) $F_2 = \sum_i q_i P_i + \epsilon \psi(q, P)$, with infinitesimal ϵ (infinitesimal transformations). Such a generating function gives rise to the transformation

$$\begin{aligned} Q_i &\simeq q_i + \epsilon \frac{\partial \psi}{\partial P_i} \simeq q_i + \epsilon \frac{\partial \psi(q, p)}{\partial p_i}, \\ p_i &\simeq P_i + \epsilon \frac{\partial \psi}{\partial q_i} \simeq P_i + \epsilon \frac{\partial \psi(q, p)}{\partial q_i}, \end{aligned}$$

i.e.

$$\delta q_i = \epsilon \frac{\partial \psi(q, p)}{\partial p_i}, \quad \delta p_i = -\epsilon \frac{\partial \psi(q, p)}{\partial q_i}.$$

Time evolution of any physical system is given by the canonical equations:

$$dq_i = \frac{\partial H}{\partial p_i} dt; \quad dp_i = -\frac{\partial H}{\partial q_i} dt.$$

This can be interpreted as a succession of infinitesimal canonical transformations with $H dt$ being their generating function.

We shall see in the main text that also in quantum mechanics the Hamiltonian determines the time evolution of the system under consideration.

20.1.5 The Hamilton–Jacobi equation

Still another formalism of classical mechanics makes use of some non-linear equations, which are, however, equivalent to the set of linear differential equations in the canonical formalism. Such a formalism turns out to be quite important in studying the relation between classical and quantum mechanics.

In the formulation of minimal action principle the action S is seen as a functional of the trajectory function $q_i(t)$ at fixed boundary conditions. We can consider the action S at various values of the final position q and at various final times t

$$\begin{aligned} S &= \int dt L = \int \left(\sum p_i \dot{q}_i - H \right) dt' \\ &= \int_{q_i}^{q_f} \sum_i p_i dq_i - \int^t dt' H = S(q_i, t), \end{aligned} \quad (20.16)$$

i.e., we consider S as an ordinary function of q_i and t . From eqn (20.16) it follows that

$$\frac{\partial S}{\partial t} = -H(q_i, p_i), \quad p_i = \frac{\partial S}{\partial q_i}, \quad (i = 1, 2, \dots, s)$$

and by combining these equations one gets a single equation

$$\frac{\partial S(q, t)}{\partial t} + H\left(q_i, \frac{\partial S}{\partial q_i}, t\right) = 0. \quad (20.17)$$

Equation (20.17) is known as the *Hamilton–Jacobi equation*. The function S is called Hamilton's principal function. It is quite remarkable that a single equation, which is however a non-linear differential equation, in general difficult to solve, replaces s Euler–Lagrange equations, or $2s$ canonical equations.

20.1.6 Adiabatic invariants

A notion of particular importance in classical mechanics is that of *adiabatic invariants*. Use of such quantities has played a key role in the discovery of quantum mechanics.

Consider a periodic motion. The trajectories $p(q)$ in the phase space—the solutions of the equation of motion—form closed curves. Suppose that one or more parameters in the system vary in time. We indicate them collectively by α . Trajectories will no longer be exactly closed curves but for sufficiently slow variations of α they will be approximately so for many periods, and it makes sense to define a quantity, integrated over a period,

$$I(\alpha) \equiv \oint dq p, \quad (20.18)$$

as a function of α . It can be shown [Landau and Lifshitz (1976 a)] in general that $I(\alpha)$ is invariant, i.e., does not depend on α when the latter varies slowly. It is an *adiabatic invariant*.²

²To be more precise, if the variation of α during a time interval T is $\Delta\alpha \sim \dot{\alpha}T$, the variation of I is of the order $\Delta I \sim \dot{\alpha}\Delta\alpha$ and tends to zero as $\dot{\alpha} \rightarrow 0$.

Instead of proving the theorem in general we shall consider the example of a pendulum with mass m and with arm length L , attached to a pulley so that L can be varied smoothly (Figure 20.1). For small amplitudes it is well known that the horizontal oscillations are described as an harmonic motion ($x \equiv L\theta$)

$$H = \frac{1}{2} m \dot{x}^2 + m g L (1 - \cos \theta) = \frac{1}{2} m \dot{x}^2 + \frac{1}{2} m \omega^2 x^2 + \dots$$

where

$$\omega = \sqrt{\frac{g}{L}}. \quad (20.19)$$

The solution of the equation of motion is

$$x(t) = A \sin(\omega t + \varphi). \quad (20.20)$$

The oscillation energy is given by

$$H = E = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2 = \frac{1}{2} m \omega^2 A^2.$$

We leave it as an exercise to show that for an oscillator

$$I(L) = 2\pi \frac{E}{\omega}. \quad (20.21)$$

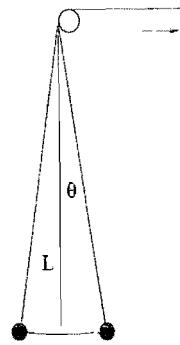


Fig. 20.1 A pendulum

Suppose now that we slowly pull the string so that the arm-length L is slowly varied, $L \rightarrow L - \delta L$. How do the oscillation energy and the frequency vary? Variation of frequency is explicitly given by eqn (20.19)

$$\delta\omega = \frac{\omega}{2} \frac{\delta L}{L}. \quad (20.22)$$

Energy variation can be found as follows. As both the amplitude A and the frequency ω vary, we shall calculate the work needed (or the work done) during the change of L to $L - \delta L$. The average tension of the string is

$$T = \overline{mg \cos \theta + mL \dot{\theta}^2} \simeq mg - \frac{1}{2} \frac{mg}{L^2} x^2 + \frac{m}{L} \dot{x}^2.$$

By using the solution (20.20) one easily finds that

$$T = mg + \frac{mg A^2}{4L^2}.$$

The work needed to shorten the arm of pendulum by δL is therefore

$$\delta W = T \delta L = mg \delta L + \frac{mg A^2}{4L^2} \delta L.$$

However, not all of the work is used up to change the oscillation energy: a part of the work is used to raise the mass of the pendulum (we shall neglect the mass of the string) by δL , i.e., to increase the potential

energy. By subtracting the latter, the net increase of the oscillation energy is:

$$\delta E = \frac{m g A^2}{4 L^2} \delta L.$$

It follows that

$$\delta E = \frac{E \delta L}{2 L}.$$

By using this and eqn (20.22) we find that

$$\frac{E}{\omega} = \text{const.}$$

³This example, in this context, was proposed by Einstein in the first Solvay Conference.

showing that $I(L)$, eqn (20.21), is indeed invariant under adiabatic variations of L .³

20.1.7 The virial theorem

A theorem which turns out to have many useful applications, is the so-called virial theorem. Consider a particle which undergoes a motion in a potential $V(\mathbf{r})$. Multiplying the Newton's equation by \mathbf{r} we have

$$m \ddot{\mathbf{r}} = -\nabla V(\mathbf{r}), \quad \Rightarrow \quad m \mathbf{r} \cdot \ddot{\mathbf{r}} = -\mathbf{r} \cdot \nabla V(\mathbf{r}).$$

Take the time average of the second formula above over an interval $(-T/2, T/2)$ much longer than the typical period of the motion. We obtain

$$\frac{1}{T} \overline{m \mathbf{r} \cdot \dot{\mathbf{r}}} \Big|_{T/2}^{T/2} - \overline{m \dot{\mathbf{r}}^2} = -\overline{\mathbf{r} \cdot \nabla V(\mathbf{r})}.$$

The first term vanishes for a finite motion in the limit $T \rightarrow \infty$ and we find that

$$\overline{m \dot{\mathbf{r}}^2} = \overline{\mathbf{r} \cdot \nabla V(\mathbf{r})}, \quad (20.23)$$

that is mean kinetic energy is equal to the time average of $\frac{1}{2} \mathbf{r} \cdot \nabla V(\mathbf{r})$. If the potential is homogeneous in r with degree ν Euler's theorem tells us that

$$\mathbf{r} \cdot \nabla V(\mathbf{r}) = \nu V(\mathbf{r}).$$

In such a case the theorem (20.23) yields a relation between average kinetic term and average potential energy

$$\overline{\frac{1}{2} m \dot{\mathbf{r}}^2} = \frac{\nu}{2} \overline{V(\mathbf{r})}.$$

20.2 The Hamiltonian of electromagnetic radiation field in the vacuum

As a warm-up exercise let us first consider a string, spun between the two end points which are fixed at $x = 0$ and at $x = R$. The Lagrangian is given by

$$L = \int_0^R dx (\dot{A}^2 - A'^2). \quad (20.24)$$

We expand $A(x)$ in Fourier components,

$$A(x) = \sum_{n=0}^{\infty} q_n(t) \sin(\pi n x / R),$$

consistently with the boundary condition. The coefficients q_n can be treated as generalized coordinates. Substituting this in eqn (20.24), and integrating over x one finds that

$$L = \frac{R}{2} \sum_{n=0}^{\infty} (\dot{q}_n^2 - k_n^2 q_n^2); \quad k_n = \frac{\pi n}{R},$$

or, by rescaling $\sqrt{R} q_n \rightarrow q_n$,

$$L = \frac{1}{2} \sum_{n=0}^{\infty} (\dot{q}_n^2 - k_n^2 q_n^2).$$

The Hamiltonian is introduced in the standard manner

$$H = \sum_n p_n \dot{q}_n - L, \quad p_n \equiv \frac{\partial L}{\partial \dot{q}_n},$$

and is

$$H = \frac{1}{2} \sum_{n=0}^{\infty} (p_n^2 + k_n^2 q_n^2); \quad k_n = \frac{\pi n}{R}, \quad n = 1, 2, \dots$$

The system is equivalent to an infinite number of uncoupled harmonic oscillators.

The description of electromagnetic field is analogous. The Lagrangian is

$$L = \frac{1}{8\pi} \int_V (\mathbf{E}^2 - \mathbf{H}^2) dv \quad (20.25)$$

with

$$\mathbf{E} = -\frac{1}{c} \frac{\partial}{\partial t} \mathbf{A}; \quad \mathbf{H} = \nabla \times \mathbf{A}, \quad (\phi = 0; \nabla \cdot \mathbf{A} = 0), \quad (20.26)$$

In order to simplify the analysis we put the system in a box, with each edge of length L . In order to simulate an isolated cavity we adopt the boundary conditions⁴ corresponding to perfect reflection: we require that the Poynting vector lie on the face of the box at the boundaries. This corresponds to selecting a particular set of Fourier components,

$$\begin{aligned} A_1(\mathbf{r}) &= \sum_{\mathbf{n}} q_1(\mathbf{n}; t) \sin \frac{\pi n_1 x}{L} \cos \frac{\pi n_2 y}{L} \cos \frac{\pi n_3 z}{L}; \\ A_2(\mathbf{r}) &= \sum_{\mathbf{n}} q_2(\mathbf{n}; t) \cos \frac{\pi n_1 x}{L} \sin \frac{\pi n_2 y}{L} \cos \frac{\pi n_3 z}{L}; \\ A_3(\mathbf{r}) &= \sum_{\mathbf{n}} q_3(\mathbf{n}; t) \cos \frac{\pi n_1 x}{L} \cos \frac{\pi n_2 y}{L} \sin \frac{\pi n_3 z}{L}, \end{aligned} \quad (20.27)$$

where $\mathbf{n} = (n_1, n_2, n_3)$, and n_i are non-negative integers. This can be easily verified considering $\mathbf{E} = -\frac{1}{c} \frac{\partial}{\partial t} \mathbf{A}$, $\mathbf{B} = \nabla \times \mathbf{A}$, and $\mathbf{E} \times \mathbf{B}$ at

⁴The bulk properties of the system do not depend on boundary conditions, we adopt a cavity with perfect reflecting boundaries for definiteness.

the boundaries, e.g. $x = 0$, $x = L$. We furthermore impose the gauge $\nabla \cdot \mathbf{A} = 0$ which means

$$\mathbf{q}_n \cdot \mathbf{n} = 0.$$

These constraints are solved by

$$\mathbf{q}_n = Q_{1n}\mathbf{i} + Q_{2n}\mathbf{j}, \quad \mathbf{n} = n\hat{\mathbf{n}},$$

where unit vectors $\hat{\mathbf{n}}, \mathbf{i}, \mathbf{j}$ satisfy

$$\hat{\mathbf{n}} \perp \mathbf{i} = \hat{\mathbf{n}} \perp \mathbf{j} = \mathbf{i} \perp \mathbf{j}, \quad \hat{\mathbf{n}} \times \mathbf{i} = \mathbf{j}, \quad \hat{\mathbf{n}} \times \mathbf{j} = -\mathbf{i}.$$

Q_{1n}, Q_{2n} are independent variables.

Substitute now eqn (20.27) into eqns (20.25) and (20.26) and integrate over $0 \leq x \leq L : 0 \leq y \leq L ; 0 \leq z \leq L$. The result is:

$$L = \frac{1}{8\pi} \left(\frac{L}{2} \right)^3 \left\{ \sum_n \frac{1}{c^2} \left(\dot{Q}_{1n}^2 + \dot{Q}_{2n}^2 \right) - \sum_n k_n^2 (Q_{1n}^2 + Q_{2n}^2) \right\},$$

where $k_n \equiv \pi n / L$. A rescaling of Q_{in} by a constant and a successive Legendre transform yields the Hamiltonian

$$H = \sum_k \left(\frac{c^2}{4} p_{(1)}^2 + k^2 Q_{(1)}^2 \right) + \sum_k \left(\frac{c^2}{4} p_{(2)}^2 + k^2 Q_{(2)}^2 \right),$$

which represents two infinite sets of independent oscillators.

20.3 Orthogonality and completeness in a system with a one-dimensional delta function potential

Consider the one-dimensional system,

$$H = \frac{p^2}{2m} - g \delta(x), \quad g > 0, \quad (20.28)$$

already discussed in Chapter 3 where we have found:

- A bound state, eqn (3.56):

$$\kappa = \frac{mg}{\hbar^2}, \quad E_0 = -\frac{mg^2}{2\hbar^2}, \quad \psi^{(0)}(x) = \begin{cases} \sqrt{\kappa} e^{\kappa x} & x < 0 \\ \sqrt{\kappa} e^{-\kappa x} & x > 0, \end{cases}.$$

- The states in the continuum, eqn (3.57):

$$E = \frac{k^2 \hbar^2}{2m}, \quad \psi(x) = \begin{cases} A e^{ikx} + B e^{-ikx}, & x < 0 \\ C e^{ikx} + D e^{-ikx}, & x > 0, \end{cases}$$

with

$$\begin{pmatrix} C \\ D \end{pmatrix} = \Omega \begin{pmatrix} A \\ B \end{pmatrix}, \quad \text{and} \quad \begin{pmatrix} A \\ B \end{pmatrix} = \Omega^{-1} \begin{pmatrix} C \\ D \end{pmatrix},$$

The transition matrix Ω is given by:

$$\Omega = \begin{pmatrix} 1 + i\alpha & i\alpha \\ -i\alpha & 1 - i\alpha \end{pmatrix}, \quad \Omega^{-1} = \begin{pmatrix} 1 - i\alpha & -i\alpha \\ i\alpha & 1 + i\alpha \end{pmatrix},$$

where

$$\alpha = \frac{mg}{k\hbar^2} = \frac{\kappa}{k} > 0.$$

For any real value of k these represent continuous eigenstates of H .

For physical applications and for the following considerations it is convenient to introduce the right-mover states R , corresponding to the particle incident from $x = -\infty$, and the left-mover states L , describing a particle entering from $x = +\infty$. They are analogous to the two independent plane waves $e^{\pm ikx}$ in the free case. They can be formed by setting either $D = 0$ or $A = 0$:

$$\psi_k^{(R)}(x) = \begin{cases} \frac{1}{\sqrt{2\pi}} [e^{ikx} - F(k) e^{-ikx}], & x < 0, \\ \frac{1}{\sqrt{2\pi}} (1 - F(k)) e^{ikx}, & x > 0, \end{cases}$$

$$\psi_k^{(L)}(x) = \begin{cases} \frac{1}{\sqrt{2\pi}} (1 - F(k)) e^{-ikx}, & x < 0, \\ \frac{1}{\sqrt{2\pi}} [e^{-ikx} - F(k) e^{ikx}], & x > 0, \end{cases}$$

where

$$F(k) = \frac{1}{1 + ik/\kappa}.$$

In these formulas we can restrict ourselves to $k \geq 0$. Normalization has been fixed so that the orthonormality relation takes the standard form.

20.3.1 Orthogonality

Orthogonality between the discrete state and those in the continuum

From

$$\kappa \pm ik = \frac{mg}{\hbar^2} \pm ik = \pm ik(1 \mp i\alpha)$$

one finds that

$$\begin{aligned} \langle \psi_{cont} | \psi_{dis} \rangle &= \int_{-\infty}^0 dx [A^* e^{-ikx} + B^* e^{ikx}] e^{\kappa x} \\ &\quad + \int_0^\infty dx [C^* e^{-ikx} + D^* e^{ikx}] e^{-\kappa x} \\ &= \frac{A^*}{\kappa - ik} + \frac{B^*}{\kappa + ik} + \frac{C^*}{\kappa + ik} + \frac{D^*}{\kappa - ik} \\ &= \frac{A^* + D^*}{\kappa - ik} + \frac{B^* + C^*}{\kappa + ik} = \frac{1}{-ik}(C^* + D^*) + \frac{1}{ik}(C^* + D^*) = 0. \end{aligned}$$

The bound state is indeed orthogonal to the states of the continuum.

Orthogonality between the states in the continuum

Consider first two states of type R :

$$\begin{aligned} {}_R\langle k'|k \rangle_R &= \frac{1}{2\pi} \int_{-\infty}^0 dx \left[e^{-ik'x} - F^*(k) e^{ik'x} \right] \left[e^{ikx} - F(k) e^{-ikx} \right] \\ &\quad + \frac{1}{2\pi} \int_0^\infty dx [1 - F^*(k)] (1 - F(k)) e^{-ik'x} e^{ikx}. \end{aligned}$$

By using

$$\int_{-\infty}^0 dx e^{ikx} = \lim_{\epsilon \rightarrow 0+} \int_{-\infty}^0 dx e^{ikx+\epsilon x} = \lim_{\epsilon \rightarrow 0+} \frac{1}{\epsilon + ik} = \pi \delta(k) - i \frac{\mathcal{P}}{k},$$

(\mathcal{P} indicates Cauchy's principal value) one has

$$\begin{aligned} {}_R\langle k'|k \rangle_R &= \frac{1}{2\pi} \left[\pi \delta(k - k') - i \frac{\mathcal{P}}{k - k'} \right. \\ &\quad - F(k) \left(\pi \delta(k + k') + i \frac{\mathcal{P}}{k + k'} \right) - F(k')^* \left(\pi \delta(k + k') - i \frac{\mathcal{P}}{k + k'} \right) \\ &\quad + F(k')^* F(k) \left(\pi \delta(k - k') + i \frac{\mathcal{P}}{k - k'} \right) \\ &\quad \left. + [1 - F(k')^*] [1 - F(k)] \left(\pi \delta(k - k') + i \frac{\mathcal{P}}{k - k'} \right) \right]. \end{aligned}$$

Noting that

$$\delta(k + k') = 0; \quad 1 + F(k')^* F(k) + (1 - F(k')^*)(1 - F(k))|_{k=k'} = 2;$$

$$1 - F(k')^* F(k) - (1 - F(k')^*)(1 - F(k)) = \frac{i(k - k')/\kappa}{(1 + ik/\kappa)(1 - ik'/\kappa)},$$

$$F(k) - F(k')^* = -\frac{i(k + k')/\kappa}{(1 + ik/\kappa)(1 - ik'/\kappa)},$$

and by using

$$(k + k') \frac{\mathcal{P}}{k + k'} = (k - k') \frac{\mathcal{P}}{k - k'} = 1,$$

one finds

$${}_R\langle k'|k \rangle_R = \delta(k - k').$$

An analogous calculation show that

$${}_L\langle k'|k \rangle_L = \delta(k - k'), \quad {}_L\langle k'|k \rangle_R = {}_R\langle k'|k \rangle_L = 0.$$

20.3.2 Completeness

Let us now illustrate the completeness relation, eqn (2.48),

$$\sum_n \psi_n(q) \psi_n^*(q') + \int df \psi_f(q) \psi_f^*(q') = \delta(q - q')$$

which in this case involves both a bound state and the continuum. Consider first the continuum contribution:

$$\int_0^\infty dk \psi_k^{(R)}(x) \psi_k^{(R)*}(x') + \int_0^\infty dk \psi_k^{(L)}(x) \psi_k^{(L)*}(x').$$

For $x > 0, x' > 0$ we find that

$$\begin{aligned} \int_0^\infty dk \psi_k^{(R)}(x) \psi_k^{(R)*}(x') &= \frac{1}{2\pi} \int_0^\infty dk \{1 - F(k)\} \{1 - F^*(k)\} e^{ik(x-x')} \\ &= \frac{1}{2\pi} \int_0^\infty dk \left[1 + \frac{i\kappa}{k-i\kappa} - \frac{i\kappa}{k+i\kappa} + \frac{\kappa^2}{(k-i\kappa)(k+i\kappa)} \right] e^{ik(x-x')} \\ &= \frac{1}{2\pi} \int_0^\infty dk \left[1 - \frac{\kappa^2}{(k-i\kappa)(k+i\kappa)} \right] e^{ik(x-x')}, \end{aligned}$$

$$\begin{aligned} \int_0^\infty dk \psi_k^{(L)}(x) \psi_k^{(L)*}(x') &= \frac{1}{2\pi} \int_0^\infty dk \left[e^{-ikx} - F(k)e^{ikx} \right] \left[e^{ikx'} - F(k)e^{-ikx'} \right] \\ &= \frac{1}{2\pi} \int_0^\infty dk \left[e^{-ik(x-x')} + \frac{i\kappa}{k-i\kappa} e^{ik(x+x')} - \frac{i\kappa}{k+i\kappa} e^{-ik(x+x')} \right. \\ &\quad \left. + \frac{\kappa^2}{(k-i\kappa)(k+i\kappa)} e^{ik(x-x')} \right], \end{aligned}$$

and therefore

$$\begin{aligned} \int_0^\infty dk &\left[\psi_k^{(R)}(x) \psi_k^{(R)*}(x') + \psi_k^{(L)}(x) \psi_k^{(L)*}(x') \right] \\ &= \frac{1}{2\pi} \int_{-\infty}^\infty dk \left[e^{ik(x-x')} + \frac{i\kappa}{k-i\kappa} e^{ik(x+x')} \right] \\ &= \delta(x-x') - \kappa e^{-\kappa(x+x')} = \delta(x-x') - \psi^{(0)}(x) \psi^{(0)*}(x'), \quad (20.29) \end{aligned}$$

where the second integral has been computed with theorem of residues. We have thus obtained explicitly (for $x > 0, x' > 0$) the completeness relation

$$\psi^{(0)}(x) \psi^{(0)*}(x') + \int_0^\infty dk \left[\psi_k^{(R)}(x) \psi_k^{(R)*}(x') + \psi_k^{(L)}(x) \psi_k^{(L)*}(x') \right] = \delta(x-x').$$

For $x < 0, x' > 0$ the contribution of the continuum is

$$\begin{aligned} \int_0^\infty dk &\left[\psi_k^{(R)}(x) \psi_k^{(R)*}(x') + \psi_k^{(L)}(x) \psi_k^{(L)*}(x') \right] \quad (20.30) \\ &= \frac{1}{2\pi} \int_0^\infty dk \left(\left[e^{ikx} - F(k) e^{-ikx} \right] (1 - F^*(k)) e^{-ikx'} + \right. \\ &\quad \left. + (1 - F(k)) e^{-ikx} \left[e^{ikx'} - F^*(k) e^{-ikx'} \right] \right) \\ &= \frac{1}{2\pi} \int_{-\infty}^\infty dk \left(e^{ik(x-x')} - \frac{i\kappa}{k+i\kappa} e^{ik(x-x')} \right) \\ &= \delta(x-x') - \kappa e^{\kappa(x-x')} = \delta(x-x') - \psi^{(0)}(x) \psi^{(0)*}(x'), \end{aligned}$$

which is again the correct answer.

In the case of a repulsive $\delta(x)$ potential, which corresponds to sign $g < 0$ in eqn (20.28), there are no bound states, so the completeness relation must be saturated by the continuum. The proof is simple. The only change as compared to the previous analysis is that now $\kappa < 0$. The passages up to eqn (20.29) remain unmodified, as the manipulations involve algebraic cancellations only. In the second term of eqn (20.29), for $x > 0, x' > 0$, however, the pole of the integrand is now in the upper half plane, the integration over k now gives zero for $x + x' > 0$ by virtue of Cauchy's theorem, so

$$\int_0^\infty dk \left[\psi_k^{(R)}(x) \psi_k^{(R)*}(x') + \psi_k^{(L)}(x) \psi_k^{(L)*}(x') \right] = \delta(x - x')$$

as expected. A similar result holds for eqn (20.30).

20.4 The S matrix; the wave packet description of scattering

⁵We shall assume that the potential tends to zero sufficiently fast as $|x| \rightarrow \infty$.

A scattering process is clearly a time-dependent process, in which a wave packet, associated with a particle with a momentum defined within certain precision, enter the region of the potential⁵ and after some time reappears as a free particle far from the interaction region, where it can be described again as a wave packet with a more or less well defined momentum. At $t \rightarrow -\infty$ and at $t \rightarrow +\infty$ the state of the particle should be describable in terms of solutions of free Schrödinger's equation. Our interest is in the probability of finding the particle in some state $|\beta\rangle$ after the scattering, knowing that the particle was initially in a state $|\alpha\rangle$.

Let S be the time evolution operator $e^{-iHt/\hbar}$ during the time interval $-T, T$ in the limit $T \rightarrow \infty$. The amplitude we are looking for is

$$\langle \beta | S | \alpha \rangle. \quad (20.31)$$

The operator S is called *S matrix*.

Now let us ask the following question: knowing the solution of the *time-independent* Schrödinger's equation how can one construct the S matrix? This would allow us to translate a complicate time-dependent problem into a relatively simple time-independent problem. We would lose some information on the details of the time evolution, but if we are only interested in amplitudes like (20.31) the time-independent solution should be sufficient.

20.4.1 The wave packet description

Let us consider a wave packet constructed as

$$\varphi(x) = \int dk f(k) \psi_R(k, x), \quad (20.32)$$

where $\psi_R(k, x)$ is a “right-mover” solution of the time independent Schrödinger’s equation with asymptotic behavior

$$\psi_R(x) \xrightarrow{x \rightarrow -\infty} e^{ikx} + A_R e^{-ikx}; \quad \psi_R(x) \xrightarrow{x \rightarrow \infty} A_T e^{ikx}. \quad (20.33)$$

(eqn (3.72)) and $f(k)$ is a function sharply peaked at some value of k , $k = k_0$ (positive). How does such a solution evolve in time? The eigenvalue of the energy is $k^2/2m$ (by setting $\hbar = 1$) so it will evolve as

$$\varphi(x, t) = \int dk f(k) \psi_R(k, x) e^{-itk^2/2m}. \quad (20.34)$$

Let us first consider t large and negative. The phase factor $e^{-itk^2/2m}$ in (20.34) oscillates very rapidly and the only contribution to the integral will come from a region of stationary phase, where the phase of ψ_R cancels this contribution. ψ_R has a large phase in the asymptotic region, i.e. for large $|x|$.

In particular,

- (1) In the region far to the right from the potential the phase of ψ_R , see eqn (20.33), is positive and large, i.e. $+ikx$, and cannot cancel the large positive phase $-i\frac{k^2}{2m}t$.
- (2) In the region far to the left, there are two contributions to ψ_R , see eqn (20.33). The only contribution with the needed large negative phase from the “incident wave” e^{ikx} . The center of the wave packet is at $x \sim k_0 t/m$.

Thus at large negative times, the solution describes an incoming free wave packet with momentum centered at k_0 , traveling towards right. If the momentum distribution were given by a Dirac’s delta function peaked at k_0 such a packet would reduce to the plane wave $e^{ik_0 x}$ which we have identified with the incident wave in the time-independent treatment of the scattering problem in Section 3.5.3.

At fixed energy, this part of solution (defined at $t \rightarrow -\infty$) specifies the ket $|\alpha\rangle$.

Let us now consider large positive times. The phase $-itk^2/2m$ is now large and negative. Analyzing the two asymptotic regions as before, we find that:

- (1) In the region to the right of the potential, $x \rightarrow +\infty$, the phase of ψ_R is positive: the wave packet is at $x \sim k_0 t/m$.
- (2) On the left of the potential, $x \rightarrow -\infty$, only the term $A_R \exp(-ikx)$ contributes now. The wave packet is at $x \sim -k_0 t/m$.

So long after the particle has left the interaction region the solution (20.32) describes a superposition of two wave packets, one moving to the right towards $x = \infty$ with the amplitude A_T , the other on the left of the potential moving toward $x = -\infty$ with the amplitude A_R . As the states propagating towards right ($|1\rangle$) and left ($|2\rangle$) together form

a complete set of states for the free particle, we can parametrize the S matrix in this basis. In this basis then

$$S_{11} = A_T \quad S_{21} = A_R$$

where the incident wave $|1\rangle$ corresponds to the “in” state, the outgoing states at $t \rightarrow \infty$ correspond to the “out” states.

Of course, we could have considered equally well the particle incident from the right, corresponding to a static solution having the asymptotic behavior,

$$x \rightarrow -\infty : a e^{-ikx} \quad x \rightarrow +\infty : e^{-ikx} + b e^{ikx}; \quad (20.35)$$

the “in” state being now $|2\rangle$. At large negative time the wave packet is on the right of the potential, moving towards the center of the potential; at large positive times the solution (similar to eqn (20.34) with $f(k)$ distributed around the central momentum $-k_0$) describes two wave packets, a “scattered wave” moving towards left with the amplitude a and the “reflected wave” moving back towards $x = +\infty$, with the amplitude, b . In other words,

$$S_{12} = b, \quad S_{22} = a,$$

thus

$$S = \begin{pmatrix} A_T & b \\ A_R & a \end{pmatrix}.$$

a and b can be determined from the definition of Ω given in Section 3.5.3

$$\begin{pmatrix} b \\ 1 \end{pmatrix} = \Omega \begin{pmatrix} 0 \\ a \end{pmatrix} \Rightarrow a = A_T, \quad b = -\frac{A_R^*}{A_T^*} A_T, \quad (20.36)$$

and so

$$S = \begin{pmatrix} A_T & -\frac{A_R^*}{A_T^*} A_T \\ A_R & A_T \end{pmatrix}.$$

It can be readily seen that the constraint $|A_R|^2 + |A_T|^2 = 1$ amounts to the unitarity condition

$$S S^\dagger = S^\dagger S = 1. \quad (20.37)$$

For simplicity we have considered only states with fixed energy, as in the scattering problem the energy remains a constant of motion. The energy eigenvalue for a free particle ($k^2/2m$) is doubly degenerate, $\exp(\pm ikx)$. The two states have been indicated as $|1\rangle, |2\rangle$ above. The operator S considered as an operator acting on the entire Hilbert space has matrix elements of the form

$$\langle E, \alpha | S | E', \beta \rangle = \delta_{E, E'} S_{\alpha\beta}.$$

Operator S is unitary on the whole Hilbert space, not only as a 2×2 matrix in a subspace of a given energy. In the following we shall continue

to talk about such a reduced S matrices, understanding that the operator acts on states with definite energy.

Let us note that it is always possible to choose a basis so as to diagonalize the matrix $S_{\alpha\beta}$. This choice is particularly interesting if the diagonalization corresponds to the choice of an observable, this is the case for a potential invariant under parity.

For a free Hamiltonian the parity eigenstates are

$$\text{Parity} = +1 : \frac{1}{\sqrt{2}}(1, 1); \quad \text{Parity} = -1 : \frac{1}{\sqrt{2}}(1, -1)$$

that is the standing waves $\cos(kx)$ and $\sin(kx)$. If parity is a good quantum number it will commutes with the Hamiltonian, so in such a basis S must be diagonal. Parity transformation interchange left and right movers then from eqn (20.35) $a = A_T$ and $b = A_R$. Using eqn (20.36) we deduce $A_R = -\frac{A_R^*}{A_T^*} A_T$. For the S matrix indicating with e and o the even and odd states

$$\begin{aligned} S_{ee} &= \frac{1}{2}(1, 1)S\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{2}\left(2A_T + A_R - \frac{A_R^*}{A_T^*}A_T\right) = A_T + A_R; \\ S_{eo} &= \frac{1}{2}(1, 1)S\begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{2}\left(\frac{A_R^*}{A_T^*}A_T + A_R\right) = 0; \\ S_{oe} &= \frac{1}{2}(1, -1)S\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{2}\left(-\frac{A_R^*}{A_T^*}A_T - A_R\right) = 0; \\ S_{oo} &= \frac{1}{2}(1, -1)S\begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{2}\left(2A_T + \frac{A_R^*}{A_T^*}A_T - A_R\right) = A_T - A_R. \end{aligned} \quad (20.38)$$

In the last equality use was made of eqn (3.81). In terms of the parametrization (3.82) we have:

$$S = \begin{pmatrix} e^{i(\theta+\alpha)} & 0 \\ 0 & e^{i(\theta-\alpha)} \end{pmatrix}.$$

The diagonal elements of S are just phases, $e^{i\varphi}$. The notation commonly used is

$$S_{\text{diag}} = \exp(2i\delta); \quad (20.39)$$

the phase δ is called *phase shift*.

Examples

- (1) Let us consider the scattering from a potential well (studied in Section 3.5.1). Setting $\hbar k' = \sqrt{2m(E + |V_0|)}$ we have (see eqn (3.50)):

$$\begin{aligned} A_R &= -e^{-ika} \frac{i(k^2 - k'^2) \sin k'a}{2kk' \cos k'a - i(k^2 + k'^2) \sin k'a}; \\ A_T &= e^{-ika} \frac{2kk'}{2kk' \cos k'a - i(k^2 + k'^2) \sin k'a}. \end{aligned}$$

From eqn (20.38) it follows that

$$S_{pp} = e^{-ika} \frac{k \cos \frac{k'a}{2} + i k' \sin \frac{k'a}{2}}{k \cos \frac{k'a}{2} - i k' \sin \frac{k'a}{2}}, \quad (20.40a)$$

$$S_{dd} = -e^{ika} \frac{k \sin \frac{k'a}{2} + i k' \cos \frac{k'a}{2}}{k \sin \frac{k'a}{2} - i k' \cos \frac{k'a}{2}}. \quad (20.40b)$$

Let us consider even waves and take S as a function of the energy. The presence of the factor $k \propto \sqrt{E}$ shows that the function $S(E)$ has a cut in the complex plane. The convention used normally is that of setting

$$ik = -\sqrt{-2mE} \quad (20.41)$$

which means that the cut is chosen to be along the real positive axis, $\text{Re}(E) > 0$.

The function $S(E)$ has poles where the denominator vanishes (see eqn (20.40a)):

$$\frac{\sqrt{-E}}{\sqrt{E + |V_0|}} = \tan \left[\frac{\sqrt{2m(E + |V_0|)}a}{2\hbar} \right]. \quad (20.42)$$

In writing eqn (20.42) we have used eqn (20.41). The condition (20.42) is exactly the condition to have an even bound state with the energy $E = -|E|$ in the potential well being considered (eqn (3.20)). In other words, $S(E)$ has poles on the negative real axis, corresponding to the (even) bound states of the system.

Analogously the reader can easily verify that the $S_o(E)$ has poles on the negative axis when the system has odd bound states.

- (2) The delta function potential. From the analysis of subsection 3.5.2 one has (see eqn (3.63))

$$\alpha = \frac{mg}{k\hbar^2}; \quad \Omega = \begin{pmatrix} 1 - i\alpha & -i\alpha \\ i\alpha & 1 + i\alpha \end{pmatrix} \Rightarrow A_R + A_T = \frac{1 + i\alpha}{1 - i\alpha}.$$

Again the pole $\alpha = -i$, by using eqn (20.41), yields the energy of the bound state $E = -mg^2/2\hbar^2$, in agreement with the result (3.55). In the case of the potential barrier ($\alpha \rightarrow -\alpha$) the pole of the S matrix lies in the second Riemann sheet, see eqn (20.41).

20.5 Legendre polynomials

To start with let us consider eqn (4.18) for $m = 0$. It is (by setting $x = \cos \theta$)

$$\left\{ \frac{d}{dx} (1 - x^2) \frac{d}{dx} + \ell(\ell + 1) \right\} \Theta = 0,$$

or

$$(1 - x^2)\Theta'' - 2x\Theta' + \ell(\ell + 1)\Theta = 0. \quad (20.43)$$

One of the solutions $P_\ell(x)$ can be taken to be finite in the interval $-1 \leq x \leq 1$: it is called Legendre polynomial. (The other solution $Q_\ell(x)$ is singular at $x = \pm 1$.)

As in the case of Hermite polynomials the properties of the Legendre polynomials can be studied by the help of a generating function which, in this case, is given by

$$T(x, s) = (1 - 2sx + s^2)^{-\frac{1}{2}} = \sum_{\ell=0}^{\infty} P_\ell(x) s^\ell, \quad s < 1, \quad (20.44)$$

where s is an arbitrary parameter. By expanding (20.44) in powers of s the first Legendre polynomials can be easily found

$$\begin{aligned} P_0(x) &= 1, \quad P_1(x) = x, \quad P_2(x) = \frac{1}{2}(3x^2 - 1), \\ P_3(x) &= \frac{1}{2}(4x^3 - 3x), \quad P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3). \end{aligned}$$

etc. A simple and explicit formula for $P_\ell(x)$ is known (Rodriguez's formula)

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{dx^\ell} (x^2 - 1)^\ell. \quad (20.45)$$

The polynomials $P_\ell(x)$ are normalized according to the condition

$$\int_{-1}^1 dx P_\ell(x) P_{\ell'}(x) = \frac{2}{2\ell + 1} \delta_{\ell, \ell'},$$

and satisfy furthermore

$$P_\ell(1) = 1; \quad P_\ell(-1) = (-1)^\ell.$$

That the polynomials $P_\ell(x)$ defined by eqn (20.44) satisfy Legendre's equation follows from the recursion relations which can be constructed by considering $\partial T(x, s)/\partial x$ and $\partial T(x, s)/\partial s$.

Another convenient representation of the Legendre polynomials is the formula (Schläfli's formula)

$$P_\ell(z) = \frac{1}{2\pi i} \oint \frac{(t^2 - 1)^\ell}{2^\ell (t - z)^{\ell+1}} dt,$$

where the integration contour is a closed curve encircling the point z . It is easy to show that

$$(1 - z^2)P_\ell(z)'' - 2zP_\ell(z)' + \ell(\ell + 1)P_\ell(z) = \frac{\ell + 1}{2\pi i} \oint dt \frac{d}{dt} \left[\frac{(t^2 - 1)^{\ell+1}}{2^\ell (t - z)^{\ell+2}} \right] = 0.$$

Rodriguez's formula (20.45) follows immediately from this representation by using the residue theorem.

The associated Legendre polynomials $P_\ell^m(x)$ can be obtained from $P_\ell(x)$ via the relation

$$P_\ell^m(x) = (1 - x^2)^{m/2} \frac{d^m}{dx^m} P_\ell(x).$$

The fact that $P_\ell^m(x)$ is the regular solution of eqn (4.18) can be shown by performing m derivations d^m/dx^m of eqn (20.43) and considering the equation for $(1 - x^2)^{m/2} d^m/dx^m \Theta$. (see [Whittaker and Watson (1927)]).

20.6 Groups and representations

20.6.1 Group axioms; some examples

A set G in which an operation called *product* or *multiplication*

$$a \in G, \quad b \in G \quad \rightarrow \quad c = a \cdot b \in G,$$

is defined for each pair of its elements, is called a *group* if the following axioms are satisfied:

- (1) associativity of the product:

$$(a \cdot b) \cdot c = a \cdot (b \cdot c);$$

- (2) existence of the unit element, e , such that

$$e \cdot a = a$$

for each element $a \in G$;

- (3) each element a possesses an (left) inverse a^{-1} ,

$$a^{-1} \cdot a = e.$$

A group G is Abelian (commutative) if the relation

$$a \cdot b = b \cdot a,$$

holds for each pair of its elements; otherwise, the group is non-Abelian (non-commutative).

Examples

- (i) The set of all integer numbers form a (commutative) group under the addition: the group "product" is defined in this case by

$$n \cdot m \equiv n + m,$$

with the unit element equal to the number 0, the inverse of n being equal to $-n$.

- (ii) The group of permutations of e.g., three objects (A, B, C) in three distinct positions 1, 2, 3 have the following elements:

$$\begin{aligned} e &: (ABC) \rightarrow (ABC); \\ (12) &: (ABC) \rightarrow (BAC); \\ (23) &: (ABC) \rightarrow (ACB); \\ (31) &: (ABC) \rightarrow (CBA); \\ (123) &: (ABC) \rightarrow (CAB); \\ (321) &: (ABC) \rightarrow (BCA). \end{aligned}$$

The multiplication rule can be found directly., i.e., $(12) \cdot (23) = (123)$; $(23) \cdot (123) = (31)$; etc. (N.B. in a product of two operations the one on the right must be performed first.) This group is indicated as S_3 . The group of permutations of N objects is called S_N .

- (iii) The set of regular complex $N \times N$ matrices with unit determinant

$$G = \{M : \det M = 1\},$$

in which multiplication is defined by the usual matrix multiplication rule, forms a group called the *special linear group*, $SL(N, \mathbb{C})$. ($SL(N, \mathbb{R})$ indicates the real special linear group.) The set of regular matrices without the condition of unit determinant also form a group called the *general linear group*, either real or complex, $GL(N, \mathbb{R})$ or $GL(N, \mathbb{C})$.

- (iv) The set of $d \times d$ orthogonal matrices with unit determinant

$$G = \{O : O^T O = \mathbf{1}; \det O = 1\},$$

forms the (special) orthogonal group $SO(d)$. The elements of this group can be identified with all possible rotations in the d -dimensional Euclidean space, which leave the length of vectors invariant

$$\mathbf{x}^T \cdot \mathbf{x}.$$

If the condition of $\det O = 1$ is dropped, one has the orthogonal group $O(d)$. As $O^T O = \mathbf{1}$ implies $\det O = \pm 1$, $O(d)$ has two disconnected components.

- (v) The set of complex unitary $N \times N$ matrices U with unit determinant

$$G = \{U : \det U = 1\}, \quad U U^\dagger = \mathbf{1},$$

form the *special unitary group*, $SU(N)$. Without the condition $\det U = 1$ one has the *unitary group* $U(N)$. The $U(N)$ group can be defined as the group of complex linear transformations in an N -dimensional vector space W which leave the scalar product

$$\mathbf{z}^\dagger \cdot \mathbf{z} = z_1^* z_1 + z_2^* z_2 + \dots + z_N^* z_N$$

invariant.

- (vi) The Lorentz group is formed by 4×4 real matrices L , which leave the metric

$$\mathbf{g} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

invariant, i.e.,

$$L^t \mathbf{g} L = \mathbf{g}.$$

Equivalently, the Lorentz group can be defined as the set of transformations among the four vectors which leave invariant the scalar product defined by

$$x_\mu x^\mu = g_{\mu\nu} x^\mu x^\nu = t^2 - x^2 - y^2 - z^2.$$

Remarks

- The groups of examples (ii)–(vi) above are all non-Abelian, except for $SO(2)$ (group of rotations in a plane) which is Abelian and is equivalent to the group $U(1)$.
- Given two groups G and H , the *direct product* group $G \otimes H$ is defined by the elements (g, h) where $g \in G$, $h \in H$, and with the product defined by

$$(g_1, h_1) \cdot (g_2, h_2) = (g_1 g_2, h_1 h_2). \quad (20.46)$$

- Given a group G , a subset $H \subset G$ of elements $h \in H \subset G$, such that

$$h_1 \cdot h_2 \in H, \quad \forall h_{1,2} \in H,$$

forms itself a group, called *subgroup* of G . If the elements h of a subgroup H satisfy the condition

$$g h g^{-1} \in H, \quad \forall h \in H, \quad \forall g \in G,$$

H is called an invariant subgroup of G .

20.6.2 Group representations

Given a group G the set R of $N \times N$ matrices (with finite or infinite N) M acting on a vector space V of dimension N , is said to form a *representation* of the group G if the map $M(g)$ from G to R respects the group multiplication rule: i.e., if for each $g \in G$ there exists an element $M(g) \in R$, such that

$$M(e) = \mathbf{1}; \quad M(g_1)M(g_2) = M(g_1 g_2).$$

The representation is indicated as $R = (M, V)$ where V is called the representation space. Note that R itself forms a group.

For any group G there always exists a particular one-dimensional representation such that $M(g) = \mathbf{1}$ for all g , which satisfies obviously all the requirements. This is called the *trivial representation*. As in this particular example a representation is not always a faithful one ($M(g) = M(g')$ does not necessarily mean $g = g'$).

The representations in terms of linear operators (matrices) can be either unitary or non-unitary. Representations in terms of unitary matrices are called *unitary representations*.

If there exists a fixed similarity transformation S , such that

$$M(g) = S \tilde{M}(g) S^{-1}, \quad \forall g \in G,$$

then the two representations (M, V) and \tilde{M} are *equivalent*.

Example

The permutation group S_3 has a representation:

$$M(e) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \quad M(12) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix};$$

$$M(13) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}; \quad M(23) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix};$$

$$M(123) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}; \quad M(321) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}.$$

Irreducible representations

A representation of a group G is called *reducible* if it is equivalent to a representation in which the matrices have a block-diagonal form

$$M(g) = \begin{pmatrix} M_1(g) & 0 & \cdots & \vdots \\ 0 & M_2(g) & 0 & 0 \\ \vdots & 0 & \ddots & \vdots \\ \cdots & 0 & \cdots & M_r(g) \end{pmatrix}, \quad \forall g.$$

Otherwise, it is *irreducible*.

In other words a representation is irreducible if the representation space V does not admit any nontrivial subspace invariant under $M(g)$, $\forall g$.

Schur's lemma

An important criterion for irreducible representations is *Schur's lemma*. It is presented in various forms:

Theorem 20.2. (Schur's lemma) *Given two irreducible representations (M, V) and (M', V') of a group G , a linear transformation A from the space V to V' , such that*

$$M'(g)A = A M(g), \quad \forall g, \tag{20.47}$$

is either a one-to-one map $V \rightarrow V'$ (isomorphism), or $A = 0$.

Proof The kernel of A , $K = \{x \in V; Ax = 0\}$ is invariant under $M(g)$, as

$$A(M(g)x) = M'(g)Ax = 0.$$

Since $M(g)$ is irreducible, this implies that either $K = V$ or $K = 0$. But $K = V$ implies $A = 0$. Assuming $A \neq 0$, we get $K = 0$. But then A is one-to-one, as $Ax = Ay$ implies $x = y$. On the other hand, the image of V , AV is invariant under $M'(g)$ by eqn (20.47) again. As $M'(g)$ is irreducible too this means that either $AV = V'$ or $AV = 0$. The latter can be excluded as $A \neq 0$. Then $AV = V'$ and A is a one-to-one map from V to V' . \square

When the condition of the above theorem is satisfied with $A \neq 0$ the two irreducible representations are said to be *equivalent*. The above theorem is valid both for real and complex representations.

If we limit our discussion to *complex* representations only, a stronger theorem holds, also known as Schur's lemma, which states:

Theorem 20.3. (Schur's lemma) Given a complex irreducible representation (M, V) of G , if a linear transformation T in V commutes with all $M(g)$, that is if

$$[M(g), T] = 0, \quad \forall g,$$

then

$$T = c \mathbb{1}, \quad c \in \mathbb{C},$$

that is, T is proportional to a unit matrix.

Proof Let c be an eigenvalue of T , $\det(T - c\mathbb{1}) = 0$. $S \equiv T - c\mathbb{1}$ obviously commutes with all $M(g)$, so by the first theorem S is either a regular, one-to-one map from V to V itself, or $S = 0$. As $\det S = 0$ the only possibility is that $S = 0$. \square

Quantum mechanics

The concept of group representation is an important one in quantum mechanics. Whenever a system possesses a symmetry, there is a symmetry group which acts on the state vectors (wave functions). The state vectors are the basis of the representation space.

Take for instance the case of three dimensional rotational symmetry. The Hamiltonian is invariant under the rotations

$$U H U^\dagger = H, \quad U = e^{i\mathbf{J} \cdot \boldsymbol{\omega}},$$

while the state vectors transform as

$$|\psi\rangle \rightarrow U |\psi\rangle.$$

In general the set of U forms a reducible representation. In the case of a multiplet with a definite angular momentum J , the rotation matrices $D_{m,m'}^{(J)}(\alpha, \beta, \gamma)$, see eqn (4.39), form a $(2J+1)$ -dimensional irreducible representation of the group $SO(3)$. Within a given multiplet of spin J the operator \mathbf{J}^2 (which obviously commutes with all U) is proportional to a unit matrix, with proportionality constant $J(J+1)$ (Schur's lemma).

20.6.3 Lie groups and Lie algebras

Consider now a continuous group G . The group elements g depend on one or more parameters $\{\alpha\}$, $g = g(\{\alpha\})$. The manifold on which the parameters $\{\alpha\}$ live is the group manifold. When the group manifold is a differential manifold, one has a Lie group. When the group manifold is furthermore compact (without being rigorous, a space closed and bounded) it is a compact Lie group. $SO(N)$ and $SU(N)$ are all compact Lie groups. We shall not be concerned with a more rigorous definition of the Lie groups here.

For instance, the group $SO(2)$ is a continuous group parametrized by an angle θ , $0 \leq \theta \leq 2\pi \sim 0$, i.e., with a value on the compact manifold S^1 .

The group $SU(2)$ is the group of 2×2 unitary matrices with unit determinant. Its elements can be expressed as

$$U = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix}$$

in terms of two complex numbers a, b satisfying

$$|a|^2 + |b|^2 = 1. \quad (20.48)$$

The group manifold is thus S^3 .

Any representation of a compact Lie group is equivalent to a unitary representation. Each element of a unitary group, which can be reached from the unit element by a continuous variation of the parameters, can be written in the exponential form,

$$U(\{\alpha\}) = \exp i\alpha_a X_a,$$

where α_a , $a = 1, 2, \dots, N$ are real parameters and X_a are Hermitian operators. X_a are called infinitesimal generators

$$U(\{\epsilon\}) \simeq \mathbf{1} + i\epsilon_a X_a + O(\epsilon^2).$$

Not all of the elements of a continuous group can be reached by a continuous variation of the parameters from the unit element. For instance, the group $O(N)$ contains elements with $\det O = -1$ which are not connected to the unit element $\mathbf{1}$ continuously.

The generators X_a of a group G close by commutation

$$[X_a, X_b] = \sum_c i f_{abc} X_c, \quad (20.49)$$

where

$$[X_a, X_b] \equiv X_a X_b - X_b X_a.$$

The relation (20.49) is called the *algebra* of the group G , and denoted as g . The constants f_{abc} , called *structure constants* characterize the algebra of a given group G (in other words, the properties of the group in the neighborhood of the origin).

The algebra of $SU(2)$ group is given by

$$[X^i, X^j] = i\epsilon_{ijk} X^k; \quad i, j, k = 1, 2, 3,$$

and ϵ_{ijk} are the totally antisymmetric tensors, $\epsilon_{123} = 1, \epsilon_{213} = -1$, etc. In other words, the algebra of the $SU(2)$ group is the same as the algebra of the three dimensional rotation group $SO(3)$, $so(3) \sim su(2)$. The latter is nothing but the *angular momentum algebra*,

$$[J^i, J^j] = i\epsilon_{ijk} J^k, \quad i, j, k = 1, 2, 3,$$

The spin (or angular momentum) operators corresponding to a given multiplet J , J_1, J_2, J_3 whose matrix form are explicitly given, e.g., by

eqns (4.23), (4.24), and (4.25), form the irreducible representation of the $so(3) \sim su(2)$ algebra. The $2J + 1$ -component state vectors corresponding to this particular multiplet transform as

$$\psi \rightarrow U\psi, \quad U = \exp(iJ_i\omega_i).$$

The set of matrices U form an irreducible representation of the group $SU(2)$.

The $SU(2)$ and $SO(3)$ groups are thus locally isomorphic (i.e., near the identity); globally they have different structures. To see this, we recall that the general $SO(3)$ elements can be expressed in terms of three Euler angles,

$$R(\alpha, \beta, \gamma) = O_z(\gamma) O_y(\beta) O_z(\alpha)$$

where

$$O_z(\alpha) = \begin{pmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

etc., and

$$0 \leq \alpha \leq 2\pi; \quad 0 \leq \beta \leq \pi; \quad 0 \leq \gamma \leq 2\pi.$$

Now $R(\pi, 0, \pi) = \mathbb{1}$, and thus the path from $(\alpha, \beta, \gamma) = (0, 0, 0)$ to $(\alpha, \beta, \gamma) = (\pi, 0, \pi)$ is a closed path which is however not contractible. The $SO(3)$ is thus not simply connected.

A manifold M which is arc-wise connected and in which all closed paths can be continuously deformed to a point (in M), is said to be *simply connected*. The circle S^1 is not simply connected. There are an infinite number of different classes of closed paths, which wind S^1 n times, $n = 0, \pm 1, \pm 2, \dots$, which cannot be unwound by a smooth deformation of the paths. These topological properties of manifolds are characterized by the *first homotopy group* or *fundamental group*, $\pi_1(M)$, defined by the equivalent classes of maps $S^1 \rightarrow M$.

More generally, homotopically equivalent (smoothly deformable) classes of maps from the N dimensional sphere S^N to M , can be shown to possess a group property under suitably defined product operation: it is called the N -th homotopy group, denoted as $\pi_N(M)$. They thus provide a finer classification scheme for manifolds. A remarkable fact is that in many instances of physics the homotopy properties of certain configurations (spin orientations, internal quantum numbers, electric and magnetic charges, etc.) lead to a *topological quantization* of various quantities. Dirac's magnetic monopoles have quantized magnetic charges corresponding to $\pi_1(S^1) \sim \mathbb{Z}$ (see Section 14.4); the 't Hooft–Polyakov magnetic monopoles, which are soliton monopoles of spontaneously broken $SO(3)$ gauge theory, have quantized charges $\pi_2(SO(3)/U(1)) \sim \mathbb{Z}$; the vortices in two dimensional liquid crystals have $\pi_1(S^1) \sim \mathbb{Z}$; the instantons in the $SU(N)$ gauge theories have charges $\pi_3(SU(2)) = \mathbb{Z}$, etc.

For $M = S^1$, one has $\pi_1(S^1) = \mathbb{Z}$. The spheres S^N , $N \geq 2$ are all simply connected, $\pi_1(S^N) = \mathbb{1}$. The torus T^1 is not simply connected, with $\pi_1(T^1) = \mathbb{Z} \times \mathbb{Z}$.

In general, a 2π rotation around any axis represents a non-contractible loop in $SO(3)$. On the other hand a 4π rotation can be undone by a smooth deformation, showing that the fundamental group of $SO(3)$ group is

$$\pi_1(SO(3)) = \mathbb{Z}_2,$$

a discrete group of order 2.

In contrast, the group manifold of $SU(2)$ is S^3 as can be seen from eqn (20.48), by writing $a = x_1 + ix_2$; $b = x_3 + ix_4$, that is, as $x_1^2 + x_2^2 + x_3^2 + x_4^2 = 1$. $SU(2)$ group is thus simply connected.

The relation between $SU(2)$ and $SO(3)$ groups is a typical example of the relation between a pair of manifolds called *covering*. Let two spaces M (with points x) and N (with points y), and map f between them, be given. f assigns to any point $x \in M$ a unique image $y \in N$,

$$f : y = f x .$$

The inverse image of a point y , however, may not be unique. When the inverse image of the neighborhood of the point y , V_j , consists of a disjoint set of neighborhoods U_{ij} , $i = 1, 2, \dots, k$, M is said to be a k -fold cover of N . If the space M is simply connected, it is called the *universal covering space* of N . $SU(2)$ group is thus a double cover of $SO(3)$: it is in fact a universal covering space of $SO(3)$.

From the theory of angular momentum we know that the smallest (nontrivial) value of spin is $\frac{1}{2}$. The wave function of a spin- $\frac{1}{2}$ particle transforms as

$$\chi \rightarrow e^{is\omega} \chi :$$

and it changes sign under the rotation of angle 2π of the coordinate system. As a representation of the $SO(3)$ group such a representation, having two images of the unit element, is called a projective (or a spinor) representation.

20.6.4 The $U(N)$ group and the quarks

The unitary groups $U(N)$ play a particularly important role in elementary particle physics, as well as in other fields of physics. The basic reason for this is that the Hamiltonian of N oscillators, in the creation and destruction operator basis, has the form

$$H = \omega \hbar \sum_{i=1}^N a_i^\dagger a_i$$

(we dropped the zero point energy). This Hamiltonian is symmetric under the transformations

$$\begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix} \rightarrow U \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix}$$

where U is a $N \times N$ unitary matrix

$$U U^\dagger = \mathbb{1}.$$

We noted in Section 6.1 that the three-dimensional isotropic harmonic oscillator ($N = 3$ above) has therefore an invariance group $U(3)$, which is *larger* than the symmetry group $SO(3)$ manifest in the standard coordinate representation

$$H = \frac{\mathbf{p}^2}{2m} + \frac{m\omega^2}{2}\mathbf{r}^2.$$

The unitary group made first appearance in nuclear physics in the form of the *isospin* symmetry group, an $SU(2)$ group. The proton and neutron are the isospin “up” and “down” states of the $I = \frac{1}{2}$ nucleon

$$|p\rangle = |\frac{1}{2}, \frac{1}{2}\rangle, \quad |n\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle,$$

while the pions π^\pm, π^0 form an isospin triplet ($I = 1$)

$$|\pi^+\rangle = |1, 1\rangle; \quad |\pi^0\rangle = |1, 0\rangle; \quad |\pi^-\rangle = |1, -1\rangle,$$

and so on. The isospin operators (acting on the isospin $\frac{1}{2}$ states) are $\frac{1}{2}\tau_i$ where

$$\tau_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \tau_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \tau_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

namely the algebra of the isospin operators is identical to that of the angular momentum, reflecting the local isomorphism between $SU(2)$ and $SO(3)$ groups. The Hamiltonian describing two nucleon interaction is invariant under $SU(2)$ isospin rotations.

$SU(3)$ group was originally introduced first as an approximate symmetry group of strongly interacting particles, generalizing the $SU(2)$ isospin group. According to the *quark model* of Ne'eman, Gell-Mann and Zweig the fundamental entity of the strongly interacting particles are the three types of quarks, *up*, *down* and *strange* quarks, which form the fundamental representation of $SU(3)$

$$q = \underline{3} = \begin{pmatrix} u \\ d \\ s \end{pmatrix}.$$

The eight infinitesimal generators of the $SU(3)$ group are the Gell-Mann matrices:

$$\lambda_1 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}; \quad \lambda_2 = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}; \quad \lambda_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix};$$

$$\lambda_4 = \begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{pmatrix}; \quad \lambda_5 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}; \quad \lambda_6 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix};$$

$$\lambda_7 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}; \quad \lambda_8 = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}.$$

Note that λ_i , $i = 1, 2, 3$ form the algebra of the isospin $SU(2)$ subgroup; λ_8 is the hypercharge.

The observed hadrons are all composite particles made either as $\bar{q}q$ bound states (mesons) or as qqq bound states (baryons).⁶ The proton (P) and neutron (N) belong to an octet representation of baryons together with $\Sigma^\pm, \Sigma^0, \Xi^0, \Xi^-$ and Λ particles. Analogously the pions and kaons (\bar{K}^0, K^-, K^+, K^0) form, together with the η particle, another octet representation of $SU(3)$.

In general the irreducible representations of $SU(3)$ groups can be constructed by decomposing the direct products,

$$\underline{3} \otimes \underline{3}^* = \underline{1} \oplus \underline{8}; \quad \underline{3} \otimes \underline{3} \otimes \underline{3} = \underline{1} \oplus \underline{8} \oplus \underline{8} \oplus \underline{10},$$

and so on, which are analogous to the familiar composition-decomposition rules of the angular momenta. The former set represents the meson ($\bar{q}q$) and the latter baryon (qqq) states. As the mass of the s quark (~ 200 MeV/ c^2) is much larger than the u and d quarks of the order of $5 - 10$ MeV/ c^2), this $SU(3)$ group represent an approximate (or broken) symmetry group of Nature. Its subgroup, $SU(2)$, is of course a much better symmetry of Nature (especially important in nuclear physics)—the isospin symmetry group.

The $SU(3)$ group however plays an even more essential role in the physics of strong interactions. Each quark comes in three *color* quantum states. The color, like the electric charge, is the charge to which the color gauge bosons (called *gluons*) are coupled. The resultant dynamical theory of the quarks is known as quantum chromodynamics [Fritzsch, Gell-Mann, and Leutwyler (1973)]. The exchange of the gluons gives rise to the strong forces. As far as we know, the color $SU(3)$ group is exact (as is the $U(1)$ gauge symmetry group of electrodynamics). Only color- $SU(3)$ singlet states can exist as physical states; particles such as quarks (in $\underline{3}$ of $SU(3)_{color}$) with non-neutralized color quantum numbers cannot exist as free particles (this phenomenon is called *quark confinement*). Understanding the mechanism of quark confinement is one of the deepest unsolved problems of the contemporary elementary particle physics.

⁶Very recently (2007) sharp resonances have been observed in the Belle experiments which are compatible with being four-quark states—the first examples of the tetraquark mesons, made of two quarks and two anti-quarks.

20.7 Formulas for angular momentum

This Supplement section is a collection of formulas used in the theory of angular momentum (see also [Messiah and Greenberg (1964)]).

Commutation relations

$$[J_x, J_y] = i J_z; \quad [J_y, J_z] = i J_x; \quad [J_z, J_x] = i J_y; \quad [J_i, J_j] = i \varepsilon_{ijk} J_k;$$

$$\mathbf{J}^2 \equiv J_x^2 + J_y^2 + J_z^2 ; \quad [\mathbf{J}^2, J_i] = 0 ;$$

$$J_{\pm} = J_x \pm i J_y ; \quad [J_+, J_-] = 2J_3 ; \quad [J_3, J_+] = J_+ ; \quad [J_3, J_-] = -J_- ;$$

$$\mathbf{J}^2 = J_+ J_- + J_3^2 - J_3 = J_- J_+ + J_3^2 + J_3.$$

Matrix elements

$$\mathbf{J}^2 |j, m\rangle = j(j+1) |j, m\rangle ; \quad J_z |j, m\rangle = m |j, m\rangle ;$$

$$\langle j, m-1 | J_- | j, m \rangle = \langle j, m | J_+ | j, m-1 \rangle = \sqrt{(j+m)(j-m+1)} .$$

$j = \frac{1}{2}$ representation

$$J_i = \frac{1}{2} \sigma_i ; \quad \sigma_i = \text{Pauli matrices}$$

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

$$\sigma_i \sigma_j = \delta_{ij} + i \epsilon_{ijk} \sigma_k ; \quad [\sigma_i, \sigma_j] = 2i \epsilon_{ijk} \sigma_k ,$$

$$\sigma_+ = \frac{\sigma_1 + i\sigma_2}{2} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} ; \quad \sigma_- = \frac{\sigma_1 - i\sigma_2}{2} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} ;$$

$j = 1$ representation

$$J_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} ; \quad J_y = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} ; \quad J_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} .$$

Sometimes it is useful to use another representation for $j = 1$:

$$(J_i)_{\alpha\beta} = -i \epsilon_{i\alpha\beta}$$

$$J_x = -i \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} ; \quad J_y = -i \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} ; \quad J_z = -i \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} .$$

Orbital angular momentum

$$L_3 = -i \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = -i \frac{\partial}{\partial \phi} ;$$

$$L_+ = -(x + iy) \frac{\partial}{\partial z} + z \left(\frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right) = e^{i\phi} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) ;$$

$$L_- = -L_+ (i \rightarrow -i) = e^{-i\phi} \left(-\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) ;$$

$$\mathbf{L}^2 = L_+ L_- + L_3^2 - L_3 = - \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] .$$

Spherical harmonics

$$Y_{\ell,m}(\theta, \phi) = (-)^{(\ell+|m|)/2} \sqrt{\frac{(2\ell+1)(\ell-|m|)!}{4\pi(\ell+|m|)!}} P_\ell^{|m|}(x) e^{im\phi}.$$

Examples

$$\begin{aligned} Y_{0,0} &= \frac{1}{\sqrt{4\pi}}, & Y_{2,0} &= \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1), \\ Y_{1,0} &= \sqrt{\frac{3}{4\pi}} \cos\theta, & Y_{2,\pm 1} &= \mp \sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta e^{\pm i\phi}, \\ Y_{1,\pm 1} &= \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi}, & Y_{2,\pm 2} &= \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{\pm 2i\phi}. \end{aligned} \quad (20.56)$$

Some properties

$$Y_{\ell,m}(\pi - \theta, \phi + \pi) = (-)^\ell Y_{\ell,m}(\theta, \phi),$$

$$Y_{\ell,m}^* = (-)^m Y_{\ell,-m}.$$

Multipole expansion

$$\begin{aligned} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} &= \frac{1}{r_>} \sum_{\ell=0}^{\infty} \left(\frac{r_<}{r_>} \right)^\ell P_\ell(\cos\gamma) = \\ &= \frac{1}{r_>} \sum_{\ell=0}^{\infty} \left(\frac{r_<}{r_>} \right)^\ell \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} Y_{\ell m}(\Omega_1) Y_{\ell m}^*(\Omega_2), \end{aligned} \quad (20.57)$$

$r_> = \max(r_1, r_2)$, $r_< = \min(r_1, r_2)$; γ is the angle between the vectors $\mathbf{r}_1, \mathbf{r}_2$:

$$\cos\gamma = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\varphi_1 - \varphi_2)$$

$$P_\ell(\cos\gamma) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} Y_{\ell m}(\Omega_1) Y_{\ell m}^*(\Omega_2). \quad (20.58)$$

Integrals

$$\int d\Omega Y_{\ell'm'}^*(\Omega) Y_{\ell'm'}(\Omega) = \delta_{\ell\ell'} \delta_{mm'}; \quad f(\Omega) \equiv f(\theta, \varphi); \quad d\Omega \equiv \sin\theta d\theta d\varphi.$$

$$\begin{aligned} &\int Y_{\ell_1 m_1} Y_{\ell_2 m_2} Y_{\ell_3 m_3} d\Omega \\ &= \sqrt{\frac{(2\ell_1+1)(2\ell_2+1)(2\ell_3+1)}{4\pi}} \cdot \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \end{aligned}$$

The definition of the 3j symbols appearing here will be given below.

Clebsch–Gordan coefficients

$$\mathbf{J} = \mathbf{j}_1 + \mathbf{j}_2$$

$$|j_1, j_2; JM\rangle = \sum_{\substack{m_1, m_2 \\ m_1 + m_2 = M}} |j_1, m_1; j_2, m_2\rangle \langle j_1, m_1; j_2, m_2 | j_1, j_2; JM\rangle ;$$

$$\langle j_1, m_1; j_2, m_2 | j_1, j_2; JM\rangle = (-1)^{j_1+j_2-J} \langle j_2, m_2; j_1, m_1 | j_2, j_1; JM\rangle ;$$

$$\sum_{m_1, m_2} \langle j_1, m_1; j_2, m_2 | j_1, j_2; JM\rangle \langle j_1, m_1; j_2, m_2 | j_1, j_2; J' M'\rangle = \delta_{JJ'} \delta_{MM'} ;$$

$$\sum_{JM} \langle j_1, m_1; j_2, m_2 | j_1, j_2; JM\rangle \langle j_1, m'_1; j_2, m'_2 | j_1, j_2; JM\rangle = \delta_{m_1 m'_1} \delta_{m_2 m'_2} ;$$

Notation:

$$[j_1, j_2, \dots, j_n] = (2j_1 + 1)(2j_2 + 1) \dots (2j_n + 1) .$$

3j symbols:

$$\langle j_1, m_1; j_2, m_2 | j_1, j_2; JM\rangle = (-1)^{j_1-j_2+M} [J]^{1/2} \begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix}$$

$$\begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} = \begin{pmatrix} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

The 3j symbols are non-vanishing only for

$$m_1 + m_2 + m_3 = 0 ; \quad j_i \leq j_j + j_k ; \quad |m_i| \leq j_i .$$

$$\begin{pmatrix} \ell & \ell & 0 \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{1}{(2\ell+1)}$$

6j and 9j symbols There are two ways to sum three angular momenta to form a given total momentum J :

$$|(j_1 j_2) J_{12} j_3; JM\rangle ; \quad |j_1 (j_2 j_3) J_{23}; JM\rangle .$$

The two representations are unitarily equivalent:

$$\begin{aligned} |j_1 (j_2 j_3) J_{23}; JM\rangle = \\ \sum_{J_{12}} |(j_1 j_2) J_{12} j_3; JM\rangle \langle (j_1 j_2) J_{12} j_3; JM | j_1 (j_2 j_3) J_{23}; JM\rangle \end{aligned}$$

The transformation matrix is given by the 6j symbols:

$$\langle (j_1 j_2) J_{12} j_3; JM | j_1 (j_2 j_3) J_{23}; JM\rangle =$$

$$(-1)^{j_1+j_2+j_3+J} [J_{12}, J_{23}]^{1/2} \begin{Bmatrix} j_1 & J_{12} & j_2 \\ j_3 & J_{23} & J \end{Bmatrix}$$

Similarly we define 9j symbols by considering two different ways to compose four angular momenta:

$$\begin{aligned} & |(j_1 j_3) J_{13}(j_2 j_4) J_{24}; JM \rangle = \\ & \sum_{J_{12} J_{24}} \langle (j_1 j_2) J_{12}(j_3 j_4) J_{34} | (j_1 j_3) J_{13}(j_2 j_4) J_{24}; J \rangle |(j_1 j_2) J_{12}(j_3 j_4) J_{34} JM \rangle ; \end{aligned}$$

$$\begin{aligned} & \langle (j_1 j_2) J_{12}(j_3 j_4) J_{34} | (j_1 j_3) J_{13}(j_2 j_4) J_{24}; J \rangle = \\ & [J_{12}, J_{34}, J_{13}, J_{24}]^{1/2} \left\{ \begin{array}{ccc} j_1 & j_2 & J_{12} \\ j_3 & j_4 & J_{34} \\ J_{13} & J_{24} & J \end{array} \right\} . \end{aligned}$$

Spherical tensors

Rank k , components $q = -k, \dots +k$. Notation $\mathbf{T}^{(k)}$, components: $T_q^{(k)}$. Transformation properties:

$$[J_z, T_q^{(k)}] = q T_q^{(k)} ; \quad [J_{\pm}, T_q^{(k)}] = \sqrt{k(k+1) - q(q+1)} T_{q \pm 1}^{(k)} .$$

Examples:

(1) Normalized spherical harmonics, $\mathbf{C}^{(k)}$:

$$C_q^{(k)} = \sqrt{\frac{4\pi}{2k+1}} Y_{kq} ;$$

(2) Vectors:

$$V_1^{(1)} = -\frac{V_x + i V_y}{\sqrt{2}} ; \quad V_0^{(1)} = V_z ; \quad V_{-1}^{(1)} = +\frac{V_x - i V_y}{\sqrt{2}} ;$$

Scalar products:

$$\mathbf{A}^{(k)} \cdot \mathbf{B}^{(k)} = \sum_q (-1)^q A_q^{(k)} B_{-q}^{(k)} ;$$

Tensor products: given two operators $\mathbf{A}^{(k_1)}, \mathbf{B}^{(k_2)}$ it is possible to construct the operators $\mathbf{X}^{(K)}$ by using the Clebsch–Gordan coefficients as:

$$X_Q^{(K)} = \left(\mathbf{A}^{(k_1)} \otimes \mathbf{B}^{(k_2)} \right)_Q^{(K)} = \sum_{q_1 q_2} \langle k_1 q_1 k_2 q_2 | k_1 k_2 K Q \rangle A_{q_1}^{(k_1)} B_{q_2}^{(k_2)} .$$

In particular, a scalar operator is

$$X_0^{(0)} = (-1)^k [k]^{-1/2} \sum_q (-1)^q A_q^{(k)} B_q^{(k)} \equiv (-1)^k [k]^{-1/2} \mathbf{A}^{(k)} \cdot \mathbf{B}^{(k)} .$$

$$\mathbf{A}^{(k)} \cdot \mathbf{B}^{(k)} = (-1)^k [k]^{1/2} \left(\mathbf{A}^{(k)} \otimes \mathbf{B}^{(k)} \right)_0^{(0)} .$$

The Wigner–Eckart theorem Indicating by γ, γ' quantum numbers other than the angular ones:

$$\langle \gamma j m | T_q^{(k)} | \gamma' j' m' \rangle = (-1)^{j-m} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} \langle \gamma j | T^{(k)} | \gamma' j' \rangle ;$$

$\langle \gamma j | T^{(k)} | \gamma' j' \rangle$ is called the *reduced matrix element*.

Particular cases:

(a) Spherical harmonics:

$$\langle \ell | C^{(k)} | \ell' \rangle = (-1)^\ell [\ell, \ell']^{1/2} \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} .$$

(b) Angular momentum:

$$\langle \gamma j | J^{(1)} | \gamma' j' \rangle = \delta_{\gamma\gamma'} \delta_{jj'} \sqrt{j(j+1)(2j+1)} .$$

Composite systems

Let 1,2 be two systems with angular momenta j_1, j_2 , respectively. A composite system with a fixed internal quantum numbers γ_1, γ_2 is given by

$$| \gamma_1 \gamma_2 j_1 j_2; JM \rangle = \sum_{m_1 m_2} \langle j_1 m_1 j_2 m_2 | j_1 j_2; JM \rangle | \gamma_1 j_1 m_1 \rangle | \gamma_2 j_2 m_2 \rangle .$$

The systems can be, e.g., ℓ , s for an atom.

Sometimes we are interested in the matrix element of operators which act only on one of the subsystems or of factorized operators, e.g., of the form, $\ell \cdot s$. Let us study the most important cases:

(a) A *scalar* operator $A^{(0)}$ acting only on the system 1:

$$\begin{aligned} \langle \gamma_1 \gamma_2 j_1 j_2; JM | A^{(0)} | \gamma'_1 \gamma'_2 j'_1 j'_2; J' M' \rangle = \\ \delta_{\gamma_2 \gamma'_2} \delta_{j_2 j'_2} \delta_{j_1 j'_1} \delta_{J J'} \delta_{M M'} \langle \gamma_1 j_1 m_1 | A^{(0)} | \gamma'_1 j'_1 m'_1 \rangle \end{aligned} \quad (20.59)$$

The last matrix element does not depend on m_1 (and $m_1 = m'_1$) as $A^{(0)}$ is a scalar.

(b) Scalar product of two operators of rank k . The reduced matrix elements c can be written in terms of $6j$ symbols:

$$\begin{aligned} \langle \gamma_1 \gamma_2 j_1 j_2 J | A^{(k)} \cdot B^{(k)} | \gamma'_1 \gamma'_2 j'_1 j'_2 J' \rangle = \\ \delta_{J J'} (-1)^{j'_1 + j_2 + J} [J]^{1/2} \begin{Bmatrix} j_1 & j_2 & J \\ j'_2 & j'_1 & k \end{Bmatrix} \\ \cdot \langle \gamma_1 j_1 | A^{(k)} | \gamma'_1 j'_1 \rangle \langle \gamma_2 j_2 | B^{(k)} | \gamma'_2 j'_2 \rangle \end{aligned} \quad (20.60)$$

(c) A tensor which acts on the system 1:

$$\begin{aligned} \langle \gamma_1 \gamma_2 j_1 j_2 J | A^{(k)} | \gamma'_1 \gamma'_2 j'_1 j'_2 J' \rangle = \\ \delta_{\gamma_2 \gamma'_2} \delta_{j_2 j'_2} (-1)^{j_1 + j_2 + J' + k} [J, J']^{1/2} \begin{Bmatrix} j_1 & j_2 & J \\ J' & k & j'_1 \end{Bmatrix} \langle \gamma_1 j_1 | A^{(k)} | \gamma'_1 j'_1 \rangle ; \end{aligned} \quad (20.61)$$

(c) A tensor acting only on the system 2:

$$\langle \gamma_1 \gamma_2 j_1 j_2 J || \mathbf{B}^{(k)} || \gamma'_1 \gamma'_2 j'_1 j'_2 J' \rangle = \quad (20.62)$$

$$\delta_{\gamma_1 \gamma'_1} \delta_{j_1 j'_1} (-1)^{j_1 + j'_1 + J + k} [J, J']^{1/2} \begin{Bmatrix} j_1 & j_2 & J \\ k & J' & j'_2 \end{Bmatrix} \langle \gamma_2 j_2 || \mathbf{B}^{(k)} || \gamma'_2 j_2 \rangle.$$

20.8 Young tableaux

We shall give here a brief account of the permutation group S_N and of the Young tableaux. Let S_N be the group of permutations of N objects. Each element of the group can be obtained as a product of the operations of exchange of two objects. The action of an element of the group can be represented, for instance, by tables such as, (e.g. S_5)

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 1 & 2 & 3 & 4 & 5 \end{pmatrix}; \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 2 & 1 & 3 & 4 & 5 \end{pmatrix}; \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 5 & 1 & 2 & 3 & 4 \end{pmatrix}; \quad (20.63)$$

in which the action of the group is the substitution of an element of the first raw with the corresponding element of the second raw. The first element of eqn (20.63) is the identity element, the second is an exchange, the third is a cyclic permutation. The order of S_N is $N!$.

As for any group one can define the representations of S_N : a representation is made of a vector space V in which the action of a matrix $g \in S_N$ is defined so as to maintain the group homomorphism

$$g(v) = v' \in V \quad g_1(g_2 v) = (g_1 g_2)(v) :$$

the product structure is maintained in the map. A representation is *reducible* if there is a subspace of V invariant under the actions of S_N , *irreducible* otherwise.

All the representation of S_N are decomposable by unitary transformations into a sum of irreducible representations. If V has dimension d each element of S_N is represented by a $d \times d$ matrix. In general the given representation is reducible and can be transformed to a block-diagonal form. (See Section 20.6). Among all possible representations there is a particular one, called regular representation, which has dimension equal to the order of the group; for the permutation group this is the one realized in the substitutions schemes 20.63.

Coming back to quantum mechanics, consider the state vectors

$$|\lambda_1, \lambda_2, \dots, \lambda_N\rangle$$

the Hilbert space \mathcal{H}^N of a system with N particles. λ_i stands for the quantum numbers of the i -th particle. There are $N!$ such state vectors which can be obtained by permuting $|\lambda_i\rangle$ in all possible ways. The action P of the group is defined naturally. The set of vectors $|\{\lambda\}\rangle$ obviously go into itself under the action of P : it forms the regular representation of the permutation group.

The irreducible representations of S_N can be classified by the so-called *Young tableaux*. They are defined as follows. Consider N boxes which

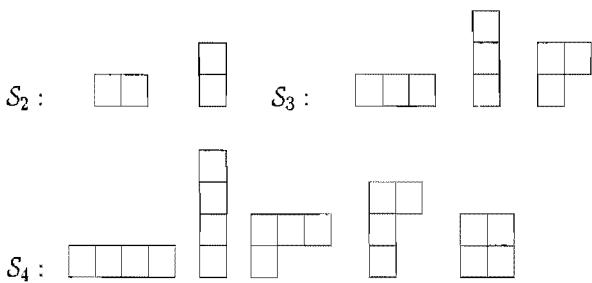


Table 20.1 Examples of Young tableaux

are arranged in rows of lengths, lower rows not longer than the higher ones. N elements are arranged in these boxes and those appearing in the same row are symmetrized and the ones in the same column are antisymmetrized. Each tableau thus corresponds to a particular scheme of symmetrization, and ensemble of arrangements corresponding to a particular tableau represents an irreducible representation of S_N .

Some examples of the smallest groups S_N are given in Table 20.1. A little thought suffices to convince ourselves that the number of tableaux of definite type is equal to the ways in which the number N can be written as a sum of integers. For instance for $N = 4$ there are 5 different ways

$$(4) ; (1 + 1 + 1 + 1) ; (3 + 1) ; (2 + 1 + 1) ; (2 + 2) .$$

corresponding to the diagrams in the table. The horizontal tableau and the vertical tableau correspond to the totally symmetric and antisymmetric representations; others are of mixed symmetry types.

In the consideration of the regular representation, which is of particular interest in quantum mechanics, the following theorem tells us about the dimension of each irreducible representation.

In the regular representation all possible representations appear and each a number of times equal to its dimension. Therefore if d_k is the dimension of an irreducible representation, $\sum d_k^2 = N!$.

A tableau which is obtained by filling up all the boxes as in Table 20.1, with increasing numbers in each row and in each column, is called *standard tableau*. Each standard tableau corresponds to a member of an irreducible representation. Writing all possible standard tableaux and counting them, we find all the possible irreducible representations, their dimensions and the decomposition of the regular representation into them.

Note that the symmetric and antisymmetric representations always appear only once: they have dimension 1.

Examples

[S_2] For S_2 there are only two tableaux, both of which are standard. That is, only the two one-dimensional representations—symmetric and

antisymmetric—appear.

1	2
2	

[S_3] For S_3 there are four standard tableaux:

1	2	1	1
2		2	3
1	2	3	2

The “mixed” representation appears twice, hence has dimension 2. The regular representation of dimension $3! = 6$ decomposes into $6 = (1) \oplus (1) \oplus 2 \cdot (2)$. A function of three variables can be written as a sum of a symmetric, an antisymmetric and two mixed-symmetry functions.

[S_4] For S_4 the standard tableaux are

1	2	3	4
1	2	3	4
4		3	2
1	2	3	1
3		2	4
4		4	
1	2		1
3	4		2
2	4		

The symmetric and antisymmetric representations have dimension 1 as always. Those in the second and third row appear three times so have dimension 3, the one in the fourth row has dimension 2. The regular representation $4! = 24$ decomposes into

$$24 = (1) \oplus (1) \oplus 3 \cdot (3) \oplus 3 \cdot (3) \oplus 2 \cdot (2)$$

For Mathematica users.

With the program Mathematica one must load the package Combinatorica by writing the input command `<< Combinatorica``. The function

```
Table[Grid[Tableaux[k][[j]], Frame -> All], {j, 1, NumberOfTableaux[k]}];
```

will print out all the standard tableaux (for instance `f[3]` for S_3). Note that, for instance, `NumberOfTableaux[10]` is 9496: the number of tableaux increases rapidly.

This function generate a Young tableau

```
youngTab[p1_List] := Module[{i, j, n = Length[p1], p =
Sort[p1]}, Grid[Table[Framed[""], {j, n, 1, -1}, {i, p[[j]]}], Spacings -> {0, 0}]];
```

and this command print the whole list of Young tableaux (those of S_5 in this example)

```
Map[youngTab, IntegerPartitions[5]]
```

To summarize, each irreducible representation of the permutation group S_N is represented by one of the Young tableaux such as those in Table 20.1.

Young tableaux analogous to the ones discussed above can be used to represent also the irreducible representations of $SO(N)$ and $SU(N)$ groups. The allowed tableaux and the dimension of each irreducible representation depend on the group considered, however. A box represents the fundamental multiplet of the group, 2 or 3 for the group $SU(2)$ or $SU(3)$ groups, respectively, for instance. Possible irreducible representation made of N particles are given by one of the Young tableaux such as those in Table 20.1. As each box takes only N possible values (for $SU(N)$ or $SO(N)$ groups), more than N particles cannot be in totally antisymmetric states.

Thus for $SU(2)$ a column of height two represents a singlet (an antisymmetric state of two spin $\frac{1}{2}$ is a singlet). Possible irreducible representations of $SU(2)$ group are therefore given, apart from the singlet, only by symmetric Young tableaux

$$\square, \quad \square\square, \quad \square\square\square, \quad \square\square\square\square, \dots$$

with dimensions 2, 3, 4, 5, ..., respectively. They correspond to the possible spin values

$$0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$$

known from the theory of angular momentum (Chapter 4.) The states of N particles are classified by all possible Young tableaux made of N boxes with up to two rows; for instance possible states of $N = 5$ spins are:

$$\begin{array}{|c|c|} \hline \square & \square \\ \hline \end{array} \sim \square, \quad \begin{array}{|c|c|c|} \hline \square & \square & \square \\ \hline \end{array} \sim \square\square\square, \quad \begin{array}{|c|c|c|c|} \hline \square & \square & \square & \square \\ \hline \end{array}.$$

For the $SU(3)$ group (which is the relevant group in the quark model, or in quantum chromodynamics), each box represents the triplet, $\underline{3}$. Irreducible representations of $SU(3)$ group are given by Young tableaux of up to three rows. There is an infinite number of irreducible representations

$$\square, \quad \begin{array}{|c|c|} \hline \square & \square \\ \hline \end{array}, \quad \begin{array}{|c|c|} \hline \square & \\ \hline \end{array}, \quad \begin{array}{|c|} \hline \square \\ \hline \end{array}, \quad \begin{array}{|c|c|} \hline \square & \square \\ \hline \end{array}, \quad \begin{array}{|c|c|} \hline \square & \\ \hline \end{array}, \quad \begin{array}{|c|c|} \hline \square & \square \\ \hline \end{array}, \quad \begin{array}{|c|c|c|} \hline \square & \square & \square \\ \hline \end{array}, \quad \dots$$

20.9 N -particle matrix elements

In several practical applications it is necessary to compute efficiently the matrix elements for operators between many particle states. To fix our

ideas we will confine ourselves to the problem of N fermions. We assume that single-particle states are described by normalized kets $|i\rangle$. In usual cases these kets are eigenstates of an effective one-particle Hamiltonian, but for the present purpose it is sufficient that they constitute a complete *orthogonal* basis in the Hilbert space of a single particle. A basis for the N particle-states is generated by the antisymmetric combinations (Slater determinants):

$$|i_1, \dots, i_N\rangle = \sqrt{N!} \mathcal{A} |i_1, \dots, i_N\rangle_0 = \sqrt{\frac{1}{N!}} \sum_P \epsilon_P P |i_1, \dots, i_N\rangle_0.$$

The interesting operators are of two kinds:

- (1) Single-particle operators. Examples are the kinetic energy, angular momentum, spin, etc. That the particles are identical implies that these operators have the form

$$F^{(1)} = \sum_{i=1}^N f_i \equiv \sum_{i=1}^N f(q_i). \quad (20.64)$$

q stands for a generalized coordinate (including spin).

- (2) Two-particle operators. Examples are the interaction Hamiltonians, like Coulomb interaction, spin-orbit coupling between different electrons, etc. The general form is

$$F^{(2)} = \sum_{a < b} g(q_a, q_b). \quad (20.65)$$

In eqn (20.65) g is symmetric in its argument.

The most general matrix element is then reduced to a matrix element between two Slater determinants.

One-particle operators

It is evident that $f(q_i)$ in eqn (20.64) can eventually act only on the i -th coordinate, i.e. at most one state can change in the matrix element, and this can happen only for non-diagonal matrix elements. Let us call $j \rightarrow i$ the possible change of state in the non-diagonal elements. We get easily

$$\langle \psi | F^{(1)} | \psi \rangle = \sum_i \langle i | f | i \rangle; \quad \text{diagonal elements.} \quad (20.66)$$

$$\langle \psi_i | F^{(1)} | \psi_j \rangle = \langle i | f | j \rangle; \quad \text{off diagonal elements.} \quad (20.67)$$

The symbol $|\psi_i\rangle$ was used to indicate a Slater determinant which contains the state i which changes, the others remaining the same. On the right-hand side of eqn (20.67) the kets refer to single-particle states.

Two-particle operators

Here the elementary term in eqn (20.65) acts on two coordinates and there are three possible cases (we write in the following only the states which change)

$$\langle \psi | F^{(2)} | \psi \rangle = \sum_{i < j} (\langle ij | g | ij \rangle - \langle ij | g | ji \rangle) ; \quad \text{diag.} \quad (20.68a)$$

$$\langle \psi_i | F^{(2)} | \psi_j \rangle = \sum_{k \neq i,j} (\langle ik | g | jk \rangle - \langle ik | g | kj \rangle) ; \quad 1 \text{ change} \quad (20.68b)$$

$$\langle \psi_{ij} | F^{(2)} | \psi_{kl} \rangle = (\langle ij | g | kl \rangle - \langle ij | g | lk \rangle) ; \quad 2 \text{ changes} \quad (20.68c)$$

As before ψ_{ij} denotes a Slater determinant with states i, j marked (those to be changed). The states on the right-hand side of eqn (20.68c) are *not* antisymmetric wave functions: for instance

$$\langle ij | f | kl \rangle = \int_{q_1, q_2} \varphi_i^*(q_1) \varphi_j^*(q_2) g(q_1, q_2) \varphi_k(q_1) \varphi_l(q_2)$$

φ_i are the basis functions.

For bosons the formulas are more complicated, as one must distinguish the occupation number of each state. We leave the relative exercise to the reader.

20.10 The Fock representation

Let us consider a system of N particles and fix once and for all a complete orthonormal basis for single particle kets, $|i\rangle$. A basis for the product space can be built by symmetric (bosons) or antisymmetric (fermions) products of single particle states. As the single particle states have been fixed, the basis vectors differ *only* in the number of particles in each state, which is necessarily 0 or 1 for fermions. We can use this *occupation numbers* to label the states: operators act only by changing these numbers. This is the *Fock representation* which we present below for bosons and fermions.

A crucial advantage of this representation is that the total number of particles becomes a variable. In other words this formalism allows to study processes where the number of particles changes during the process, an essential feature in relativistic quantum mechanics. (See also Chapter 17)

20.10.1 Bosons

A special role is played by the state in which there are no particles, the *vacuum*, $|\Omega\rangle$. All other states can be constructed from $|\Omega\rangle$ by acting with creation operators a_i^\dagger and annihilation operators, a_i , which increase or decrease the occupation number of the state i by one. By definition

$$a_i^\dagger |\Omega\rangle = |0, 0, \dots, 1, \dots\rangle , \quad a_i |\Omega\rangle = 0 ; \quad (20.69)$$

where 1 is at the i-th state. With a shorthand notation we shall write only the occupied states and the previous equation will be written in such simple cases

$$a_i^\dagger |\Omega\rangle = |i\rangle .$$

For each state (or *mode*) of the system a tower of states (for bosons) can be constructed by successive applications of a_i^\dagger . The various modes are independent thus we have the algebra

$$[a_i, a_j^\dagger] = \delta_{ij} ; \quad [a_i, a_j] = [a_i^\dagger, a_j^\dagger] = 0 . \quad (20.70)$$

These relations are particularly important as they automatically ensure the symmetric nature of states

$$|i, j\rangle = a_i^\dagger a_j^\dagger |\Omega\rangle = a_j^\dagger a_i^\dagger |\Omega\rangle = |j, i\rangle .$$

The first commutation relation in eqn (20.70) is fixed consistently with the normalization

$$\langle i | j \rangle = \delta_{ij} .$$

As the algebra we are using is identical to the corresponding algebra of the harmonic oscillator, it is obvious that the correct normalized n -particles state (in mode i) is given by

$$|n_i\rangle = \frac{1}{\sqrt{n_i!}} (a_i^\dagger)^{n_i} |\Omega\rangle . \quad (20.71)$$

The continuous spectrum

Everything works also for the continuous case provided that the commutation relations are properly normalized. Let us take for example the common case of momentum eigenstates, normalized by

$$\langle \mathbf{p}' | \mathbf{p} \rangle = (2\pi\hbar)^3 \delta^3(\mathbf{p} - \mathbf{p}') .$$

In this case

$$[a_{\mathbf{p}}, a_{\mathbf{p}'}^\dagger] = (2\pi\hbar)^3 \delta^3(\mathbf{p} - \mathbf{p}') ; \quad [a_{\mathbf{p}}, a_{\mathbf{p}'}] = [a_{\mathbf{p}}^\dagger, a_{\mathbf{p}'}^\dagger] = 0 .$$

Operators

To complete the description of the representation we must give an explicit expression for the operators. As discussed in the previous section the most important cases are one-particle and two-particle operators.

It is easy to see that one- and two-particle operators are represented by

$$F^{(1)} = \sum_{\alpha\beta} f_{\alpha\beta} a_\alpha^\dagger a_\beta . \quad (20.72)$$

$$F^{(2)} = \frac{1}{2} \sum_{\alpha\beta,\gamma\delta} \langle \alpha\beta | g | \gamma\delta \rangle a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta . \quad (20.73)$$

The single-particle operators f, g are defined by eqns (20.64) and (20.65). The content of these equations is quite intuitive: the first enumerates all possible changes for a single state, the second all possible changes for two particles. Being operator equations it is sufficient to check their normalization on the simplest case, for one- and two-particle states. We leave it as an exercise (see also Problems for this chapter).

Matrix elements of operators expressed through a_i and a_j^\dagger can be easily computed by a systematic use of the commutation relations. One brings all a_i to the right, until they act on the vacuum state and give 0. Similarly one brings a_j^\dagger to the left, until it acts on the vacuum to the left.

The most important example of eqn (20.72) is the Hamiltonian for a system of independent particles. If the states are chosen to be eigenstates of the Hamiltonian we have trivially

$$H = \sum_i \varepsilon_i a_i^\dagger a_i \quad (20.74)$$

where ε_i are the eigenvalues. It should be stressed that eqn (20.74) has a very general meaning and requires only that particles are independent, i.e. the energy is additive, and as such it has the same form for the free relativistic or non-relativistic particles, and for every kind of bosonic excitation in a system, like phonons in a solid, particles in superfluid helium, etc. The difference between the systems is in the *dispersion law*, i.e. the energy spectrum ε_i . For example, for non-relativistic and relativistic free particles, one has

$$H_{NR} = \sum_{\mathbf{p}} \frac{\mathbf{p}^2}{2m} a_{\mathbf{p}}^\dagger a_{\mathbf{p}} ; \quad H_R = \sum_{\mathbf{p}} \sqrt{\mathbf{p}^2 c^2 + m^2 c^4} a_{\mathbf{p}}^\dagger a_{\mathbf{p}} .$$

As already noted, the number of particles is an operator in this formalism

$$N = \sum_i a_i^\dagger a_i \quad (20.75)$$

Whether it is conserved or not depends on the dynamics, i.e. if it commutes with the Hamiltonian.

20.10.2 Fermions

A Fock representation for fermions requires the Pauli principle to be satisfied, i.e. the occupation number can only take the values 0 or 1. This can be achieved by changing the algebra of the creation and annihilation operators. Instead of the commutation relations one must use the *anti-commutators*:

$$\{a_\alpha, a_\alpha^\dagger\} = 1 ; \quad \{a_\alpha, a_\beta\} = \{a_\alpha^\dagger, a_\beta^\dagger\} = 0 . \quad (20.76)$$

where

$$\{f, g\} = fg + gf .$$

It is clear from eqn (20.76) that the Pauli principle is satisfied. The states constructed by using these operators are automatically antisymmetric. For instance

$$(a_i^\dagger)^2 |\Omega\rangle = 0 , \quad a_i^\dagger a_j^\dagger |\Omega\rangle = -a_j^\dagger a_i^\dagger |\Omega\rangle .$$

The formula for the operators are identical to the bosonic case, but are a little easier to verify. Examples of systems described by this formalism are the electrons in an atom, in a metal, in relativistic quantum electrodynamics, etc. Again the formula (20.74) is quite general and is valid in this case also.

20.11 Second quantization

The Fock representation allows a smooth transition to one of the most powerful formalism of quantum mechanics, the so-called *second quantization*.⁷

Let us see how it works in the simple case of a non-relativistic spinless particle, in particular let us consider a free particle. The Fock operators a_p describe completely a system of one or more particles by assigning the momentum eigenvalue p , a "point" in momentum space. To be precise, $p \rightarrow a_p$ is an operator valued function in momentum space, i.e. the result is an operator.

The idea of second quantization is to take a Fourier transform of these operators, to the usual three-dimensional space. We define a *field operator*

$$\Phi(\mathbf{x}) = \int \frac{d^3 k}{(2\pi)^3} a(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{x}} \quad (20.77)$$

where $a(\mathbf{k})$ satisfies the commutation relation⁸

$$[a(\mathbf{k}), a^\dagger(\mathbf{k}')] = (2\pi)^3 \delta^{(3)}(\mathbf{k} - \mathbf{k}') . \quad (20.78)$$

This way we associate an operator to each point in the space, the field operator. As any operator in Fock representation is written in terms of a_i and a_j^\dagger it can be expressed in terms of $\Phi(\mathbf{x})$.

The operator $\Phi(\mathbf{x})$ has some peculiar and very important properties.

- (1) First of all from eqn (20.78) it is easy to show that

$$\begin{aligned} [\Phi(\mathbf{x}), \Phi(\mathbf{y})] &= [\Phi^\dagger(\mathbf{x}), \Phi^\dagger(\mathbf{y})] = 0 ; \\ [\Phi(\mathbf{x}), \Phi^\dagger(\mathbf{y})] &= \delta^{(3)}(\mathbf{x} - \mathbf{y}) . \end{aligned}$$

This means that operators in different points are mutually compatible, a satisfying property as it imply that observables built with Φ at space-like separation can be simultaneously measured.

- (2) Acting on a single-particle state

$$|\psi\rangle = \int \frac{d^3 q}{(2\pi)^3} f(\mathbf{q}) |\mathbf{q}\rangle$$

⁷This is a notorious misnomer: of course, there is only *one* quantization, i.e. the usual quantum theory. The name has nevertheless historically stuck; it simply refers to the standard quantization procedure applied to systems with an infinite degrees of freedom, such as the electromagnetic field.

⁸We use the wave number $\mathbf{k} = \mathbf{p}/\hbar$ to simplify the formulas.

the operator “extracts” the wave function

$$\Phi(\mathbf{x})|\psi\rangle = \Phi(\mathbf{x}) \int \frac{d^3\mathbf{q}}{(2\pi)^3} f(\mathbf{q}) |\mathbf{q}\rangle = \int \frac{d^3\mathbf{q}}{(2\pi)^3} f(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{x}} |0\rangle = \psi(\mathbf{x}) |0\rangle \quad (20.79)$$

- (3) It is easy to construct “local” operators, i.e. operators which act on a finite part of the space, in particular on a single point.

For example, let us consider the density operator, which in the usual Schrödinger picture for a single particle is written as

$$\rho_x = \delta^{(3)}(\hat{\mathbf{q}} - \mathbf{x}).$$

The transcription in terms of Φ is immediate:

$$\rho(\mathbf{x}) = \Phi^\dagger(\mathbf{x}) \Phi(\mathbf{x}).$$

In fact, it follows easily from eqn (20.79) that

$$\langle \psi | \Phi^\dagger(\mathbf{x}) \Phi(\mathbf{x}) | \psi \rangle = |\psi(\mathbf{x})|^2.$$

Finally it is easy to show that the “second quantized” form of the Hamiltonian is given by

$$\begin{aligned} H = & \int d^3\mathbf{x} \Phi^\dagger(\mathbf{x}) \left[-\hbar^2 \frac{\nabla^2}{2m} \right] \Phi(\mathbf{x}) \\ & + \frac{1}{2} \int d^3\mathbf{x}_1 d^3\mathbf{x}_2 |\Phi(\mathbf{x}_1)|^2 U(\mathbf{x}_1 - \mathbf{x}_2) |\Phi(\mathbf{x}_2)|^2 \end{aligned}$$

20.12 Supersymmetry in quantum mechanics

An extremely elegant idea born in the context of elementary particle physics is that of supersymmetry—symmetry under the exchanges of boson and fermion. It could turn out to be an important ingredient of the future theory of fundamental interactions, which will include the Glashow–Weinberg–Salam theory of electroweak interactions as well as the quantum chromodynamics (strong interactions) as a part, and perhaps, even gravity.

The basic structure of supersymmetric theories is given by the relation

$$\{Q_\alpha, Q_\beta^\dagger\} = 2(\sigma^\mu)_{\alpha\beta} P_\mu, \quad \alpha, \beta = 1, 2. \quad (20.80a)$$

$$\{Q_\alpha, P^\mu\} = \{Q_\alpha^\dagger, P^\mu\} = \{Q_\alpha, Q_\beta\} = 0, \quad (20.80b)$$

where P_μ is the space-time translation operator

$$P_\mu = (H, \hat{P}) = i\hbar \frac{\partial}{\partial x^\mu};$$

$\sigma^\mu \equiv (\mathbf{1}, \sigma_i)$ are 2×2 matrices, σ_i being the standard Pauli matrices. Q^α are the fermionic generators of supersymmetry transformation. These

convert a bosonic state into a fermionic state and vice versa. The supersymmetry commute with the Hamiltonian: it is a symmetry operator of the theory.

To work out even a simplest model of supersymmetric (quantum field) theory goes beyond the scope of the book. But an example of supersymmetry can be found in a simple one-dimensional quantum mechanical model [Witten (1981)]. Let us consider a spin- $\frac{1}{2}$ particle which moves along one dimension, the Hamiltonian being

$$H = \frac{1}{2m} [p^2 + W(x)^2 + \hbar\sigma_3 W'(x)] \quad (20.81)$$

($W(x)$ real). For simplicity let us take $|W| \rightarrow \infty$ for $x \rightarrow \pm\infty$, so that the spectrum is purely discrete. The Hamiltonian (20.81) turns out to be a square of the operators $Q_{1,2}$:

$$Q_1^2 = Q_2^2 = H, \quad (20.82)$$

where

$$Q_1 \equiv \frac{1}{\sqrt{2m}} [\sigma_1 p + \sigma_2 W(x)]; \quad Q_2 \equiv \frac{1}{\sqrt{2m}} [\sigma_2 p - \sigma_1 W(x)]. \quad (20.83)$$

Clearly

$$[Q_{1,2}, H] = 0 :$$

Q generates a symmetry of the system, in view of the fact that there exists another operator (σ_3) which also commutes with H but not with $Q_{1,2}$. The function $W(x)$ is an example of "superpotential".

The first consequence of eqn (20.82) is:

$$\langle \psi | H | \psi \rangle \geq 0,$$

in any state, and in particular

$$E_0 \geq 0 :$$

the energy of the system is positive semi-definite. We leave as an exercise for the reader to show the following commutators and anti-commutators (the latter defined by $\{A, B\} = A B + B A$):

$$\begin{aligned} \{Q_1, Q_2\} &\equiv Q_1 Q_2 + Q_2 Q_1, & [\sigma_3, H], \\ [\sigma_3, Q_1]; & \quad [\sigma_3, Q_2]; & \quad \{\sigma_3, Q_1\}; \quad \{\sigma_3, Q_2\}, \end{aligned}$$

and to prove that:

- (i) The necessary and sufficient condition for the ground state to have $E_0 = 0$ is that there exists a normalizable solution of the linear equation

$$p \psi_0(x) \equiv -i\hbar \frac{d}{dx} \psi_0(x) = -iW(x) \sigma_3 \psi_0(x). \quad (20.84)$$

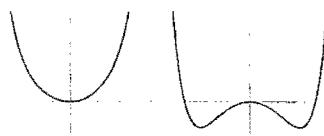


Fig. 20.2 Potentials $V^{(1,2)}$ having (almost) identical spectra.

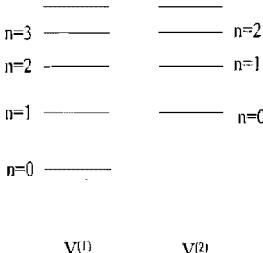


Fig. 20.3 The two potentials of Figure 20.2 have the same energy levels except one.

- (ii) Each eigenstate of H with positive energy is doubly degenerate, while the state with $E_0 = 0$, if there, is single (non-degenerate).
- (iii) The existence of a zero-energy ground state does not depend on the behavior of the superpotential $W(x)$ at finite x , but depends on its asymptotic behavior at $x \rightarrow \pm\infty$; more precisely a zero-energy ground state exists when the number of zeros of $W(x)$ is odd, it does not if $W(x)$ have an even number of zeros.

In fact, by choosing the states as simultaneous eigenstates of (H, σ_3) ,

$$H |E_n, \pm\rangle = E_n |E_n, \pm\rangle, \quad \sigma_3 |E_n, \pm\rangle = \pm |E_n, \pm\rangle,$$

one finds that the operators Q_1 ($\circ Q_2$) act as:

$$\begin{aligned} Q_1 |E_n, +\rangle &= \sqrt{E_n} |E_n, -\rangle, & Q_1 |E_n, -\rangle &= \sqrt{E_n} |E_n, +\rangle, \\ Q_2 |E_n, +\rangle &= i \sqrt{E_n} |E_n, -\rangle, & Q_2 |E_n, -\rangle &= -i \sqrt{E_n} |E_n, +\rangle, \end{aligned}$$

Q_1, Q_2 are examples of *supersymmetry* operators.

It might appear surprising that two one-dimensional systems with distinct Hamiltonians ($\sigma_3 = \pm 1$ in eqn (20.81)) possess an identical spectrum, except possibly the ground state. In the simple case of harmonic oscillator, $W(x) = m\omega x$, the two potentials (for $\sigma_3 = \pm 1$) are $V^{(1,2)} = \frac{1}{2}m\omega^2 x^2 \pm \omega \hbar$, and such a situation is quite obvious, but in a more general case, e.g., for the potentials $V^{(1)} = x^6 + 3x^2$ and $V^{(2)} = x^6 - 3x^2$ (Figure 20.2) the identity of the spectrum (except for the ground state) is quite intriguing.

The properties of systems with supersymmetry indeed look quite extraordinary and this might mislead the reader into believing that we are talking about rather exceptional situations, of academic interest.

Actually, the structure of this type is very general. Quite independently of the original physical idea of supersymmetry in elementary particle physics (symmetry under the exchange of bosons and fermions), one can, in a more general context of quantum mechanics, ask whether, given a Hamiltonian H , it is possible to find another Hamiltonian which has exactly the same spectrum as H except for one or more states. It turns out that there is a simple procedure which works for *any* system. The procedure can furthermore be iterated. Thus, given a system H_1 (with potential $V^{(1)}$) with spectrum $E_0 = 0, E_1, E_2, E_3, E_4, \dots$, a second system H_2 (with potential $V^{(2)} \neq V^{(1)}$) can be constructed, endowed with energy levels $E_1, E_2, E_3, E_4, \dots$; starting from the system H_2 a third system H_3 can be constructed which has the energy levels E_2, E_3, E_4, \dots , etc.

This general property of quantum mechanical spectrum is, perhaps not commonly appreciated.

The central role is played by the two non-Hermitian operators Q, Q^\dagger such that

$$Q = \frac{1}{\sqrt{2m}}(ip + W(x)), \quad Q^\dagger = \frac{1}{\sqrt{2m}}(-ip + W(x)).$$

The Hamiltonians of the two sister systems are then given by⁹

$$\begin{aligned} H^{(1)} &= Q^\dagger Q = \frac{p^2}{2m} + V^{(1)}(x), \\ H^{(2)} &= Q Q^\dagger = \frac{p^2}{2m} + V^{(2)}(x), \end{aligned} \quad (20.85)$$

where

$$V^{(1)}(x) = \frac{1}{2m}(W^2(x) - \hbar W'(x)), \quad V^{(2)}(x) = \frac{1}{2m}(W^2(x) + \hbar W'(x)).$$

The property

$$E_n^{(1)} \geq 0; \quad E_n^{(2)} \geq 0, \quad n = 0, 1, 2, 3, \dots$$

readily follows from eqn (20.85).

Suppose that one has a system with potential $V^{(1)}(x)$, with a ground state $\psi_0(x)$ with zero energy $E_0 = 0$. Clearly the condition for the existence of such a system is that

$$Q |\psi_0\rangle = 0,$$

i.e.,

$$W(x) = -\hbar \frac{\psi'_0(x)}{\psi_0(x)}, \quad \therefore \quad \psi_0(x) = e^{-\frac{1}{\hbar} \int^x dx W(x)}, \quad (20.86)$$

$$\begin{aligned} H^{(1)} &= \frac{1}{2m} Q^\dagger Q = \frac{p^2}{2m} + V^{(1)}(x), \\ V^{(1)}(x) &= \frac{1}{2m} (W^2(x) - \hbar W'(x)). \end{aligned} \quad (20.87)$$

The hypothesis that $\psi_0(x)$ is normalizable ($\psi_0 \in L^2$) implies the behavior of the superpotential be such that the integral

$$\int^x dx W(x) \rightarrow +\infty, \quad x \rightarrow \pm\infty, \quad (20.88)$$

diverges sufficiently rapidly ($|\int^x dx W(x)| > \frac{1}{2} \log x$). As $\psi_0(x)$ has no nodes W is finite for finite values of x .

The above discussion shows that actually it is sufficient to know the ground-state wave function $\psi^{(0)}(x)$, to start the whole construction. Indeed, given $\psi^{(0)}(x)$, it is always possible to find the potential of the system through eqns (20.86) and (20.87), and then construct the rest.

Once the superpotential $W(x)$ is found it is a simple matter to construct a second Hamiltonian

$$\begin{aligned} H^{(2)} &= \frac{1}{2m} Q Q^\dagger = \frac{p^2}{2m} + V^{(2)}(x), \\ V^{(2)}(x) &= \frac{1}{2m} (W^2(x) + \hbar W'(x)). \end{aligned} \quad (20.89)$$

Note that in view of the behavior of the superpotential, eqn (20.88), the new system $H^{(2)}$ cannot have a state with $E = 0$ (i.e., a normalizable

⁹In fact, the operators Q, Q^\dagger are equivalent to the two operators $\sigma_2 Q_1$ or $\sigma_1 Q_2$ (see eqns (20.83)). However, in what follows we shall forget about the original interpretation and consider the possible states associated with $\sigma_3 = \pm \frac{1}{2}$ as belonging to two separate systems. It is possible to reinstate a spin interpretation if one wishes, at any moment.

state annihilated by Q^\dagger), therefore the two systems do not have the same spectrum. But it is easy to show that *all* the non-zero energy eigenvalues are identical. Given the eigenstates of $H^{(1)}$

$$H^{(1)} \psi_n^{(1)} = E_n^{(1)} \psi_n^{(1)}, \quad (20.90)$$

one has

$$H^{(2)} (Q \psi_n^{(1)}) = Q Q^\dagger Q \psi_n^{(1)} = Q H^{(1)} \psi_n^{(1)} = E_n (Q \psi_n^{(1)}).$$

Obviously this argument is valid except for $n = 0$, for which $Q \psi_0^{(1)} = 0$. Thus

$$\begin{aligned} \psi_n^{(2)} &= \frac{1}{\sqrt{E_{n+1}^{(1)}}} Q \psi_{n+1}^{(1)}, & n &= 0, 1, 2, \dots \\ E_n^{(2)} &= E_{n+1}^{(1)}, & n &= 1, 2, \dots \end{aligned}$$

The ground-state energy of the second system is positive, $E_0^{(2)} > 0$. Now by shifting the origin of the energy, we define

$$H^{(2')} \equiv H^{(2)} - E_0^{(2)}.$$

The eigenfunctions are not affected by such a shift. $\psi_0^{(2)}(x)$ is now the ground state wave function of $\tilde{H}^{(2)}$ with zero energy. We can then find $W^{(2)}$ from eqn (20.86) but with $\psi_0^{(2)}(x)$ instead of $\psi_0(x)$, and reconstruct $\tilde{H}^{(2)} = Q^{(2)\dagger} Q^{(2)}$ exactly as in eqns (20.86)–(20.89), with

$$Q^{(2)} = \frac{1}{\sqrt{2m}} (ip + W^{(2)}(x)). \quad (20.91)$$

At this point we find another system $H^{(3)} = Q^{(2)} Q^{(2)\dagger}$, which has the same spectrum as $H^{(2')}$ except the ground state of the latter. The third system $H^{(3)}$ has an identical spectrum as the first $H^{(1)}$ except for the lowest two states of the latter, and so on.

Many new interesting results can be found by following this method, see [Cooper, et. al. (2002)].

An example: an infinite potential well of width a

The eigenstates and energy levels of this system are well known (Section 3.1):

$$\psi_n^{(1)}(x) = \sqrt{\frac{2}{a}} \sin \frac{\pi n x}{a}, \quad E_n = \frac{\pi^2 (n^2 - 1) \hbar^2}{2ma^2}, \quad n = 1, 2, \dots$$

We added a constant to the Hamiltonian so that the ground state ($n = 1$) has a vanishing energy.

From eqn (20.86) one finds that

$$W(x) = -\frac{\hbar}{\sqrt{2m}} \frac{\pi}{a} \cot \frac{\pi x}{a}.$$

$$W(x)^2 = \frac{\hbar^2}{2m} \frac{\pi^2}{a^2} \cot^2 \frac{\pi x}{a}; \quad W'(x) = \frac{\hbar}{\sqrt{2m}} \frac{\pi^2}{a^2} \frac{1}{\sin^2 \frac{\pi x}{a}}.$$

For consistency,

$$V^{(1)}(x) = W^2(x) - \frac{\hbar W'(x)}{\sqrt{2m}} = \frac{\hbar^2}{2m} \frac{\pi^2}{a^2} \left[\cot^2 \frac{\pi x}{a} - \frac{1}{\sin^2 \frac{\pi x}{a}} \right] = -\frac{\hbar^2 \pi^2}{2m a^2},$$

as expected. The potential $V^{(2)}$ is however nontrivial (Figure 20.4):

$$V^{(2)}(x) = W^2(x) + \frac{\hbar}{\sqrt{2m}} W'(x) = \frac{\hbar^2}{2m} \frac{\pi^2}{a^2} \frac{1 + \cos^2 \frac{\pi x}{a}}{1 - \cos^2 \frac{\pi x}{a}}, \quad 0 \leq x \leq a,$$

$$V^{(2)}(x) = \infty, \quad x < 0, \quad x > a.$$

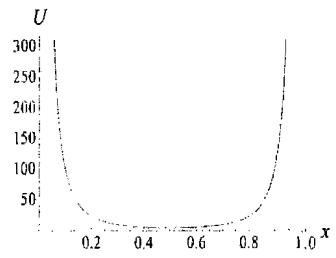


Fig. 20.4 The potential with energy eigenvalues $\frac{\pi^2 n^2 \hbar^2}{2m a^2}$, $n = 1, 2, \dots$

20.13 Two- and three-dimensional delta function potentials

Consider a particle moving in a three-dimensional (or two-dimensional) delta function potential

$$H = \frac{\mathbf{p}^2}{2m} + G_0 \delta^3(\mathbf{r}),$$

where the constant G_0 can have either sign. Unlike the one-dimensional problem discussed in Chapter 3 the potential is highly singular in two or three dimensions. Below we shall study this problem, following the paper by R. Jackiw [Jackiw (1991)].

For concreteness we shall consider first the three dimensional case. To simplify the notation let us use the natural units $\hbar = 1 = m$ and set $m G_0 / \hbar^2 = g_0$. The Schrödinger equation for the stationary states is

$$-\frac{1}{2} \Delta \psi + g_0 \delta^3(\mathbf{r}) \psi(\mathbf{r}) = -\frac{1}{2} \Delta \psi + g_0 \delta^3(\mathbf{r}) \psi(\mathbf{0}) = E \psi(\mathbf{r}). \quad (20.92)$$

It is clear that a solution of eqn (20.92) must be singular: the potential term implies a factor $\delta^3(\mathbf{r})\psi(\mathbf{0})$, a δ function in three dimension can arise only from a singularity $1/r$, as $\Delta 1/r = -4\pi \delta^3(\mathbf{r})$, and this implies $\psi(\mathbf{0}) = \infty$. This is the crucial difference from the one-dimensional case, where a δ factor is generated by $|x|$ (as $\partial_x^2 |x| = 2\delta(x)$) which is continuous.

To understand the nature of the singularity let us solve eqn (20.92) for the continuous spectrum. We have to fix boundary condition and we choose the usual one: we require that asymptotically the solution behaves as a plain wave plus a spherical divergent wave (this point is fully discussed in Chapter 15)

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} + f(\theta) \frac{e^{ikr}}{r}, \quad (20.93)$$

where $E = \mathbf{k}^2/2$. A δ function can only affect the s -waves so $f(\theta)$ must be independent of θ . For $r > 0$ the function $\exp(ikr)/r$ is an exact solution for the s -wave. Indeed, apart a normalization factor it is the

Hankel function $h_0(kr)$, see Section 6.1.3. This means that eqn (20.93) is the *exact* solution for $r > 0$. This implies $\psi(0) = \infty$, if f is finite.

The exact solution can be easily written down by using the Green function $G_k(r)$

$$G_k(r) = \frac{1}{4\pi} \frac{e^{ikr}}{r}, \quad (\Delta + k^2)G_k(r) = -\delta^3(\mathbf{r}).$$

One has immediately:

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} - 2g_0 G_k(r)\psi(0); \quad f = -\frac{g_0}{2\pi}\psi(0).$$

$\psi(0)$ is undefined and we have to interpret the meaning of this solution.

To clarify this point let us solve eqn (20.92) in the p -representation, performing a Fourier transform:

$$\frac{1}{2}(p^2 - k^2)\varphi_{\mathbf{k}}(\mathbf{p}) = -g_0 \psi(0). \quad (20.94)$$

φ is the Fourier transform of ψ . The solution of this linear equation is given by a superposition of a particular solution with a solution of the homogeneous equation:

$$\varphi_{\mathbf{k}}(\mathbf{p}) = (2\pi)^3 \delta^3(\mathbf{p} - \mathbf{k}) - \frac{2g_0}{p^2 - k^2 - i\varepsilon} \psi(0). \quad (20.95)$$

The infinitesimal ε is the well-known “epsilon-prescription” which fixes the way the Fourier transform is computed; it selects the outgoing spherical wave in the solution, see Section 6.1.3. The first term in eqn (20.95) is the homogeneous solution, its normalization has been chosen so as to agree with the plane wave in eqn (20.93). Integrating over \mathbf{p} and using

$$\psi(0) = \int \frac{d^3 p}{(2\pi)^3} \varphi_{\mathbf{k}}(\mathbf{p}),$$

one finds

$$g_0 \psi(0) = \left(\frac{1}{g_0} + 2I(-k^2 - i\varepsilon) \right)^{-1}.$$

where

$$I(z) = \int \frac{d^3 p}{(2\pi)^3} \frac{1}{\mathbf{p}^2 + z}.$$

I clearly diverges in three dimensions. It can be defined by introducing a cutoff Λ in the momenta:

$$I(z) \simeq \frac{1}{2\pi^2} \Lambda - \frac{1}{4\pi} \sqrt{z}$$

and

$$g_0 \psi(0) = \left(\frac{1}{g_0} + \frac{\Lambda}{\pi^2} + i \frac{k}{2\pi} \right)^{-1}.$$

The sign in the imaginary term has been chosen using the $i\varepsilon$ prescription.

If g_0 would be taken as a fixed physical parameter, the problem would look ill-defined. Actually, *all* physical information enters in the model

through the combination $g_0\psi(0)$. This observation allows us to define the theory by taking g , where

$$\frac{1}{g_0} + \frac{\Lambda}{\pi^2} = \frac{1}{g}, \quad g : \text{finite},$$

as the physical parameter of the system. In other words, the model is defined by a curve in the parameter space, (g_0, Λ) , corresponding to a given value of g . The system is then perfectly well defined.

This is an analogue of an idea familiar in relativistic quantum field theories, such as the quantum electrodynamics or the Standard Model of fundamental interactions. The procedure is called *renormalization*, g is known as *renormalized coupling*, while g_0 is what is known as the *bare coupling*.

The scattering amplitude as a function of g is

$$f(k) = -\left(\frac{2\pi}{g} + ik\right)^{-1}. \quad (20.96)$$

Scattering amplitude is usually parametrized by phase shifts (see Chapter 15):

$$f = \frac{1}{2ik}(e^{2i\delta} - 1), \quad \Rightarrow \quad \tan(\delta) = \frac{\text{Im}(f)}{\text{Re}(f)} = -\frac{gk}{2\pi}. \quad (20.97)$$

Remarks

- Note that no new parameters have been added in the theory: we have traded one bare parameter, g_0 , with a renormalized parameter, g (which is the physical parameter).
- If this is to be taken as a “realistic” model, the effectively measured parameter is g , not g_0 . g is to be determined experimentally, for instance, by measuring the angular distribution, $|f|^2$ which is a function only of g at fixed k .
- The physical reason that renormalization is necessary in three (also in two) dimensions, whereas the one-dimensional delta function potential does not require renormalization, is that the potential is more singular than (or as singular as) the kinetic term.
- Two different attitudes can be taken with respect to these results: either we consider the procedure as a coherent mathematical framework to define a generalized Hamiltonian, i.e. assign a consistent meaning to the limit $\Lambda \rightarrow \infty$ (in other words, these can be defined as a self-adjoint extension of the free Hamiltonian system, defined however in $\mathbf{R}^3/\{0\}$); or we can consider it as an effective way to describe the physics at scales $k \ll \Lambda$. This second point of view is the one currently preferred in analogous situations in quantum field theory, and even more in statistical mechanics.

20.13.1 Bound states

The scattering amplitude (20.96) has a pole for $g > 0$ on the positive imaginary k axis, $k = ik_0$, $k_0 = 2\pi/g$. This corresponds to a bound

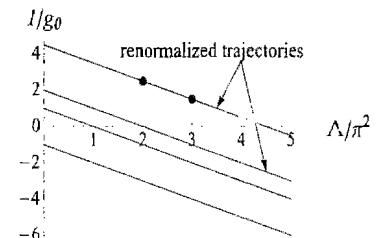


Fig. 20.5 Renormalized trajectories (fixed g) in the plane of bare coupling-cutoff; points on the same curve give the same physics.

state with energy

$$E_B = -\frac{k_0^2}{2} = -\frac{2\pi^2}{g^2}, \quad \sqrt{-2E_B} = \frac{2\pi}{g}. \quad (20.98)$$

Let us verify directly this point. The Schrödinger equation is

$$-\frac{1}{2}\Delta\psi - \frac{k_0^2}{2}\psi + g_0\delta^3(\mathbf{r})\psi(0).$$

For $r > 0$ the *normalized* solution is (expressing it as a function of E_B):

$$\psi(r) = \left(\frac{-E_B}{2\pi^2}\right)^{1/4} \frac{e^{-\sqrt{-2E_B}r}}{r}. \quad (20.99)$$

This function is in \mathbb{L}^2 , so if it satisfies the Schrödinger equation it represents a bound state. Consider again eqn (20.94), now for negative energies $E_B = -k_0^2/2$:

$$\frac{1}{2}(\mathbf{p}^2 + k_0^2)\varphi_B(\mathbf{p}) = -g_0\psi_B(0).$$

The solution is

$$\varphi_B(\mathbf{p}) = -\frac{2g_0}{\mathbf{p}^2 + k_0^2}\psi_B(0)$$

Integration in \mathbf{p} gives

$$\psi_B(0) = -2g_0I(k_0^2)\psi_B(0).$$

The condition for the existence of a bound state is therefore

$$\frac{1}{g_0} = -2I(k_0^2) = -2\left(\frac{1}{2\pi^2}\Lambda - \frac{1}{4\pi}k_0\right) = -\frac{\Lambda}{\pi^2} + \frac{k_0}{2\pi}.$$

This is the same condition for the finiteness of the renormalized coupling constant obtained before. That is the bound state energy is indeed given by eqn (20.98), the corresponding wave function is given by eqn (20.99).

An alternative approach to the momentum cutoff adopted above, would be to work directly in the coordinate space. A δ function can be regularized by

$$\delta^3(\mathbf{r}) = \frac{1}{4\pi R^2}\delta(r-R).$$

In the limit $R \rightarrow 0$ one recovers the original singularity. In Problem 5 of Chapter 6 the necessary computations are done in this representation.

20.13.2 Self-adjoint extensions

The whole machinery exposed so far can be summarized by the statement that to deal with a δ function potential in three dimensions we have to relax the condition that $\psi(0)$ is finite. A question naturally arises: is this legitimate? Is the resulting Hamiltonian a self-adjoint operator? The answer is yes.

We have seen that the only problem is for the s -wave solution, so let us consider the Schrödinger equation for the reduced radial wave function for $L = 0$. The relevant one-dimensional Hamiltonian problem is

$$-\frac{1}{2}\chi''(r) = E\chi(r). \quad (20.100)$$

χ is the reduced wave function. As the origin is singular we consider the Hamiltonian for $r > 0$ and we want to understand how we can define a self-adjoint Hamiltonian in this domain.

In the Section 20.15.5 we will discuss the possible extensions of operators, in particular we will show that for the region $[0, \infty]$ the most general (free) Hamiltonian is parametrized by the boundary conditions (see Section 20.15.5)

$$\lim_{r \rightarrow 0} \chi(r) = -\frac{\lambda}{2\pi} \lim_{r \rightarrow 0} \chi'(r); \quad (20.101)$$

$\lambda = 0$ is the usual choice.

The generic solution for the continuum spectrum, with an arbitrary normalization, is ($E = k^2/2$):

$$\chi(r) = \sin(kr) + C \cos(kr).$$

The condition (20.101) fixes $C = -\frac{\lambda}{2\pi} k$ and

$$\chi(r) = \sin(kr) - \frac{\lambda}{2\pi} k \cos(kr).$$

The asymptotic behavior for scattering states is

$$A \sin(kr + \delta) = A \cos \delta (\sin(kr) + \tan(\delta) \cos(kr)).$$

Then

$$\tan \delta = -\frac{\lambda}{2\pi} k.$$

Comparing this with eqn (20.97) we see that the extension parameter λ is nothing but the renormalized coupling constant g .

This conclusion is confirmed by considering the bound state for $g > 0$. The solution must be of the form

$$\chi(r) = Ae^{-\mu r}$$

By using eqn (20.101) we get for the bound state the same condition (20.98):

$$A = \frac{\lambda}{2\pi} \mu A \quad \Rightarrow \quad \mu = \frac{2\pi}{\lambda} = \frac{2\pi}{g}.$$

20.13.3 The two-dimensional delta-function potential: a quantum anomaly

An analogous treatment of the delta function potential in two dimensions, $g_0 \delta^2(x)$, shows interesting phenomena, not very common in non-relativistic quantum mechanics, but very analogous to what typically occurs in a “renormalizable” quantum field theory in four dimensions.

In the two-dimensional case, the classical system has a scale invariance, under $r_i \rightarrow \lambda r_i$. The coupling constant g_0 is dimensionless (in the natural unit, $c = \hbar = 1$), as the two-dimensional delta function behaves as r^{-2} just as the kinetic term. The discussion is fairly parallel though to the three-dimensional case above, and leads to the following result on the scattering amplitude:

$$f(k, E_B) = -\frac{1}{i\sqrt{2\pi k}} \left(\frac{1}{g} - \frac{1}{\pi} \log \frac{k}{\mu} + \frac{i}{2} \right)^{-1}.$$

g is the “renormalized” coupling constant,

$$\frac{1}{g} = \frac{1}{g_0} + \frac{1}{\pi} \log \frac{\Lambda}{\mu}, \quad g : \text{finite},$$

defined at μ , while Λ is the ultraviolet cutoff, g_0 is the *bare* coupling constant. There is again a (unique) bound state with energy

$$\sqrt{-2E_B} = \mu e^{\pi/g}, \quad E_B = -\frac{\mu^2}{2} e^{2\pi/g},$$

and the wave function

$$\psi(r) = \sqrt{\frac{-2E_B}{\pi}} K_0 \left(\sqrt{-2E_B} r \right).$$

K_0 is a Bessel function of purely imaginary argument. Again, the bound-state energy is not calculable; it is a physical quantity to be determined experimentally (if such a system is applied to a concrete physical system, such as an impurity in a crystal). g is a finite *renormalized* coupling constant. Note that both the scattering amplitude and the bound state wave function (binding energy) depend only on the finite physical parameters.

Unlike the three-dimensional case, however, here a new scale parameter μ seems to appear in the physical expressions. We are, in fact, obliged to introduce this in order to define a finite “renormalized” coupling constant g out of apparently divergent expressions. Nevertheless, the bound-state wave function and the scattering amplitude are functions only of k and E_B ; they do not depend on g or on μ separately.¹⁰ In this sense the “physical” coupling constant g must be understood as depending on μ , $g \equiv g(\mu)$. Its dependence is given by

$$\mu \frac{d}{d\mu} g(\mu) = \frac{1}{\pi} g(\mu)^2 = \beta(g(\mu)).$$

This is an example of the so-called *renormalization group equation*; the right-hand side is known as the beta function for g .

To summarize, the classical scale invariance has been broken by the necessity of introducing a quantity of dimension of momentum (or mass), μ , in order to *define* a finite renormalized coupling constant—that is in order to define a quantum theory. This is an example of what is known as a *quantum anomaly*: a rather common phenomenon in four-dimensional renormalizable quantum field theories. At the end of the

¹⁰Exercise. Check this.

day, we find that the ultraviolet cutoff Λ or the bare coupling constant g_0 has been traded with a single physical quantity, $|E_B|$, and the scattering amplitude is expressed in terms of it (and of the physical momentum) only. These are the typical features occurring in any four-dimensional renormalizable quantum field theory, such as quantum electrodynamics, the Glashow–Weinberg–Salam theory, or quantum chromodynamics.

20.14 Superselection rules

In Section 7.1 we asserted that to each observable is associated a self-adjoint operator (P2) and that each physical state corresponds to a ray in the Hilbert space (P1). We now wish to examine briefly whether the inverse holds true also, i.e.,

- (b1) Does each self-adjoint operator correspond to a physical observable?
- (b2) Does each vector in the Hilbert space describe a physical state?

Clearly we are forced to examine more closely the superposition principle itself: if $|\alpha\rangle$, $|\beta\rangle$ are two physical states, is the state $|\alpha\rangle + |\beta\rangle$ also a physical state, for *whatever* $|\alpha\rangle$ and $|\beta\rangle$?

In most cases treated in this book, and in the majority of systems considered in quantum mechanics, the answer is affirmative, and we have indeed presented it as one of the basic principles of quantum mechanics. As it turns out, however, it is not at all obvious that we can extend this principle (or better, postulate) to *whatever* system; it must be consolidated by the experimental facts and/or strong theoretical motivations.

The conclusion of the discussion below will be that we need certain conditions to answer affirmatively the questions (b1), (b2); in other words, *superposition principle admits exceptions*.

Remarks

- (1) What specifies a system physically is what we can, at least in principle, experimentally verify, that is, the ensemble of the observables of the system. To each observable is associated a self-adjoint operator: they will be identified below. However what qualifies an observable as such is not mathematics but a physical requirement: when we say that q is an observable, we are asserting that there exists an apparatus, such as a microscope, which is capable of measuring the position. The same holds for the momentum operator.
- (2) Let us call *realizable* a state which can be produced by an observable, i.e., as a result of a measurement (more precisely, a set of compatible measurements). Namely a self-adjoint operator or a set of commuting operators, acting upon some vector Φ , produce as one of the possible results of the measurement, the state in question. In other words a state is realizable if it is an eigenstate of some observable(s).

It is easy to show that if all self-adjoint operators would correspond to an observable, then all states in the Hilbert space are realizable, and vice versa, so the questions (b1),(b2) are equivalent. In fact, assume that every self-adjoint operator corresponds to some observable. Then so is $|\psi\rangle\langle\psi|$: acting on any state $|\Phi\rangle$ it generates a state $|\psi\rangle(\langle\psi|\Phi\rangle)$, that is, $|\psi\rangle$. Of course, there must be at least one such state $|\Phi\rangle$; otherwise the operator would be a null operator. It follows that each state is realizable.

Vice versa, each self-adjoint operator A admits a spectral representation, which has the form (assuming a discrete spectrum, for simplicity of writing),

$$A = \sum_i \lambda_i |e_i\rangle\langle e_i|. \quad (20.102)$$

So if we assume that all states are realizable then the projector $|e_i\rangle\langle e_i|$ is observable, as the latter is a filter to create such a state. All the projection operators commute among each other, they are compatible observables, and they are simultaneously observable and thus A is an observable.

Let us now examine in a simple example in which way physics enters. Let us consider a one-dimensional potential well, symmetric with respect to parity, $x \leftrightarrow -x$. Let us assume that energy is an observable, in the sense that there exists an apparatus able to measure it. Consider first the bound states. As there are no degenerate bound states in one dimension, the energy specifies uniquely the state. The situation is different in the continuous spectrum. Each energy level is doubly degenerate, and as the potential is invariant under parity each state will be either symmetric or antisymmetric (e.g., $\cos(px)$ or $\sin(px)$ in the free case).

Let us assume, just as a logical possibility, that all observables A are even. Then in any state of type

$$\psi = c_+ |+\rangle + c_- |-\rangle$$

where $|+\rangle$ and $|-\rangle$ are even or odd under parity, the expectation value of A takes the form,

$$\langle\psi|A|\psi\rangle = |c_+|^2 \langle +|A|+\rangle + |c_-|^2 \langle -|A|-\rangle. \quad (20.103)$$

There would be no ways of measuring the effects due to the interferences between $|+\rangle$ and $|-\rangle$. The system would effectively be a mixed state described by the density matrix,

$$\rho = |c_+|^2 (|+\rangle\langle +|) + |c_-|^2 (|-\rangle\langle -|)$$

rather than being a pure state. If there were indeed no observables at all which have non-vanishing matrix elements connecting vectors of the type $|+\rangle$ and vectors of the type $|-\rangle$, the Hilbert space would be effectively a direct sum, $\mathcal{H} = \mathcal{H}_+ \oplus \mathcal{H}_-$, without any communications between them.

Of course, this is actually not the case in these simple systems: there are perfectly sensible operators such as x or p , which are odd under parity.

Even so, our argument clearly illustrates the following possibility. Suppose that there exists a self-adjoint operator Q , which commutes with all observables. In particular Q commutes with the Hamiltonian, i.e., it is conserved. Let us assume for the moment that there is only one such operator. The operator Q can be diagonalized and in such a basis all the states are eigenstates of Q . If A is a possible observable (represented by a self-adjoint operator A), $[Q, A] = 0$ by assumption. It is then easy to show that

$$\langle \psi, q | A | \psi', q' \rangle \neq 0,$$

only for $q = q'$. There are no observables having non-vanishing matrix elements between two states of different eigenvalues of Q . That is to say: the Hilbert space decomposes into subspaces corresponding to definite value of Q . In such a case, the charge Q is said to be “superselected”. No pure states exist which are nontrivial superposition of states with different values of q . Only the superposition of states of the same q makes sense. Any state and observation involving different eigenvalues of Q can be described in terms of a density matrix rather than a wave function. This state of affair is called *superselection rule*. The generalization to more than one such charge Q is straightforward.

Are there known examples of superselection rule in Nature?

Two examples are well known: the fermionic charge and the electric charge. The first concerns the “charge” $P_F = (-1)^F$, where F is the total fermion number of the system. As seen in the Chapter 4, there are in Nature two different types of elementary particles, those with integer spin (called bosons) and those with half-integer spin (fermions). Instances of the former are: photon, pion, kaon, W and Z bosons, (graviton); electron, proton, neutron, neutrino, etc., are examples of the latter. As we know from the theory of angular momentum, the behavior of the wave function under 2π space rotations is different in the two cases, the fermionic wave functions changing sign, while the bosonic system does not. Now a natural requirement on any sensible theory is that the physics does not change when the coordinate system is rotated by 360 degrees. If the state is either bosonic or fermionic, no problem arises as the overall sign change (in the case of a fermionic state) does not modify the quantum state. But if the state under consideration is a superposition of a bosonic and fermionic state, then there is a problem:

$$|B\rangle + |F\rangle \xrightarrow{\text{rot. } 2\pi} |B\rangle - |F\rangle .$$

As the relative phase is important, the state would not come back to the original state after 360 degree rotation. Thus we are forced to exclude superpositions of this sort, from possible quantum states. If F is the operator which counts the fermion number, the operator which distinguishes whether the system contains an even number or odd number of fermions is $P_F = (-1)^F$. This operator is superselected. Only the superposition of states among the states of the same P_F are allowed.

Another famous example is the electric charge. It is absolutely conserved, and *superselected*. No pure states are allowed which are nontrivial superpositions of states with different electric charges. This example nicely illustrates the difference of any *conserved* charges and superselected ones. For example, the energy is conserved, but certainly superposition of states of different energies is not only allowed but is a most common concept in quantum mechanics (e.g., wave packets).

The basic point is that while a conserved charge R always commutes with the Hamiltonian, in general there are in the system under consideration other observables with which R does not commute. In other words, the fact that R is conserved does not exclude the existence of some physical variables (possible measurements) which are capable of changing its value. In the case of the energy which is absolutely conserved, for instance, there are operators such as x or p which are measurable and which do not commute with H . In the presence of observables having non-diagonal elements, a pure state which is a nontrivial superposition of states with different eigenvalues of R perfectly makes sense: the relative coefficients in such a linear combination have observable consequences.

Vice versa, in the case of a superselected charge Q , no observables exist having non-diagonal matrix elements corresponding to transitions between different eigenstates of Q . In such a situation a “pure state”

$$|\psi\rangle = \sum c_i |q_i\rangle$$

is for all purposes equivalent to a mixed state described by the density matrix:

$$\rho = \begin{pmatrix} |c_1|^2 & 0 & 0 & 0 \\ 0 & \ddots & 0 & 0 \\ 0 & 0 & |c_n|^2 & 0 \\ 0 & 0 & 0 & \ddots \end{pmatrix}.$$

20.15 Quantum representations

In this Supplement we try to answer in a simple manner the following questions.

- (1) The usual assignment $q \rightarrow x, p \rightarrow -i\hbar\partial/\partial x$ gives a representation of the abstract algebra of commutation relation, this *defines* what we mean by a quantum theory. Is this representation unique?
- (2) What is the relation between equivalent quantum representations and equivalent classical representations (canonical transformations) of a system?
- (3) Does a formal assignment of the Hamiltonian fix uniquely the dynamics of the theory?

These questions have some practical issues, apart their conceptual importance:

- (a) The study of the representations of the canonical algebra and of its generalization is important in the study of abstract dynamical models both in quantum field theory and statistical mechanics.
- (b) The relation between canonical transformations and quantum unitary transformations has some deep relations with the very possibility of obtaining the classical mechanics as a limit of the quantum theory. This is a highly nontrivial problem, both from physical and mathematical point of view.
- (c) The problem of the possible extensions of the Hamiltonian in the case of nontrivial topological configuration space is important in several physical problems.

20.15.1 Weyl's commutation relations

First we must decide on the object of our investigation. To work directly with Heisenberg's relations is quite difficult as we face immediately the domain problems for the unbounded operators q and p . It is much easier and mathematically sound to switch to a "continuous" version of these operators by considering the unitary (and by consequence continuous) operators of q and p translation:

$$T(a)\psi(x) = \psi(x+a); \quad V(b)\psi(x) = e^{ibx/\hbar} \psi(x). \quad (20.104)$$

These operators preserve scalar products, as can be easily verified, then they are unitary. Their infinitesimal generators (for small a and b) are exactly momentum and position operators

$$T(a) = e^{ipa/\hbar} = \simeq 1 + i \frac{a}{\hbar} \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right); \quad V(b) \simeq 1 + i \frac{b}{\hbar} x.$$

From the definition (20.104) or using the Baker–Haussdorff expansion it is trivial to show that

$$T(a)V(b) = e^{iab/\hbar} V(b)T(a).$$

(20.105)

These commutation relations are the *Weyl commutation relations*. The point is that if there is no problem they are equivalent to Heisenberg's relations, but actually are more general as they are formulated in term of continuous operators, thus avoiding complicated problems of domains for unbounded operators q and/or p .

The problem set in the introduction can now be stated: how many (nonequivalent) realizations of Weyl relations exist? A theorem due to von Neumann answers this question.

20.15.2 Von Neumann's theorem

Theorem 20.4 *Given two one-parameter families of unitary operators $T(a)$ and $V(b)$ satisfying Weyl's algebra on a Hilbert space \mathcal{H} then there exist a set of closed subspaces \mathcal{H}_k such that*

- (a) $\mathcal{H} = \bigoplus_{k=1}^N \mathcal{H}_k$
- (b) $T(a) : \mathcal{H}_k \rightarrow \mathcal{H}_k$ e $V(b) : \mathcal{H}_k \rightarrow \mathcal{H}_k$
- (c) $\forall k$ there exists a unitary operator $U_k : \mathcal{H}_k \rightarrow \mathbb{L}_2(\mathbb{R})$ such that $U_k T(a) U_k^{-1}$ acts as a translation (i.e. $\psi(x) \rightarrow \psi(x+a)$) and $U_k V(b) U_k^{-1}$ acts as $e^{ibx/\hbar}$.

The proof of this theorem can be found in [Reed and Simon (1980a)]. Statements (a), (b) mean simply that the representation can be reduced to act on subspaces of the whole Hilbert space, like a usual group representation. (c) is the main point: the theorem states that the representation is *unique*, up to a unitary transformation.

A crucial point to understand is that in the thesis of the theorem appear $\mathbb{L}_2(\mathbb{R})$; i.e. we are speaking about unconstrained variables, i.e. *usual cartesian coordinates* on \mathbb{R} . This is why cartesian coordinates have a special role in quantum mechanics: only for them we have a “unique” quantum mechanics.

From the theorem it is possible to proof a corollary which is what is usually needed:

Corollary. Let $T(a), V(b)$ be as in von Neumann's theorem, let P, Q be their infinitesimal generators, then it exists a dense domain $D \in \mathcal{H}$ such that

- (a) $P : D \rightarrow D$, $Q : D \rightarrow D$;
- (b) $PQ\varphi - QP\varphi = -i\hbar\varphi \quad \forall \varphi \in D$;
- (c) P and Q are essentially self-adjoint operators on D , i.e. they can be extended as self-adjoint operators.

20.15.3 Angular variables

A simple example can help to clarify the meaning of the von Neumann theorem and the importance of Weyl's algebra.

Let us consider a particle moving on a circle of length L (this is equivalent to a problem of an angular variable $\varphi \in [0, 2\pi]$ if we put $L = 2\pi R$). The Hilbert space is $\mathbb{L}^2[0, L]$. Clearly one can limit oneself to the study of periodic functions, for the moment. It is an elementary exercise to show that Q and P are self-adjoint operators, Q is bounded ($\|Q\| = L$) and that P has a discrete spectrum

$$p_n = \hbar \frac{2\pi n}{L}. \quad (20.106)$$

Equation (20.106) is clearly incompatible with Heisenberg's relations, as $\Delta P = 0$ on eigenstates while Q is bounded. Let us consider the origin of this phenomenon. The domain of P is the set of periodic functions. If we consider a state $\varphi(x) = V(b)\psi(x)$, with ψ periodic, $\varphi(x)$ is not periodic, so it does not belong to the domain of P . This is true for every periodic function. The intersection between the domain of $V(b)$ and P is zero. The Weyl or Heisenberg commutation relations cannot even be written

down. To get fully convinced one can compute the norm of the state $P\varphi_k(x)$, with $\varphi_k(x)$ obtained applying $V(b)$ to an eigenstate of P :

$$\varphi_k(x) = e^{iab/\hbar} \frac{1}{\sqrt{L}} \exp\left(i\frac{2\pi k}{L}x\right).$$

One easily gets

$$\|P\varphi_k\|^2 = \sum_n \left(\frac{2\pi n}{L}\right)^2 \left| \frac{1}{L} \frac{e^{ibL/\hbar} - 1}{\frac{2\pi(k-n)}{L} + \frac{b}{\hbar}} \right|^2.$$

The series diverges. The state does not belong to $\mathbb{L}^2[0, L]$.

From this calculation it is clear that while it is not possible to define consistently the commutation relations for $V(b)$ and P , it is possible to define them if one restricts the possible values of b . For $b = 2\pi/L$, $V(b)$, the translation operator for the momentum, acts in a simple way

$$W \equiv V\left(\frac{2\pi}{L}\right) = \exp\left(\frac{2\pi i}{L} Q\right),$$

$$W\psi_n(x) = e^{2\pi ix/L} \frac{1}{\sqrt{L}} e^{i\frac{2\pi n}{L}x} = \psi_{n+1}(x) \Rightarrow W|n\rangle = |n+1\rangle.$$

$|n\rangle$ label the eigenstates of p . Acting on $|n\rangle$ it is trivial to show that

$$PW - WP = \hbar \frac{2\pi}{L} W.$$

These are the correct Heisenberg commutation relations for angular variables. Using

$$|n\rangle = W^n |0\rangle, \quad P|n\rangle = \frac{2\pi n \hbar}{L} |n\rangle, \quad n = 0, \pm 1, \pm 2, \dots$$

and (using induction):

$$P^n W = \sum_{k=0}^n \binom{n}{k} W P^k \left(\frac{2\pi \hbar}{L}\right)^{n-k};$$

one can also write the Weyl form of the commutation relations:

$$T(a)W = e^{i2\pi a/L} WT(a). \quad (20.107)$$

It follows from this discussion that what is missing in the hypothesis of von Neumann's theorem in this case is the existence of a one-parameter group of operators $V(b)$, only a discrete subgroup $\{W^n\}$ exists. One can suspect a non-uniqueness of the representation of the Weyl algebra.

A generalization of the model has been already met in Section 3.2.2. In the present notation one can define the states periodic up to an angle θ

$$\psi_k^{(\theta)}(x) = \frac{1}{\sqrt{L}} \exp\left[i\left(\frac{2\pi k}{L} + \frac{\theta}{L}\right)x\right].$$

It can be immediately shown that

$$T(a)\psi_k^{(\theta)}(x) = \psi_k^{(\theta)}(x+a); \quad W\psi_k^{(\theta)}(x) = e^{i\frac{2\pi}{L}x}\psi_k^{(\theta)}(x).$$

The Weyl algebra (20.107) always holds, but this representation is not unitarily equivalent to the previous one (the special case $\theta = 0$) as the momentum spectrum changes

$$p_n = \hbar \frac{2\pi n + \theta}{L},$$

while the spectrum should be invariant under unitary transformations for equivalent systems.

It is interesting that the same conclusion can be reached, starting directly from the algebra. The translations $T(a)$ form an Abelian group. It is well known from group theory that the only irreducible representation of such a group are one dimensional. There exists then a state $|0\rangle$ such that

$$T(a) = \exp(i\lambda a)|0\rangle. \quad (20.108)$$

The usual periodicity requirement is $T(L) = T(0)$ but we can allow a generalized condition $T(L) = T(0)\exp(i\theta)$. λ is quantized then as $\lambda = 2\pi n/L + \theta/L$. At fixed θ for each n , one has a different representation of the $U(1)$ group.

It is here that W which acts as an “interwining operator” between different group representations enters. From the Weyl algebra it follows that if $|n\rangle$ is a state belonging to the representation n of $U(1)$ then $W|n\rangle$ belongs to the representation $n+1$. In fact,

$$\begin{aligned} T(a)W|n\rangle &= e^{i2\pi a/L}WT(a)|n\rangle = \\ &e^{i2\pi a/L}W e^{i(2\pi n a + \theta)/L}|n\rangle = e^{i[2\pi(n+1)a + \theta]/L}W|n\rangle. \end{aligned}$$

The representation of the algebra (20.107) requires a whole “tower” of representations of $U(1)$. This tower of representations is the Hilbert space on which the algebra is represented. Two different θ correspond to two non-equivalent representations.

20.15.4 Canonical transformations

By changing the variable to $\varphi = x/L$ one can recognize in the discussion of the previous subsection the quantization procedure for an angular variable and its conjugate momentum $p_\varphi = -i\hbar\partial_\varphi$. The failure of the usual Heisenberg relation for these variables implies that the standard correspondence rule between the Poisson brackets and commutators

$$\{p_\varphi, \varphi\} = 1 \quad \Rightarrow \quad [p_\varphi, \varphi] = -i\hbar$$

breaks down in this case.

This observation, if taken in connection with canonical transformations, has some interesting consequences. Consider in fact any integrable

system. In classical mechanics such a system can always be brought to an action-angles variables by a canonical transformation. The action variables are defined by

$$I = \frac{1}{2\pi} \oint pdq.$$

In these variables the classical Hamiltonian is a function of I 's only, $H = f_H(I)$.¹¹ Now note that the spectrum of p_φ ($p_n = 2\pi n\hbar$), the quantum momentum conjugated to φ , does not depend on the dynamics, but only on the periodicity and on the commutation relations with φ . This would imply that, if the same quantization procedure were possible for every classically canonically conjugate pair (q, p) , the quantum spectrum of the associated Hamiltonian would be

$$E_n = f_H(2\pi n\hbar).$$

This is not true, as can be easily verified, for instance by solving the Schrödinger equation for the anharmonic oscillator. This implies that *canonical transformations are not necessarily translated into unitary operators (i.e. symmetries) in quantum systems*, for otherwise the Hamiltonian spectrum would be invariant.

This also means, as we have already noted, that the canonical quantization procedure selects Cartesian coordinates. For these, and only for these, the von Neumann theorem ensures the uniqueness of the quantization procedure.

One may ask also another question: does an alternative quantization procedure exist which maintains the correspondence between the Poisson brackets and the commutators? If such a procedure existed, one could translate each canonical transformation to a quantum transformation in a consistent way. The answer is no!

Let \mathcal{Q} be the function which associates to a classical variable (q, p) the corresponding quantum variable (Q, P) :

$$\mathcal{Q}(1) = 1; \quad \mathcal{Q}(q) = Q; \quad \mathcal{Q}(p) = P.$$

One would require

$$[\mathcal{Q}(A), \mathcal{Q}(B)] = i\hbar \mathcal{Q}(\{A, B\}).$$

It is easy to show that:

- (1) Up to polynomials of order 2 the correspondence can be found, with

$$\mathcal{Q}(q^2) = Q^2; \quad \mathcal{Q}(p^2) = P^2; \quad \mathcal{Q}(qp) = \frac{1}{2}(QP + PQ).$$

- (2) For polynomials of third order the procedure does not exist. This can be checked by comparing the results of \mathcal{Q} on the two sides of the classical identity

$$\frac{1}{9}\{q^3, p^3\} = \frac{1}{3}\{q^2p, p^2q\}.$$

The conclusion is that there does not exist *any* such quantization procedure which gives a correspondence between the canonical structure and commutators in quantum mechanics.

¹¹More details on this point will be given in Chapter 11.

20.15.5 Self-adjoint extensions

Let us now discuss the third question asked at the beginning of this Supplement. A necessary condition for a self-adjoint operator is to be symmetric, i.e.

$$\forall x, y \in \mathcal{D}(A) \quad (x, Ay) = (Ax, y).$$

The key point in checking whether A can be extended to be a self-adjoint operator is the range of A , $\text{Ran}(A)$, i.e. the image of its domain (the co-domain). Indeed one can prove the following theorem:

Theorem 20.5 *If A is symmetric and $\text{Ran}(A) = \mathcal{H}$ then A is self-adjoint.*

This theorem suggests that if A is not self-adjoint something is missing in $\text{Ran}(A) \subset \mathcal{H}$.

The following theorem links the lack of surjectiveness of A to the structure of the kernel of $A^\dagger + i$:

Theorem 20.6 *If A is symmetric the following properties are equivalent:*

- (i) A is self-adjoint.
- (ii) A is closed and $\text{Ker}(A^\dagger + i) = 0$.
- (iii) $\text{Ran}(A^\dagger + i) = \mathcal{H}$.

This theorem is important as it reduces the problem of self-adjointness to the computation of the dimension of a space, $\text{Ker}(A^\dagger + i)$, i.e. to counting the independent solutions of the linear equation $(A^\dagger + i)\psi = 0$.

This approach is fully realized in a theorem by Weyl and von Neumann which in principle allows a classification of adjoint operators and of their possible extensions. To state the theorem we need a definition, that of the deficiency indexes.

Let A, A^\dagger be an operator and its adjoint. The deficiency spaces \mathcal{N}_+ and \mathcal{N}_- are defined as

$$\mathcal{N}_+ = \{\psi \in D(A^\dagger) : A^\dagger \psi = \lambda_+ \psi; \text{Im}(\lambda_+) > 0\} \quad (20.109a)$$

$$\mathcal{N}_- = \{\psi \in D(A^\dagger) : A^\dagger \psi = \lambda_- \psi; \text{Im}(\lambda_-) < 0\} \quad (20.109b)$$

The dimensions (n_+, n_-) of these subspaces are the deficiency indexes. The crucial point is that these subspaces do not depend on the particular value λ chosen, as long as $\text{Im}(\lambda_+) > 0$ and $\text{Im}(\lambda_-) < 0$. The subspaces \mathcal{N}_\pm are the kernel of $(A^\dagger \pm i)$ appearing in the previous theorem.

Let us assume (n_+, n_-) to be finite for simplicity. Then the Weyl–von Neumann theorem states that:

Theorem 20.7 *If A is a symmetric operator with deficiency indexes (n_+, n_-) there are three possibilities*

- (1) *If $n_+ = n_- = 0$, then A is self-adjoint (see the previous theorem).*

- (2) If $n_+ = n_- = n \geq 1$ then A has infinite self-adjoint extensions parametrized by a unitary $n \times n$ matrix.
- (3) If $n_+ \neq n_-$ then A has no self-adjoint extensions.

As a simple application, let us consider the “radial momentum” p_r , i.e. the operator $-i\hbar\partial_x$ defined on $[0, \infty]$. We have to solve (we put $\lambda_{\pm} = \pm i\hbar a$)

$$-i\hbar\partial_x\psi_{\pm}(x) = \pm i a \psi_{\pm}(x); \Rightarrow \partial_x\psi_{\pm}(x) = \mp a \psi_{\pm}(x).$$

The first of these equations has a solution in $L^2[0, \infty]$, $\psi_+(x) = C \exp[-ax]$; the second one has no solutions. The deficiency indexes are $(1, 0)$ therefore no self-adjoint extensions exist for p_r .

As a second example let us consider the Hamiltonian in the same system. With $\lambda = \pm i \frac{1}{2m} \hbar^2 \alpha^2$, $\alpha > 0$, one must solve

$$-\frac{\partial^2}{\partial x^2} \psi_{\pm}(x) = \pm i \alpha^2 \psi_p m(x).$$

Both equations have a unique normalizable solution:

$$\psi_{\pm}(x) = C \exp(-\alpha_{\pm} x); \quad \alpha_{\pm} = \frac{1 \pm i}{\sqrt{2}} \alpha.$$

The deficiency indexes are $(1, 1)$ and the self-adjoint extensions are parametrized by a phase (a one by one unitary matrix). The mechanism is easy to understand. For self-adjoint Hamiltonians one must have

$$\int_0^{\infty} (\phi''(x)\psi(x) - \phi(x)\psi''(x)) dx = 0.$$

Integrating by parts and using $\phi(\infty) = \psi(\infty) = 0$ one has the condition

$$\phi'(0)\psi(0) - \psi(0)\phi'(0) = 0 \quad \Rightarrow \quad \frac{\psi'(0)}{\psi(0)} = \lambda. \quad (20.110)$$

The same condition can be put in a form which shows explicitly a phase:

$$\psi'(0) - i\psi(0) = e^{i\alpha}(\psi'(0) + i\psi(0)); \quad \lambda = -\cot\left(\frac{\alpha}{2}\right).$$

Let us note that the condition (20.110) can be used to make a self-adjoint extension for radial Schrödinger equation. ψ is the reduced radial wave function in this case.

20.16 Gaussian integrals and Feynman graphs

Ordinary Gaussian integrals play a basic role in understanding many physical situations, serve as the starting point of perturbative expansion in path integral formalism of quantum mechanics and in quantum

field theories. Here are some useful formulas for such ordinary multiple integrals. Consider

$$I(A, \mathbf{b}) \equiv \int \prod_{i=1}^N dx_i e^{-\frac{1}{2} \mathbf{x}^T A \mathbf{x} + \mathbf{b}^T \cdot \mathbf{x}},$$

where A is a $N \times N$ real symmetric matrix, \mathbf{b} is a constant N component vector. By completing the square and shifting the variable,

$$\mathbf{x} \rightarrow \mathbf{x} - A^{-1} \mathbf{b},$$

one finds easily

$$I(A, \mathbf{b}) = (2\pi)^{N/2} (\det A)^{-1/2} e^{\frac{1}{2} \mathbf{b}^T A^{-1} \mathbf{b}}. \quad (20.111)$$

The “propagator” $\langle x_i x_j \rangle$ is found to be equal to A_{ij}^{-1} :

$$\langle x_i x_j \rangle = \frac{1}{I(A, \mathbf{0})} \int \prod dx_i x_j e^{-\frac{1}{2} \mathbf{x}^T A \mathbf{x}} = \frac{1}{I(A, \mathbf{0})} \frac{\partial^2 I}{\partial b_i \partial b_j}|_{\mathbf{b}=0} = A_{ij}^{-1}.$$

The “ n -point function”

$$\langle x_{i_1} x_{i_2} \dots x_{i_n} \rangle = \frac{1}{I(A, \mathbf{0})} \int \prod dx_i x_{i_1} x_{i_2} \dots x_{i_n} e^{-\frac{1}{2} \mathbf{x}^T A \mathbf{x}}$$

has a simple expression

$$\frac{1}{I(A, \mathbf{0})} \frac{\partial^n I(A, \mathbf{b})}{\partial b_{i_1} \partial b_{i_2} \dots \partial b_{i_n}}|_{\mathbf{b}=0}.$$

But as $I(A, \mathbf{b})$ is given by eqn (20.111), the n -th derivative with respect to the “source” \mathbf{b} gives

$$\langle x_{i_1} x_{i_2} \dots x_{i_n} \rangle = \sum_{pairings} (A^{-1})_{k_1 k_2} (A^{-1})_{k_3 k_4} \dots (A^{-1})_{k_{n-1} k_n}$$

where $(k_1, k_2), (k_3, k_4), \dots (k_{n-1}, k_n)$ are possible ways to paring up the n indices i_1, i_2, \dots, i_n . (For odd n the integral vanishes by symmetry).

Now consider the nontrivial interaction terms

$$V(x) = \frac{g_{ijk}}{3!} x_i x_j x_k + \frac{g_{ijkl}}{4!} x_i x_j x_k x_\ell + \dots,$$

in the exponent, i.e.,

$$I(A, \mathbf{b}; \{g\}) \equiv \int \prod dx e^{-\frac{1}{2} \mathbf{x}^T A \mathbf{x} + \mathbf{b}^T \cdot \mathbf{x} - V(\mathbf{x})}.$$

Our aim is to compute $I(A, \mathbf{0}; \{g\})$ or n derivatives of $I(A, \mathbf{b}; \{g\})$ with respect to b (n point functions) perturbatively in $\{g\}$.

For simplicity let us just consider $V(\mathbf{x}) = g \sum_i x_i^3$. First we note that

$$I(A, \mathbf{b}; g) = e^{-V(\frac{g}{8\pi})} I(A, \mathbf{b}; 0) = (2\pi)^{N/2} (\det A)^{-1/2} e^{-V(\frac{g}{8\pi})} e^{\frac{1}{2} \mathbf{b}^T A^{-1} \mathbf{b}}.$$

Then the required results can be obtained by expanding the exponential factor $e^{-V(\frac{g}{\partial b})}$ in powers of g up to the desired order and by setting $b = 0$. To first order in g there is no contribution to $I(A, 0; \{g\})$. To second order, there are six derivatives with respect to b_i 's, so that we must expand $e^{\frac{1}{2}b^T A^{-1} b}$ to third order to get a non-vanishing result upon setting $b = 0$. We find

$$\frac{I(A, 0; g)}{I(A, 0; 0)} = 1 + c g^2 + \dots,$$

$$\begin{aligned} c &= \frac{1}{2!} \frac{1}{3!} \left[\sum_i \frac{\partial^3}{\partial b_i^3} \sum_j \frac{\partial^3}{\partial b_j^3} \frac{1}{3!} \left(\frac{1}{2} b^T A^{-1} b \right) \left(\frac{1}{2} b^T A^{-1} b \right) \left(\frac{1}{2} b^T A^{-1} b \right) \right]_{b=0} \\ &= \frac{9}{2} \sum_{i,j} A_{ii}^{-1} A_{ij}^{-1} A_{jj}^{-1} + 3 \sum_{ij} (A_{ij}^{-1})^3, \end{aligned}$$

after some calculations. The origin of various factorials should be fairly obvious.

Although such a direct calculation can be pushed to higher orders of g things become quickly intractable. What makes life easier is the fact that these contributions can be diagrammatically rearranged (Feynman). Indeed the above two contributions correspond to the graphs A and B of Figure 20.6.

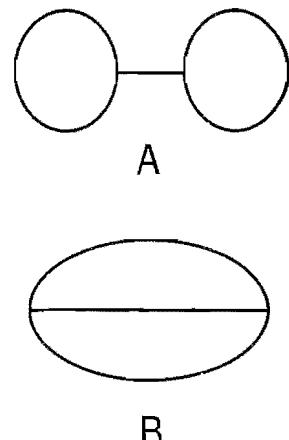
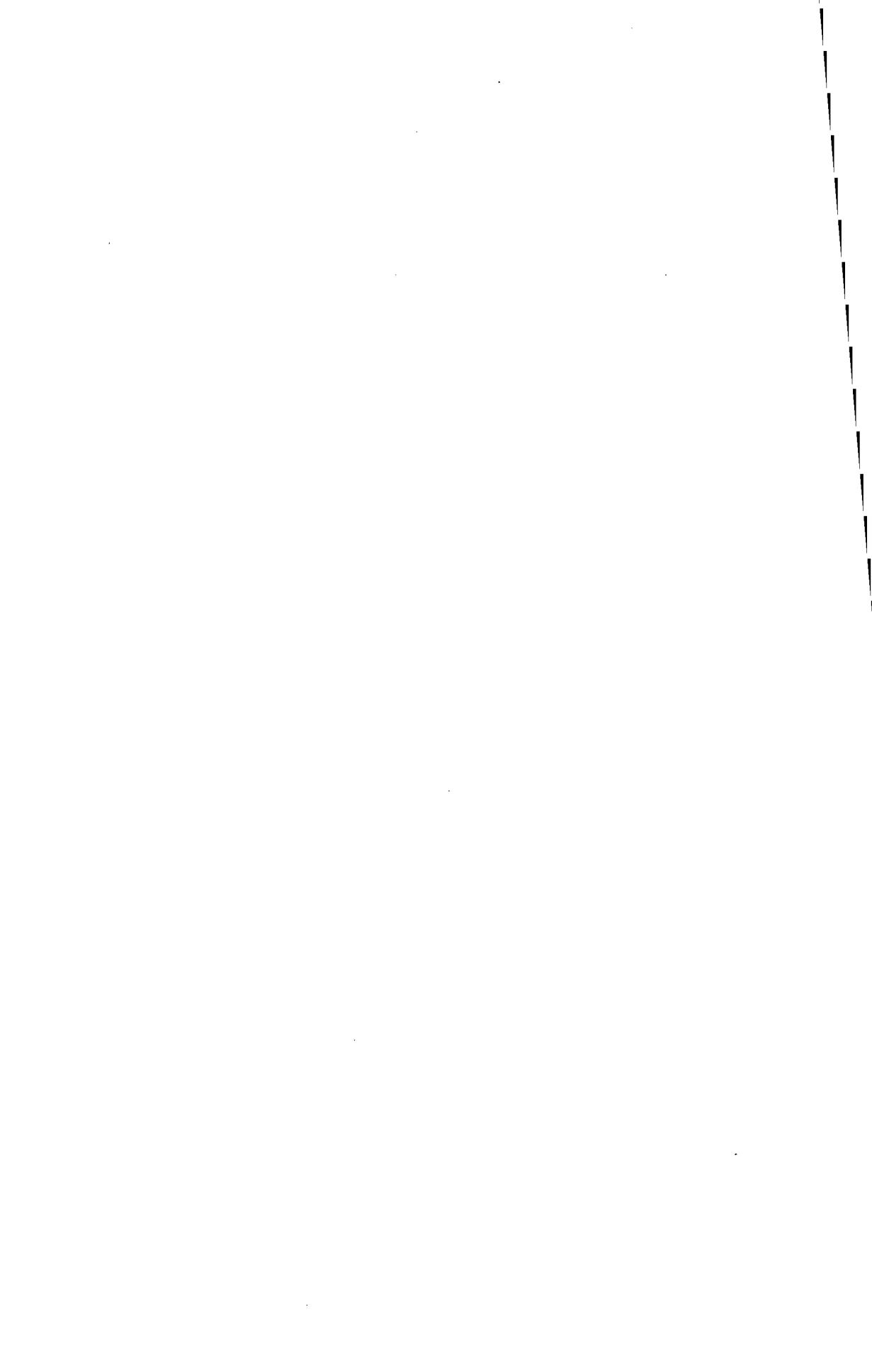


Fig. 20.6



21

Supplements for Part II

21.1 Supplements on perturbation theory

21.1.1 Change of boundary conditions

Some problems in quantum mechanics can be approximated by a motion of a particle confined in a definite region of space, bounded by certain surface,

$$S_0(x) = 0.$$

In the case of Schrödinger's equation a typical eigenvalue problem is of the form,¹:

$$H\psi = E\psi ; \quad \psi|_{S_0} = 0. \quad (21.1)$$

Supposing that we know how to solve the problem (21.1), what about the problem in which the boundary is slightly changed, i.e., in which the boundary is now given by

$$S(x) = 0 ?$$

A possible strategy is to seek for a change of the variables such that

$$x = f(\xi) : \quad S(x(\xi)) = S_0(\xi) ,$$

i.e., such that in terms of the new variables the equation determining the boundary has the original form S_0 and therefore with the same problem as the original one (whose solution is known). Let us write $H(x)$ for the Hamiltonian written in terms of x variables and use the identity

$$H(x) = H(\xi) + (H(x) - H(\xi)) \equiv H(\xi) + V .$$

The problem in terms of the variables ξ is the one whose solution is known, with the boundary condition $S_0(\xi) = 0$. Then for small a variation of the surface the variation of the Hamiltonian can be treated as a perturbation. The variation of the energy levels will therefore be

$$\delta E = \langle \psi | H(x(\xi)) - H(\xi) | \psi \rangle , \quad (21.2)$$

where $|\psi\rangle$ are the eigenvectors of the original Hamiltonian.

In the nuclei the levels can be obtained in a first approximation by considering free particles moving in a spherical potential. Collective excitations of the nuclei can be schematized as a deformation of the potential well. In such a case eqn (21.2) can be used to calculate the shifts of the energy levels. Some applications of this approach are in problems 9.18 and 9.19.

21.1 Supplements on perturbation theory	615
21.2 The fine structure of the hydrogen atom	621
21.3 Hydrogen hyperfine interactions	630
21.4 Divergences of perturbative series	633
21.5 The semi-classical approximation in general systems	648

¹ What follows can be applied to cases with a more general boundary condition of the form, $\alpha\psi + \beta\partial_n\psi = 0$, where ∂_n is the derivative normal to the surface.

21.1.2 Two-level systems

Consider a quantum system having two independent states only, $|+\rangle, |-\rangle$. Let the Hamiltonian of the system be given by $H = H_0 + V$:

$$H = E_0 + \begin{pmatrix} -E_1 & -\Delta \\ -\Delta^* & E_1 \end{pmatrix}, \quad H_0 = \begin{pmatrix} -E_1 & 0 \\ 0 & E_1 \end{pmatrix}, \quad V = \begin{pmatrix} 0 & -\Delta \\ -\Delta^* & 0 \end{pmatrix}. \quad (21.3)$$

E_0 is an additive constant which plays no special role and will be neglected below. Suppose for simplicity that Δ is real. The system can be easily diagonalized by solving the secular equation $\det(H - \lambda) = 0$.

As an exercise let us now follow a path which is more instructive. System (21.3) can be thought as a spin- $\frac{1}{2}$ in a “magnetic field” with components²

$$B_z = E_1, \quad B_x = \Delta, \quad H = -\sigma_3 B_z - \sigma_1 B_x \equiv -\boldsymbol{\sigma} \cdot \mathbf{B}.$$

In polar coordinates, with θ the polar angle between \mathbf{B} and z axis:

$$\begin{aligned} B_z &= B \cos \theta, \quad B_x = B \sin \theta, \quad H = -B \begin{pmatrix} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{pmatrix}, \quad (21.4) \\ B &= \sqrt{E_1^2 + \Delta^2}, \quad \tan \theta = \frac{\Delta}{E_1}. \end{aligned}$$

We can diagonalize H with an anti-clockwise rotation of θ around the y axis of the frame system (or we can rotate clockwise \mathbf{B}). In spin- $\frac{1}{2}$ representation the rotation is

$$R = \exp \left(i \frac{\theta}{2} \sigma_2 \right) = \cos \frac{\theta}{2} + i \sin \frac{\theta}{2} \sigma_2 = \begin{pmatrix} \cos \frac{\theta}{2} & \sin \frac{\theta}{2} \\ -\sin \frac{\theta}{2} & \cos \frac{\theta}{2} \end{pmatrix}.$$

It is easy to verify that

$$R \sigma_3 R^\dagger = \cos \theta \sigma_3 - \sin \theta \sigma_1; \quad R \sigma_1 R^\dagger = \sin \theta \sigma_3 + \cos \theta \sigma_1.$$

Substitution in eqn (21.4) gives a diagonal matrix

$$R H R^\dagger = -B \sigma_3 = \begin{pmatrix} -B & 0 \\ 0 & B \end{pmatrix}.$$

The two eigenvectors, $|g\rangle$ for the ground state and $|e\rangle$ for the excited state are obtained by a rotation on $|+\rangle, |-\rangle$

$$|g\rangle = R^\dagger |+\rangle = R^\dagger \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \cos \frac{\theta}{2} \\ \sin \frac{\theta}{2} \end{pmatrix} \quad (21.5a)$$

$$|e\rangle = R^\dagger |-\rangle = R^\dagger \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} -\sin \frac{\theta}{2} \\ \cos \frac{\theta}{2} \end{pmatrix} \quad (21.5b)$$

The reader can easily verify the procedure by checking that

$$H|g\rangle = -B|g\rangle, \quad H|e\rangle = +B|e\rangle.$$

Let us consider now these results from the perturbative point of view. As long as $E_1 \neq 0$ the level is non-degenerate; there is not first-order correction to the energy as $\langle +|V|+ \rangle = \langle -|V|- \rangle = 0$ while the correction on states is

$$|g\rangle = |+\rangle + \frac{\langle -|V|+ \rangle}{E_+ - E_-} \cdot |-\rangle = |+\rangle + \left(\frac{-\Delta}{-2E_1} \right) |-\rangle \simeq |+\rangle + \left(\frac{\theta}{2} \right) |-\rangle,$$

$$|e\rangle = |-\rangle + \frac{\langle +|V|- \rangle}{E_- - E_+} \cdot |+\rangle = |-\rangle + \left(\frac{-\Delta}{2E_1} \right) |+\rangle \simeq |-\rangle - \left(\frac{\theta}{2} \right) |+\rangle.$$

This fits with the first-order expansion in θ of eqn (21.5).

As $E_1 \rightarrow 0$ the system becomes degenerate and the angle θ is no more small. As $\tan \theta = \Delta/E_1$ the value of θ for small E_1 depends on the sign of E_1

$$\lim_{E_1/\Delta \rightarrow 0} \theta = \begin{cases} +\frac{\pi}{2} & E_1/\Delta > 0 \\ -\frac{\pi}{2} & E_1/\Delta < 0 \end{cases}$$

For states $|g\rangle$ and $|e\rangle$

$$\lim_{E_1 \rightarrow 0^+} |g\rangle = \begin{cases} \frac{1}{\sqrt{2}} (|+\rangle + |-\rangle) \equiv |S\rangle & \Delta > 0 \\ \frac{1}{\sqrt{2}} (|-\rangle - |+\rangle) \equiv |A\rangle & \Delta < 0 \end{cases}$$

The symmetric and antisymmetric states $|S\rangle, |A\rangle$ are eigenvectors of the

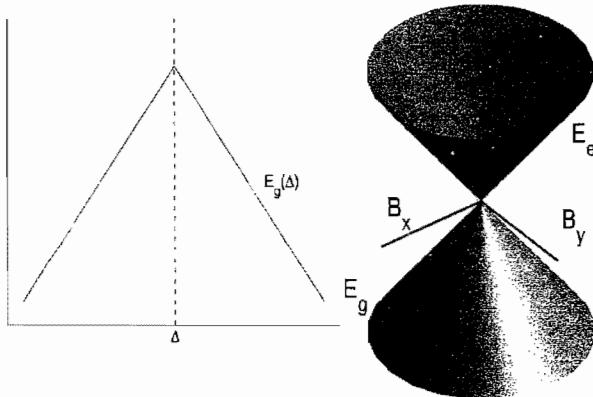


Fig. 21.1 Ground state energy as a function of Δ and B_x, B_y .

degenerate Hamiltonian, but we see that vector $|g\rangle$ is not analytic in Δ : there is a discontinuity as $\Delta \rightarrow 0$.

This is exactly what one expects in general for a perturbation on a degenerate level: the energy is continuous but its derivative is discontinuous, the states are not continuous. In different words: as $\Delta \rightarrow 0$ the state $|g\rangle$ becomes a vector in the two-dimensional linear space generated by $|+\rangle, |-\rangle$, but the limit vector is not fixed in a unique way.

It is simple to generalize the problem to complex Δ , adding an y component to the B field. In polar coordinates \mathbf{B} is

$$B_x = B \sin \theta \cos \varphi, B_y = B \sin \theta \sin \varphi, B_z = B \cos \theta; B = \sqrt{E_1^2 + |\Delta|^2}.$$

The y component can be removed by a rotation of φ around z , $R_z(\varphi) = \exp(i\varphi/2 \cdot \sigma_3)$. In the new basis

$$|+\rangle' = R_z^\dagger(\varphi)|+\rangle = e^{-i\frac{\varphi}{2}}|+\rangle, \quad |-\rangle' = R_z^\dagger(\varphi)|-\rangle = e^{i\frac{\varphi}{2}}|-\rangle,$$

we recover the preceding model.

In this case the off-diagonal term is there for $|\Delta| > 0$, then in the degeneracy limit

$$E_g = -|\Delta| = -\sqrt{B_x^2 + B_y^2}, \quad |g\rangle = \frac{1}{\sqrt{2}}(|+\rangle' + |-\rangle') = \frac{1}{\sqrt{2}}\left(e^{-i\frac{\varphi}{2}}|+\rangle + e^{+i\frac{\varphi}{2}}|-\rangle\right).$$

The singularity is a cone in the parameter space (B_x, B_y) , while the ground state now depends on φ .

In the general case from (21.5) we have

$$|g\rangle = \cos\frac{\theta}{2}|+\rangle' + \sin\frac{\theta}{2}|-\rangle' = \cos\frac{\theta}{2}e^{-i\frac{\varphi}{2}}|+\rangle + \sin\frac{\theta}{2}e^{i\frac{\varphi}{2}}|-\rangle. \quad (21.6)$$

As φ grows from 0 to 2π , $|g\rangle$ get a phase π , i.e. change sign. This change of phase is linked to the topological properties of the singularity of E_g and will be discussed in connection with Berry's phase, in Chapter 12.

We remark a last point, which is in fact at the origin of Berry's phase. Let us consider H for given values of B, θ, φ . In general the system is not degenerate. Let us suppose now to make a small change in θ e φ and let us use perturbation theory to compute the change of $|g\rangle$. In the text we have shown that is always possible, locally, to satisfy the constraint (9.23), which in our case reads

$$\langle g|\partial_\lambda g\rangle = 0.$$

From eqn (21.6) we can compute the derivatives:

$$\left\langle g \left| \frac{\partial}{\partial \theta} \right| g \right\rangle = 0 \quad (21.7a)$$

$$\left\langle g \left| \frac{\partial}{\partial \varphi} \right| g \right\rangle = -\frac{i}{2} \cos \theta \quad (21.7b)$$

The purely imaginary term (21.7b) can be locally reabsorbed by a change of phase $\alpha(\varphi)$ (see eqn (9.25)):

$$\frac{d\alpha}{d\varphi} = \frac{1}{2} \cos \theta \quad \alpha = \frac{\varphi}{2} \cos \theta.$$

This procedure cannot be extended globally, as $\alpha(2\pi) \neq \alpha(0)$, i.e. the phase is discontinuous.

21.1.3 Van der Waals interactions

Let us consider two atoms in their ground state. We can consider at a first approximation nuclei as fixed and electrons bounded by the two

separated nuclei. As atoms approach the tunnel effect of electrons between the atoms become relevant and this is one of the origin of chemical binding. We think of atoms far enough to neglect this kind of effect.

In this approximation the system is described by the Hamiltonian

$$H = H_1 + H_2 + H_{12} .$$

H_1, H_2 are the single atom Hamiltonians and H_{12} their (dipole) electrostatic interaction. Remembering the field due to a dipole

$$V = \frac{dr}{r^3} ; \quad \mathbf{E} = -\frac{1}{r^3}(\mathbf{d} - 3(\mathbf{n}\mathbf{d})\mathbf{n}) , \quad (21.8)$$

we can write

$$H_{12} = -\mathbf{d}_2 \cdot \mathbf{E}_1 = \frac{1}{R^3}[\mathbf{d}_1 \mathbf{d}_2 - 3(\mathbf{d}_1 \cdot \mathbf{n})(\mathbf{d}_2 \cdot \mathbf{n})] \equiv \frac{e^2}{R^3} A ,$$

where R is the distance between atoms and \mathbf{n} a unit vector from atom 1 to atom 2. The operator A has the dimension of length².

For independent systems (i.e. neglecting exchange effects) the unperturbed wave function of the atoms can be taken in a factorized form

$$|\psi\rangle \simeq |\psi_1\rangle |\psi_2\rangle .$$

As atoms do not admit intrinsic dipole the first-order perturbative correction to energy vanishes

$$\langle \psi | H_{12} | \psi \rangle = 0 .$$

The first nontrivial correction is at second-order in perturbation theory

$$U = \frac{e^4}{R^6} \sum'_n \langle \psi | A | n \rangle \frac{1}{E_0 - E_n} \langle n | A | \psi \rangle . \quad (21.9)$$

This correction depend on R and, as far as the motion of the nuclei is concerned, acts as a potential energy.

Remarks

- For the ground state $U < 0$, this give an attractive force for the nuclei, the *Van der Waals force*, $F \sim R^{-7}$.
- We consider the force as “instantaneous”. This is not true, if time delay is considered the potential energy goes as R^{-7} . If $\Delta\omega$ is a typical transition frequency these delay effects become important at distances $c/\Delta\omega$.

21.1.4 The Dalgarno–Lewis method

In many problems the first-order correction is sufficient but if this correction vanishes, for symmetry reasons or otherwise, it is necessary to perform a second-order calculation. This usually involves the computation of an infinite sum, see eqn (9.15), usually quite difficult to perform.

The recursive nature of the perturbation expansion however allows us to reduce the problem to the determination of the first-order correction to the state, $|\psi^{(1)}\rangle$, see eqn (9.18b). $|\psi^{(1)}\rangle$ is obtained by solving the equation (9.8)

$$(H_0 - E^{(0)}) |\psi^{(1)}\rangle + (V - \varepsilon_1) |\psi^{(0)}\rangle = 0.$$

The Dalgarno–Lewis [Dalgarno and Lewis (1955)] method is based on the solution of this equation. In the following we consider for simplicity the spectrum of a particle, described by the unperturbed Hamiltonian

$$H_0 = -\frac{\hbar^2}{2m} \Delta + U$$

and a perturbation $V(x)$. The function $\psi^{(1)}$ is a solution of the inhomogenous equation

$$(H_0 - E_0) \psi^{(1)} + (V - \varepsilon_1) \psi^{(0)} = 0. \quad (21.10)$$

Suppose that a regular solution $\varphi(\mathbf{x})$ of this equation has been found. The kernel of $H_0 - E_0$ is not zero and for a non-degenerate level is spanned by functions $c \psi^{(0)}$, with c constant. If φ is a solution so is $\varphi - c \psi^{(0)}$. The constant c is fixed by the orthogonality condition between $\psi^{(1)}$ and $\psi^{(0)}$, i.e.

$$c = \int \psi^{(0)*} \varphi.$$

If the first-order correction to energy vanishes, as usually happens when this method is useful, it is not even necessary to compute c , as its contribution to energy is

$$c \langle \psi^{(0)} | V | \psi^{(0)} \rangle = c \varepsilon_1 = 0.$$

The search of the solution φ is simplified by a change of variables, we look for solutions in the form $\varphi = F(\mathbf{x}) \psi^{(0)}(\mathbf{x})$. By substitution in eqn (21.10) we get

$$-\frac{\hbar^2}{2m} \left[\psi^{(0)} \Delta F + 2 \nabla F \nabla \psi^{(0)} \right] + (V - \varepsilon_1) \psi^{(0)} = 0;$$

which does not depend explicitly on the unperturbed potential U .

Polarizability of hydrogen

For example let us consider the second-order Stark effect on the ground state of the hydrogen atom. Let z the direction of the external electric field \mathcal{E} . The perturbation is $V = -e z \mathcal{E}$. There is no first-order effect due to parity conservation. At second-order

$$\varepsilon_2 = -e \mathcal{E} \langle \psi^{(0)} | z | \psi^{(1)} \rangle = -\frac{1}{2} \alpha \mathcal{E}^2.$$

The equation for $|\psi^{(1)}\rangle$ is

$$\left(-\frac{\hbar^2}{2m} \Delta + U(r) \right) \psi^{(1)} = e z \mathcal{E} \psi^{(0)}. \quad (21.11)$$

From now on we use atomic units. The right-hand side of eqn (21.11) transforms like the spherical harmonics Y_{10} , thus it is natural to look for a solution in the form

$$\psi^{(1)} = \mathcal{E} z F(r) \psi^{(0)}(r).$$

Inserting this expression in eqn (21.11) a short computation gives

$$\psi^{(0)} \left[\frac{2z}{r} F' + \frac{z}{2} F'' \right] + \psi^{(0)'} \left[\frac{z}{r} F + z F' \right] = -z \psi^{(0)},$$

or

$$\left(\frac{2}{r} F' + \frac{1}{2} F'' \right) + \frac{\psi^{(0)'}}{\psi^{(0)}} \left(\frac{F}{r} + F' \right) = -1. \quad (21.12)$$

Where $F' = dF/dr$, etc.

This equation is true for any central potential. For the hydrogen atom

$$\psi^{(0)} = \frac{1}{\sqrt{\pi}} e^{-r}, \quad \frac{\psi^{(0)'}}{\psi^{(0)}} = -1,$$

and eqn (21.12) reads

$$\frac{r}{2} F'' + F'(2-r) - F = -r.$$

The regular solution is simply $F(r) = 1 + \frac{r}{2}$, the correction to the wave function is then

$$\psi^{(1)} = \mathcal{E} z \left(1 + \frac{r}{2} \right) \psi^{(0)}.$$

Let us note that $\psi^{(1)}$ is odd and orthogonal to $\psi^{(0)}$.

For the correction to ground state energy level one finds that

$$\varepsilon_2 = -\mathcal{E}^2 \int d^3x \psi_0^2 z^2 \left(1 + \frac{r}{2} \right) = -\mathcal{E}^2 \frac{4}{3} \int r^2 dr r^2 e^{-2r} \left(1 + \frac{r}{2} \right) = -\frac{9}{4} \mathcal{E}^2.$$

The polarization follows

$$\alpha = \frac{9}{2} \text{ a.u.} = \frac{9}{2} a_B^3. \quad (21.13)$$

In notebook **NB-9.2** the reader can find the next-order correction, computed with the same method.

21.2 The fine structure of the hydrogen atom

An hydrogen-like atom is built from a nucleus of mass $M \gg m$ and charge $Z|e|$ and an electron of mass m . Neglecting corrections of order m/M we can consider the electron as moving in the external electromagnetic field due to nucleus. In Chapter 14 (see also its Supplements)

we see that the effective Hamiltonian for an electron in an external electromagnetic field is given, up to order $\mathcal{O}(v^2/c^2)$, by:

$$H = \frac{1}{2m} \left(\mathbf{p} - \frac{e}{c} \mathbf{A} \right)^2 - \frac{\mathbf{p}^4}{8m^3 c^2} + e\Phi - \frac{e\hbar}{2mc} \boldsymbol{\sigma} \cdot \mathbf{B} - \frac{ie\hbar^2}{8m^2 c^2} \boldsymbol{\sigma} \cdot \nabla \times \mathbf{E} - \frac{e\hbar}{4m^2 c^2} \boldsymbol{\sigma} \cdot (\mathbf{E} \times \mathbf{p}) - \frac{e\hbar^2}{8m^2 c^2} \nabla \cdot \mathbf{E}.$$

We can specialize to the hydrogen atom using $\mathbf{B} = 0$, $\mathbf{E} = Z|e|/r^3 \mathbf{r}$. The effective Hamiltonian becomes

$$H = \frac{\mathbf{p}^2}{2m} - \frac{\mathbf{p}^4}{8m^3 c^2} - \frac{Ze^2}{r} + \frac{Ze^2 \hbar}{4m^2 c^2} \frac{1}{r^3} \boldsymbol{\sigma} \cdot \mathbf{L} + \frac{Ze^2 \hbar^2}{8m^2 c^2} 4\pi \delta^{(3)}(\mathbf{r}). \quad (21.14)$$

A simple estimate of various contributions can be given using virial theorem and Heisenberg principle. Let a be the characteristic radius of the system

$$p \sim \frac{\hbar}{a}, \quad \frac{p^2}{m} \sim \frac{Ze^2}{a} \Rightarrow a \sim \frac{1}{Z} a_B = \frac{1}{Z} \frac{\hbar^2}{me^2}.$$

$a_B = \hbar^2/me^2$ is the Bohr radius.

The small parameter in a non-relativistic expansion is v/c and from previous relations

$$\frac{v}{c} \sim Z\alpha, \quad \alpha = \frac{e^2}{\hbar c} \sim \frac{1}{137}.$$

The dimensionless constant α is the *fine-structure constant*.

The characteristic energy in the system is p^2/m or Ze^2/a and the order of magnitude of the terms in eqn (21.14) is

$$\begin{aligned} \frac{\mathbf{p}^4}{8m^3 c^2} &\sim E Z^2 \alpha^2; & \frac{Ze^2 \hbar}{4m^2 c^2} \frac{1}{r^3} \boldsymbol{\sigma} \cdot \mathbf{L} &\sim \frac{Ze^2 \hbar}{4m^2 c^2} \frac{\hbar}{a^3} \sim E Z^2 \alpha^2; \\ \frac{Ze^2 \hbar^2}{8m^2 c^2} 4\pi \delta^{(3)}(\mathbf{r}) &\sim \frac{\pi Ze^2 \hbar^2}{2m^2 c^2} \frac{1}{a^3} \sim E Z^2 \alpha^2. \end{aligned}$$

The expansion parameter is $(Z\alpha)^2$. For hydrogen or ionized He this parameter is of the order 10^{-4} , then the fine-structure corrections to Bohr energies are

$$E_{FS} \sim (Z\alpha)^2 E \sim 10^{-4} \text{ Ry}.$$

As relativistic correction involve even powers in v/c the approximation should be correct up to order $v^4/c^4 E \sim 10^{-8}$ Ry. There are instead at least three major corrections bigger than v^4/c^4 terms:

- (1) The mass of the nucleus is not infinite, this introduce corrections of order $m/M E \sim 10^{-3} E$, this is bigger than first-order relativistic correction. In non-relativistic hydrogen atom all these effects are reabsorbed in the definition of reduced mass, $\mu = mM/(m+M)$, this means that once μ is used in our results the first nontrivial correction will be of the form $(m/M)v^2/c^2 \sim (10^{-7}-10^{-8})E$.

- (2) The nucleus can have a spin and a magnetic moment, as in the hydrogen case. The interaction between nucleus magnetic field and electron magnetic moment will be of the order

$$\mu_1 \mu_2 \frac{1}{r^3} \sim \frac{e^2 \hbar^2}{m M c^2} \frac{1}{a^3} \sim E Z^2 \alpha^2 \frac{m}{M}.$$

This interaction is “small” but do not commute with electron angular momentum j , then it split the levels with fixed j (*hyperfine interaction*).

- (3) In eqn (21.14) the electromagnetic field is a classic field, but of course also this field has to be considered at the quantum level. This induces an additional contribution to energy levels, the *Lamb shift*. The experimental and theoretical investigation of this effect was a milestone for the birth of modern quantum electrodynamics.

Let us consider now quantitatively the fine-structure splittings. We will limit ourselves to lowest levels with principal quantum numbers $n = 1, 2$. In the following we will use atomic units and $Z = 1$. The results will be written in the form $E = E_0(1 + c\alpha^2)$. The general case is obtained with the substitutions $E_0 \rightarrow Z^2 E_0$, $c \rightarrow c Z^2$. In these units

$$H = \frac{\mathbf{p}^2}{2} - \frac{1}{r} - \frac{\alpha^2}{8} \mathbf{p}^4 + \frac{\alpha^2}{2} \frac{1}{r^3} \boldsymbol{\ell} \cdot \mathbf{s} + \frac{\pi \alpha^2}{2} \delta^{(3)}(\mathbf{r}). \quad (21.15)$$

Fine structure results

In non-relativistic approximation each level has quantum numbers ℓ, s and a degeneracy $(2\ell+1)(2s+1) = 2(2\ell+1)$. The $\ell \cdot s$ coupling can be computed using the Wigner–Eckart theorem: within a degenerate level with ℓ, s fixed

$$\boldsymbol{\ell} \cdot \mathbf{s} = \frac{1}{2} (\mathbf{j}^2 - \ell^2 - \mathbf{s}^2). \quad (21.16)$$

Using Clebsch–Gordan coefficients we can write the eigenstates $|n, j, j_z\rangle$ of j, j_z , with $\mathbf{j} = \boldsymbol{\ell} + \mathbf{s}$, and these diagonalize $\ell \cdot s$ coupling. As all other terms in eqn (21.15) commute with \mathbf{j} we can apply in this basis the usual perturbation theory for non-degenerate levels.

Using for non-relativistic eigenstates the identity

$$\left\langle n\ell \left| \frac{\mathbf{p}^4}{8} \right| n\ell \right\rangle = \frac{1}{2} \left\langle n\ell \left| \left(E_n + \frac{1}{r} \right)^2 \right| n\ell \right\rangle,$$

we have

$$\begin{aligned} \Delta E(n; j, \ell, s) = & -\frac{\alpha^2}{2} (E_n^2 + 2E_n \langle nl | r^{-1} | nl \rangle + \langle nl | r^{-2} | nl \rangle) \\ & + \frac{\alpha^2}{4} \left(j(j+1) - \ell(\ell+1) - \frac{3}{4} \right) \langle nl | r^{-3} | nl \rangle + \frac{\pi \alpha^2}{2} |\psi_{nl}(0)|^2. \end{aligned}$$

From the hydrogen radial eigenfunctions it is easy to compute

$$\begin{aligned}\langle nl|r^{-1}|nl\rangle &= \frac{1}{n^2} ; & \langle nl|r^{-2}|nl\rangle &= \frac{1}{n^3} \frac{1}{(\ell + \frac{1}{2})} ; \\ \langle nl|r^{-3}|nl\rangle &= \frac{1}{n^3} \frac{1}{\ell(\ell + \frac{1}{2})(\ell + 1)} ; & |\psi_{nl}(0)|^2 &= \frac{1}{\pi n^3} \delta_{\ell 0} .\end{aligned}$$

For $\ell = 0, j = \frac{1}{2}$ it follows that

$$\begin{aligned}\Delta E(n; j, 0, s) &= -\frac{\alpha^2}{2} \left(-\frac{3}{4n^4} + \frac{2}{n^3} \right) + \frac{\alpha^2}{2} \frac{1}{n^3} \\ &= -\frac{\alpha^2}{2n^3} \left(1 - \frac{3}{4n} \right) \text{ a.u.}\end{aligned}\quad (21.17)$$

For $\ell \geq 1, j = \ell \pm \frac{1}{2}$, or $\ell = j \pm \frac{1}{2}$. It is convenient to express matrix elements in terms of j :

$$\begin{aligned}\langle nl|r^{-2}|nl\rangle &= \frac{1}{n^3} \begin{cases} 1/(j+1) & \ell = j + \frac{1}{2} \\ 1/j & \ell = j - \frac{1}{2} \end{cases} \\ j(j+1) - \ell(\ell+1) - \frac{3}{4} &= \begin{cases} -(j + \frac{3}{2}) & \ell = j + \frac{1}{2} \\ j - \frac{1}{2} & \ell = j - \frac{1}{2} \end{cases} \\ \langle nl|r^{-3}|nl\rangle &= \frac{1}{n^3} \begin{cases} [(j + \frac{1}{2})(j + \frac{3}{2})(j + 1)]^{-1} & \ell = j + \frac{1}{2} \\ [(j - \frac{1}{2})(j + \frac{1}{2})]^{-1} & \ell = j - \frac{1}{2} \end{cases}\end{aligned}$$

Summing the different contributions one gets

$$\begin{aligned}\Delta E(n; j, \ell, s) &= -\frac{\alpha^2}{2} \left(-\frac{3}{4n^4} \right) - \frac{\alpha^2}{2n^3} \begin{cases} 1/(j+1) \\ 1/j \end{cases} \\ &\quad + \frac{\alpha^2}{4n^3} \begin{cases} -1/(j+1)(j+\frac{1}{2}) \\ 1/j(j+\frac{1}{2}) \end{cases} \\ &= -\frac{\alpha^2}{2} \left(-\frac{3}{4n^4} \right) - \frac{\alpha^2}{2n^3} \begin{cases} 1/(j+\frac{1}{2}) \\ 1/(j+\frac{1}{2}) \end{cases} ;\end{aligned}$$

All terms have the same form and the result can be written as

$$\boxed{\Delta E(n; j, \ell, s) = -\frac{\alpha^2}{2n^3} \left[\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right] \text{ a.u.}} \quad (21.18)$$

For $j = \frac{1}{2}, \ell = 0$, eqn (21.17) is recovered also.

From eqn (21.18) we see that fine-structure corrections, in hydrogen, depend only on j , this means that Coulomb degeneracy is only partially resolved: levels with the same j but different ℓ continue to be degenerate. This is in particular true for $ns_{1/2}, np_{1/2}$ levels.

To write explicit energies it is convenient to introduce the reduced mass, keeping in this way m/M corrections. The non-relativistic energies are

$$E_n = -\frac{1}{n^2} Z^2 R_A ; \quad R_A = R \times \frac{m}{m + M} .$$

R is the Rydberg constant (in literature one finds also the notations R_∞ or Ry). The final result for energy levels is

$$E(n,j) = -R_A \frac{Z^2}{n^2} \left(1 + \frac{(Z\alpha)^2}{n} \left[\frac{1}{j+1/2} - \frac{3}{4n} \right] \right) + \mathcal{O}\left(\frac{m}{M}\alpha^2, \alpha^3\right). \quad (21.19)$$

A comparison with experimental data is given in Table 21.1.

	H	eqn (21.19)	He*	eqn (21.19)
$1s_{1/2}$	-0.999 466 509	-0.999 468 985	-3.999 631 998	-3.999 664 828
$2s_{1/2}$	-0.249 867 761	-0.249 868 078	-0.999 925 149	-0.999 929 518
$2p_{1/2}$	-0.249 868 082	-0.249 868 078	-0.999 929 417	-0.999 929 518
$2p_{3/2}$	-0.249 864 748	-0.249 864 751	-0.999 876 044	-0.999 876 274
$3s_{1/2}$	-0.111 052 015	-0.111 052 109	-0.444 405 774	-0.444 407 203
$3p_{1/2}$	-0.111 052 111	-0.111 052 109	-0.444 407 046	-0.444 407 203
$3p_{3/2}$	-0.111 051 123	-0.111 051 124	-0.444 391 231	-0.444 391 427
$3d_{3/2}$	-0.111 051 124	-0.111 051 124	-0.444 391 257	-0.444 391 427
$3d_{5/2}$	-0.111 050 795	-0.111 050 795	-0.444 385 986	-0.444 386 168

Table 21.1 Energies for H, He*. Values are in Rydberg.

The agreement is good but it has to be stressed the the greatest corrections to the Bohr energies for infinite mass nuclei is purely kinematic and come from the substitution $R \rightarrow R_A$.³

A sharper test on the fine-structure levels is obtained by reporting the differences between levels. Here we use the standard notation in spectroscopy, reporting the frequencies $\Delta E/\hbar$. The conversion factor is

$$\text{Ry} = 3\,289\,841.958\,0 \text{ GHz}. \quad (21.20)$$

We obtain Table 21.2.

The biggest discrepancy of order 1 GHz is in hydrogen. To measure this effect we need a precision of about 10^{-6} on the frequency lines⁴.

Remarks

Equation (21.18) predicts an exact degeneracy for $2s_{1/2}$ – $2p_{1/2}$ etc. levels, this is not verified in the high-precision data of Table 21.2. The shift

³ The data are taken from <http://physics.nist.gov/PhysRefData/Handbook>.

⁴The first measurement of the fine structure of hydrogen is due to Michelson and Morley in 1887.

	H	eqn (21.18)	He*	eqn (21.18)
$2s_{1/2}-2p_{1/2}$	1.058	0.000	14.041	0.000
$2p_{3/2}-2p_{1/2}$	10.969	10.943	175.589	175.165
$3s_{1/2}-3p_{1/2}$	0.315	0.000	4.185	0.000
$3p_{3/2}-3p_{1/2}$	3.250	3.242	52.029	51.901
$3p_{3/2}-2d_{3/2}$	0.003	0.000	0.086	0.000
$3d_{5/2}-3d_{3/2}$	1.082	1.081	17.341	17.300

Table 21.2 Energy differences for H and He* in GHz.

between these states is called the *Lamb shift*. The crucial point is that from the discussion at the beginning of this Supplement any correction in form of mass correction or relativistic correction is *at least* of order $10^{-3} E_{FS}$ while the shift is of order $E_{FS}/10$ (compare the $2p_{3/2}-2p_{1/2}$ shift with the $2s_{1/2}-2p_{1/2}$ shift). Some completely new physical effect is at work: this is the quantum nature of the electromagnetic field.

The first experimental measure of $2s_{1/2}-2p_{1/2}$ energy difference is due to Lamb and Rutherford in 1947. To convince ourselves of the extreme difficulty of the measurement, it suffices to recall that it required microwave techniques which simply did not exist a few years earlier.

21.2.1 A semi-classical model for the Lamb shift

A complete study of the Lamb shift correction is far beyond the purposes of this book, but a simple semi-classical description of the effect can clarify its origin.

In several occasions we stated that the quantum electromagnetic field can be viewed as an ensemble of quantum oscillators (see Section 20.2). So we can assume that the effective electric field acting on the electron in an hydrogen atom has the form $\mathbf{E} = \mathbf{E}_{cl} + \mathbf{E}_q$, where the first is the classical field produced by the nucleus, while \mathbf{E}_q is the quantum field. In absence of external sources the oscillators describing the quantum field are in the lowest state, usually called “vacuum”, for obvious reasons. The quantum field will affect the motion of the electron:

$$\mathbf{x}_e = \mathbf{x}_{cl} + \boldsymbol{\xi},$$

where \mathbf{x}_{cl} is the classical motion and $\boldsymbol{\xi}$ the fluctuation due to the quantum field. In the vacuum we will have $\langle \mathbf{E}_q \rangle = 0$, so the mean trajectory will be unaffected, but the potential energy of the electron will change.

In effect assuming isotropy for the fluctuations

$$\langle U(\mathbf{x}_e) \rangle_\gamma = U(\mathbf{x}) + \langle \xi_i \rangle \partial_i U(x) + \frac{1}{2} \langle \xi_i \xi_j \rangle \partial_i \partial_j U(x) = U(x) + \frac{1}{6} \langle \xi^2 \rangle \nabla^2 U.$$

U is the classical electrostatic energy. This means that energy levels will be shifted by an amount

$$\begin{aligned} \Delta E_{n\ell} &= \langle \xi^2 \rangle \langle \psi | \frac{Ze^2 4\pi}{6} \delta^{(3)}(\mathbf{r}) | \psi \rangle = Ze^2 \frac{2\pi}{3} |\psi(0)|^2 \langle \xi^2 \rangle = \\ &= Z^4 e^2 \frac{2}{3a_B^3} \frac{1}{n^3} \langle \xi^2 \rangle \delta_{\ell,0}. \end{aligned} \quad (21.21)$$

We used for the Coulomb field the relation

$$\nabla^2 U = Ze^2 4\pi \delta^{(3)}(\mathbf{r}).$$

In this approximation only s -states are affected, their energies grow, in agreement with experimental data of Table 21.2.

To compute the quadratic fluctuation of the electron position we write the equation of motion for ξ , and perform a Fourier transform

$$m\ddot{\xi} = e\mathbf{E}_q; \Rightarrow \xi_\omega = -\frac{e}{m\omega^2} \mathbf{E}_\omega.$$

\mathbf{E}_ω is the Fourier component at frequency ω of the quantum field. Each component can be considered as statistically independent, as the oscillators describing the electromagnetic field, then

$$\langle \xi^2 \rangle = \int d\omega \langle \xi_\omega^2 \rangle = \frac{e^2}{m^2} \int d\omega \frac{1}{\omega^4} \mathbf{E}_\omega^2. \quad (21.22)$$

The quantity \mathbf{E}_ω^2 is clearly connected to the energy stored in the frequency ω oscillator of the electromagnetic field. In the vacuum (ground) state each oscillator has frequency $\hbar\omega/2$, and remembering that each photon has two polarization degrees

$$\frac{1}{8\pi} \int d^3x (\mathbf{E}^2 + \mathbf{B}^2) = \frac{1}{4\pi} \int d^3x \mathbf{E}^2 = 2 \sum_{osc.} \frac{\hbar\omega_k}{2}.$$

We imagine the system immersed in a large box of size L^3 , ω_k is the frequency relative to the k -th oscillation mode of this box. Then we can write

$$\langle \mathbf{E}^2 \rangle = \int d\omega \mathbf{E}_\omega^2 = \frac{1}{L^3} \int d^3x \mathbf{E}^2 = \frac{4\pi}{L^3} \sum_{osc.} \hbar\omega_k = 4\pi \int \frac{d^3k}{(2\pi)^3} \hbar\omega.$$

We used the usual numbering of modes in a cavity: $k = 2\pi n/L$, $n = 0, \pm 1, \pm 2, \dots$. The integral over angles and the substitution $k = \omega/c$ finally gives

$$\int d\omega \mathbf{E}_\omega^2 = \frac{2}{\pi c^3} \int d\omega \omega^3.$$

The spectral density of the field is then

$$\mathbf{E}_\omega^2 = \frac{2}{\pi} \frac{\hbar}{c^3} \omega^3 ,$$

and substitution in eqn (21.22) gives

$$\langle \xi^2 \rangle = \frac{2}{\pi} \frac{e^2}{m^2} \frac{\hbar}{c^3} \int d\omega \frac{1}{\omega} .$$

This expression is logarithmically divergent, we need some cutoff. It is reasonable to assume $\omega_{max} \sim mc^2/\hbar$ as we used a non-relativistic model and as we expect that at frequencies of the order ω_{max} the inertia of the electron do not allow to follow the too rapid field oscillations. The low frequency cutoff is obviously of the order of $\hbar\omega_{min} \sim Z^2 e^2/a_B$, as for these energies the motion is dominated by the usual “classical” nucleus field. Our estimate for $\langle \xi^2 \rangle$ is then

$$\langle \xi^2 \rangle = \frac{2}{\pi} \frac{e^2}{m^2} \frac{\hbar}{c^3} \log \frac{\omega_{max}}{\omega_{min}} \equiv \frac{2}{\pi} \alpha r_e^2 \log \frac{\omega_{max}}{\omega_{min}} .$$

Substitution in eqn (21.21) gives, for s -states

$$\Delta E_{n0} = Ry \cdot \frac{1}{n^3} \frac{8}{3\pi} Z^4 \alpha^3 \log \left(\frac{1}{Z^2 \alpha^2} \right) .$$

For the $2s$ level the number is

$$\Delta E_{2s} \simeq 1.33 \text{ GHz} ,$$

in qualitative agreement with the experimental data.

We now understand why this effect overcomes higher-order relativistic corrections, it is of the order

$$E_0 \alpha^3 \log \alpha \sim E_{FS} \alpha \log \alpha ,$$

larger than $\alpha^2 E_{FS}$ corrections due to higher orders in v/c .

We give here for reference the result of the exact calculation of the shifts $\Delta E(n, \ell)$ for states with quantum numbers (n, ℓ) :

$$\Delta E(n, 0) = \frac{8Z^4}{n^3} \frac{\alpha^3}{3\pi} \cdot Ry \cdot \left[2 \log \frac{1}{Z\alpha} + \log \frac{1}{K(n, 0)} + \frac{19}{30} \right] ; \quad (21.23a)$$

and for $\ell > 0$:

$$\Delta E(n, \ell) = \frac{8Z^4}{n^3} \frac{\alpha^3}{3\pi} \cdot Ry \cdot \left[\log \frac{1}{K(n, \ell)} + \frac{3}{8} \frac{j(j+1) - \ell(\ell+1) - 3/4}{\ell(\ell+1)(2\ell+1)} \right] .$$

⁵The first computation of the Lamb shift is due to H. Bethe, 1947.

The dimensionless coefficients $K(n, \ell)$ are defined by⁵

$$\log(K_{n\ell}) \sum_s \mathbf{p}_{n_0 s} \mathbf{p}_{sn_0} (E_s - E_{n_0}) = \sum_s \mathbf{p}_{ns} \mathbf{p}_{sn} (E_s - E_n) \log \left| \frac{E_s - E_n}{Z^2 R} \right| .$$

	H	FS,L	He*	FS,L
$2s_{1/2}-2p_{1/2}$	1.058	1.052	14.041	13.826
$2p_{3/2}-2p_{1/2}$	10.969	10.969	175.589	175.571
$3s_{1/2}-3p_{1/2}$	0.315	0.313	4.185	4.118
$3p_{3/2}-3p_{1/2}$	3.250	3.250	52.029	52.021
$3p_{3/2}-2d_{3/2}$	0.003	0.004	0.086	0.064
$3d_{5/2}-3d_{3/2}$	1.082	1.083	17.341	17.340

Table 21.3 Energy differences taking into account the Lamb shift.

The state n_0 in this equation refers to the s -state. These coefficients can be evaluated numerically:

$$K(1,0) \simeq 19.8; \quad K(2,0) \simeq 16.6398; \quad K(2,1) \simeq 0.970430 \dots$$

The most relevant effect is on s -states, they are shifted upward as in the above elementary model. Adding this effect Table 21.2 becomes Table 21.3.

The agreement is good. The small difference has two sources

- (1) The correction to the Lamb shift. The most important term for s -states has the form

$$\Delta E_{n0} = \frac{1}{n^3} 8Z^5 \alpha^4 \left(1 + \frac{11}{128} - \frac{1}{2} \log(2) + \frac{5}{192} \right) \text{Ry}.$$

- (2) The mass corrections. In Chapter 14 it is shown that the order m/M corrections to the relativistic effects are

$$H_M = \frac{1}{Mc^2} \left[\frac{3\mathbf{p}^4}{8m^2} - \frac{Ze^2\hbar^2\pi}{m} \delta^{(3)}(\mathbf{r}) - \frac{Ze^2}{2mr} (\mathbf{p}^2 + \hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \mathbf{p})\mathbf{p}) \right].$$

An easy calculation left to the reader gives a shift independent on ℓ :

$$\Delta E_{n\ell} = -\frac{1}{4n^2} \frac{m}{M} (Z\alpha)^2 \frac{Z^2}{n^2} \text{Ry}.$$

Taking into account these corrections we can write Table 21.4, where the *levels* are reported, then there is no room for overall shifts in energy. The quantities reported are written as $10^4(E_{\text{Bohr}} - E)$

Level	H	FS + LS	FS,LS, δ	He*	FS + LS	FS,LS, δ
$1s_{1/2}$	0.108 29	0.108 36	0.108 26	1.801 46	1.807 73	1.802 47
$2s_{1/2}$	0.038 41	0.038 42	0.038 40	0.621 86	0.624 15	0.623 47
$2p_{1/2}$	0.041 62	0.041 62	0.041 62	0.664 54	0.666 18	0.666 20
$2p_{3/2}$	0.008 28	0.008 28	0.008 28	0.130 81	0.132 50	0.132 52
$3s_{1/2}$	0.013 84	0.013 84	0.013 84	0.222 35	0.224 30	0.224 09
$3p_{1/2}$	0.014 79	0.014 79	0.014 80	0.235 07	0.236 81	0.236 82
$3p_{3/2}$	0.004 92	0.004 92	0.004 92	0.076 92	0.078 69	0.078 69
$3d_{3/2}$	0.004 93	0.004 93	0.004 93	0.077 18	0.078 88	0.078 89
$3d_{5/2}$	0.001 64	0.001 64	0.001 64	0.024 47	0.026 17	0.026 18

Table 21.4 $10^4(E_{\text{Bohr}} - E)$. The values are in Rydberg. The third column for each case includes mass corrections and corrections due to the Lamb shift.

The agreement is quite impressive now, one part in 10^9 , and is one of the great successes of modern quantum field theory. Modern improvement both in theoretical computations and in experimental precision are important as they can reveal new physical effects, as the Lamb shift signaled the necessity of field quantization.

21.3 Hydrogen hyperfine interactions

In Subsection 14.1.6 it is shown that the electron–nucleus magnetic interaction is

$$V = -\frac{e}{mc} \left(\frac{1}{r^3} \boldsymbol{\mu}_N \cdot \boldsymbol{\ell} \right) - \frac{e}{mc} \left\{ \frac{8\pi}{3} \boldsymbol{\mu}_N \cdot \mathbf{s} \delta^{(3)}(\mathbf{r}) - [\boldsymbol{\mu}_N \cdot \mathbf{s} - 3(\boldsymbol{\mu}_N \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} \cdot \mathbf{s}] \frac{1}{r^3} \right\} .$$

It is useful to define a gyromagnetic factor for the nucleus in analogy to the electron

$$\boldsymbol{\mu}_N = g_N \frac{|e|}{2m_p c} \mathbf{s}_N , \quad \mu_p \equiv \frac{|e|\hbar}{2m_p c} .$$

The proton mass is used in the definition. All nuclei have magnetic moments of order μ_p , known also as the *Bohr nuclear magneton*. As

$m_e/m_p \sim 1/2000$ the nuclear magnetic moment is smaller than electron magnetic moment by a factor or order 10^{-3} .

Extracting the implicit \hbar factors we have

$$V = A \left\{ \frac{8\pi}{3} \mathbf{I} \cdot \mathbf{S} \delta^{(3)}(\mathbf{r}) - (\mathbf{I} \cdot \mathbf{S} - 3(\mathbf{I} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} \cdot \mathbf{S}) \frac{1}{r^3} + \frac{\mathbf{I} \cdot \mathbf{L}}{r^3} \right\},$$

where

$$A = -\frac{e\hbar}{2mc} \mu_p g g_N \equiv |\mu_B| \mu_p g g_N > 0; \quad \ell = \hbar \mathbf{L}; \quad \mathbf{s} = \hbar \mathbf{S}; \quad \mathbf{s}_N = \hbar \mathbf{I}.$$

The order of magnitude for V matrix elements is easily computed, as the characteristic length is $a \sim a_B = \hbar^2/me^2$:

$$\frac{A}{a_B^3} = \frac{m_e}{m_p} \alpha^2 \frac{e^2}{a_B}; \quad \alpha \equiv \frac{e^2}{\hbar c} \sim \frac{1}{137} \text{ (fine-structure const.)}.$$

The effects are of the order 10^{-7} times a typical electronic energy or 10^{-3} times the fine-structure splittings, nevertheless the splittings due to V , the so called *hyperfine structure*, are very important as they are the first effects probing directly the effects of nuclear structure on the atomic spectra. The radiation emitted in transitions between these levels have wavelengths of order $10^3 \text{ \AA} \times (10^6-10^7) \sim 10-100 \text{ cm}$, in the range of radio-frequency, a very important range for applications.

We will limit our analysis to a single electron, this case covers the hydrogen atom and alkali metals. First let us note that for s waves only the first term contributes: the last term has an explicit \mathbf{L} while the second is proportional to the second rank tensor

$$\delta_{ij} - 3 \frac{x_i x_j}{r^2},$$

which transforms as an $L = 2$ tensor. Both terms give a vanishing contribution of $L = 0$ matrix elements by the Wigner-Eckart theorem. For s waves the Hamiltonian has the same structure as that of the $L-S$ interaction:

$$V^{(S)} = A \frac{8\pi}{3} \mathbf{I} \cdot \mathbf{S} \delta^{(3)}(\mathbf{r}).$$

The unperturbed energy level has degeneracy $(2S+1)(2I+1)$, the eigenstates have the form $|\alpha, S, S_z, I, I_z\rangle$. $V^{(S)}$ does not commute with electronic spin and nuclear spin but, being a scalar, commutes with total angular momentum, which for $L = 0$ states has the form

$$\mathbf{F} = \mathbf{J} + \mathbf{I} = \mathbf{S} + \mathbf{I}.$$

The Hamiltonian can be diagonalized by using Clebsch-Gordan series, i.e. switching to the eigenstates of F, F_z . Exactly as in the case of $L-S$ coupling within a multiplet we can write

$$\mathbf{I} \cdot \mathbf{S} = \frac{1}{2} (\mathbf{F}^2 - \mathbf{S}^2 - \mathbf{I}^2) = \frac{1}{2} (F(F+1) - S(S+1) - I(I+1)).$$

The Hamiltonian is diagonal in the basis $|F, F_z\rangle$ and its eigenvalues are

$$E_F = A \frac{8\pi}{3} |\psi(0)|^2 \frac{1}{2} (F(F+1) - S(S+1) - I(I+1)). \quad (21.24)$$

Hydrogen atom

In this case $S = \frac{1}{2}$, $I = \frac{1}{2}$ and from the addition rules for angular momentum F can take the values $F = 0, 1$. Using $|\psi(0)|^2 = 1/\pi n^3 a^3$ for ns states:

$$E_F = \frac{1}{n^3} \frac{2}{3} \frac{A}{a^3} \begin{cases} 1 & F=1 \\ -3 & F=0 \end{cases} = \frac{2}{3n^3} g g_N \frac{\mu_p |\mu_B|}{a^3} \begin{cases} 1 & F=1 \\ -3 & F=0 \end{cases}$$

In particular for the $1s$ level

$$\Delta E = E_1 - E_0 = \frac{8}{3} g g_N \frac{\mu_p |\mu_B|}{a^3} .$$

a is expressed through the reduced electron mass

$$a = (1 + \frac{m_e}{m_p}) a_B ; \quad \frac{e^2}{a_B} = 1 \text{ a.u.} = 2 \text{ Ry} ,$$

and we have

$$\Delta E = \frac{g}{2} g_N \frac{m_e}{m_p} \left(1 + \frac{m_e}{m_p}\right)^{-3} \frac{4}{3} \alpha^2 \text{ a.u.} = \frac{g}{2} g_N \frac{m_e}{m_p} \left(1 + \frac{m_e}{m_p}\right)^{-3} \frac{8}{3} \alpha^2 \text{ Ry} .$$

For the proton $g_N = 5.585 7$ and the numerical result is, in frequency:

$$f = \frac{\Delta E}{\hbar} \simeq 1425.13 \text{ MHz} ; \quad \lambda = \frac{c}{f} = 21.060 5 \text{ cm.} \quad (21.25)$$

This is a famous line in astrophysical research, its detection allows us to reveal the presence of hydrogen clouds in the galaxy. The experimental value for f has an astonishing precision

$$1420405751.768 \pm 0.001 \text{ Hz.} \quad (21.26)$$

The first correction is of order α as for the electron $g - 2 \sim \alpha/\pi$, we used this value in eqn (21.25), this is why the results agree up to order α^2 .

The discrepancy of order 10^{-4} is due to the fact that we have neglected relativistic corrections. The present knowledge of the nucleus is not enough to explain all significant digits in (21.26).

The extension to $L > 1$ angular momenta is a useful exercise on the Wigner-Eckart theorem (see Problem 14.3); we quote here the result

$$\delta E_F = A \langle r^{-3} \rangle \frac{L(L+1) F(F+1) - J(J+1) - I(I+1)}{J(J+1)} . \quad (21.27)$$

For hydrogen atom, using the values

$$\langle nl | \frac{1}{r^3} | nl \rangle = \frac{1}{n^3 a^3} \frac{1}{\ell(\ell + \frac{1}{2})(\ell + 1)} ; \quad |\psi(0)|^2 = \frac{1}{\pi n^3 a^3} ,$$

eqns (21.27) and (21.24) give for s and p states

$$\begin{aligned} \delta E_{ns_{1/2}} &= A \frac{4\pi}{3} \left[F(F+1) - \frac{3}{2} \right] |\psi(0)|^2 = \frac{1}{n^3 a^3} A \frac{4}{3} \left[F(F+1) - \frac{3}{2} \right] ; \\ \delta E_{np_{1/2}} &= A \frac{4}{3} \left[F(F+1) - \frac{3}{2} \right] \left\langle \frac{1}{r^3} \right\rangle = \frac{1}{n^3 a^3} A \frac{4}{9} \left[F(F+1) - \frac{3}{2} \right] ; \\ \delta E_{np_{3/2}} &= A \frac{4}{15} \left[F(F+1) - \frac{9}{2} \right] \left\langle \frac{1}{r^3} \right\rangle = \frac{1}{n^3 a^3} A \frac{4}{45} \left[F(F+1) - \frac{9}{2} \right] . \end{aligned}$$

$F = 0, 1$ for the first two cases, $F = 1, 2$ for the third one. The energy difference can be written as

$$f_{ns_{1/2}} = \frac{8A}{3n^3a^3}; \quad f_{np_{1/2}} = \frac{1}{3} \times \frac{8A}{3n^3a^3}; \quad \dot{f}_{np_{3/2}} = \frac{2}{15} \times \frac{8A}{3n^3a^3}.$$

21.4 Divergences of perturbative series

Most perturbative series we encounter in quantum mechanics are divergent and, often, asymptotic. The origin of the divergence, the possibility of reconstructing the exact result from an asymptotic expansion, the analyticitic structure of the quantity under study, the stability of the system, and the non-perturbative (tunneling) effects, all turn out to be intimately related. A thorough discussion of these questions would take us too far: here we shall content ourselves with some most significant aspects of these problems. See the book [Le Guillou and Zinn-Justin (1990)] for a collection of papers on the subject.

21.4.1 Perturbative series at large orders: the anharmonic oscillator

We start by illustrating in a concrete example a typical large-order behavior of the perturbation series. Let us consider an anharmonic oscillator, (setting $m = 1, \omega = 1$)

$$H = \frac{1}{2} p^2 + \frac{1}{2} x^2 + \frac{1}{2} g x^4.$$

The perturbation expansion for the energy has the form

$$E = \frac{1}{2} + \sum E_n g^n.$$

The unperturbed ground-state wave function has the form, $\psi_0 = e^{-x^2/2}$. To each order of perturbation the matrix elements of x^4 can mix at most the states with n differing by 4. The unperturbed wave functions of the excited states are a degree n polynomial multiplying ψ_0 . It is therefore natural to seek for a solution of Schrödinger's equation (by setting $\hbar = 1$):

$$-\frac{1}{2} \frac{d^2}{dx^2} \psi + \frac{1}{2} x^2 \psi + \frac{1}{2} g x^4 \psi = E \psi, \quad (21.28)$$

in the form

$$\psi = B(x) e^{-x^2/2},$$

where B is a polynomial (in perturbation theory). By substituting this Ansatz into eqn (21.28) we find for B the equation

$$\frac{d^2 B}{dx^2} - 2x \frac{dB}{dx} - g x^4 B + (2E - 1)B = 0.$$

We expand B in powers of x , by keeping only up to terms of the degree $4k$, to the k -th-order of perturbation. We set therefore

$$B(x) = \sum_{k=0}^{\infty} g^k B_k(x); \quad B_k(x) = \sum_{j=0}^{2k} A_{k,j} x^{2j}; \quad A_{k,0} = 1;$$

$$2E = \sum_{k=0}^{\infty} \varepsilon_k g^k; \quad \varepsilon_0 = 1.$$

The wave functions are normalized by $B_k(0) = 1$. Upon substitution of this into Schrödinger's equation and equating term by term in g^k :

$$B_k'' - 2B_k' - x^4 B_{k-1} + \sum_{s=0}^k \varepsilon_s B_{k-s} - B_k = 0.$$

By using the expression for B_k one finds that

$$\sum_{\ell=1}^{2k} (2\ell)(2\ell-1) A_{k,\ell} x^{2\ell-1} - 2 \sum_{j=1}^{2k} 2j A_{k,j} x^{2j}$$

$$- \sum_{\ell=0}^{2k-2} A_{k-1,\ell} x^{2\ell+4} - \sum_{j=0}^{2k} A_{k,j} x^{2j} + \sum_{s=0}^k \varepsilon_s \sum_{j=0}^{2k-2s} A_{k-s,j} x^{2j} = 0.$$

We use the convention $A_{k,j} \equiv 0$ if $j > 2k$, this way the sum over j in the last expression can be extended to $2k$. Substituting into the first sum $\ell = j+1$ and into the third $\ell = j-2$ and using this convention one finds that

$$\sum_{j=0}^{2k} x^{2j} \left[(2j+2)(2j+1) A_{k,j+1} - 4j A_{k,j} \right.$$

$$\left. - A_{k-1,j-2} - A_{k,j} + \sum_{s=0}^k \varepsilon_s A_{k-s,j} \right] = 0.$$

The coefficients of this polynomial must all be zero. Using $\varepsilon_0 = 1$ we see that term with $s = 0$ in the sum cancels the term $-A_{k,j}$ and we have

$$(2j+2)(2j+1) A_{k,j+1} - 4j A_{k,j} - A_{k-1,j-2} + \sum_{s=1}^k \varepsilon_s A_{k-s,j} = 0.$$

The term with $s = k$ in the sum has as coefficient $A_{0,j}$ which is non-vanishing only for $j = 0$, and in this case is equal to 1. Therefore the term with $j = 0$ implies

$$\varepsilon_k = -2A_{k,1} - \sum_{s=1}^{k-1} \varepsilon_s,$$

which provides a recursion relation for ε_k once $A_{k,1}$ is known. The terms with $j \neq 0$ are thus determined by

$$(2j+2)(2j+1) A_{k,j+1} - 4j A_{k,j} - A_{k-1,j-2} + \sum_{s=1}^{k-1} \varepsilon_s A_{k-s,j} = 0.$$

Let us note that in this expression ε_k no longer appears. We start with $j = 2k$, the first term is zero: $A_{k,2k+1} = 0$, and this allows $A_{k,j}$ to be determined recursively:

$$A_{k,j} = \frac{1}{4j} \left((2j+2)(2j+1)A_{k,j+1} - A_{k-1,j-2} + \sum_{s=1}^{k-1} \varepsilon_s A_{k-s,j} \right),$$

with the sequence $j = 2k, 2k-1, 2k-2 \dots 1$. Once $A_{k,1}$ are found, ε_k can be calculated. As can be seen from the Table 21.5 and from Figure 21.2, the series is of alternative signs and grows very fast. In the figure are the first 50 coefficients in logarithmic scale.

$E_1 = \frac{3}{8}$	$E_2 = -\frac{21}{32}$
$E_3 = \frac{333}{128}$	$E_4 = -\frac{30885}{2048}$
$E_5 = \frac{916731}{8192}$	$E_6 = -\frac{65518401}{65536}$
$E_7 = \frac{2723294673}{262144}$	$E_8 = -\frac{1030495099053}{8388608}$
$E_9 = \frac{54626982511455}{33554432}$	$E_{10} = -\frac{6417007431590595}{268435456}$
$E_{11} = \frac{413837985580636167}{1073741824}$	$E_{12} = -\frac{116344863173284543665}{17179869184}$
$E_{13} = \frac{8855406003085477228503}{68719476736}$	$E_{14} = -\frac{1451836748576538293163705}{549755813888}$
$E_{15} = \frac{127561682802713500067360049}{2199023255552}$	$E_{16} = -\frac{191385927852560927887828084605}{140737488355328}$

Table 21.5

Such a calculation can be easily done with any program which allows algebraic manipulation (see the problems at the end of Chapter 9)

As can be seen in Figure 21.2 the behavior of the asymptotic coefficients is $E_n \sim n!$. The series diverges and it raises the question of what sense we can make out of such a series.

21.4.2 The origin of the divergence

Let us first try to understand the reason for the divergences of the perturbative series. We note that the divergence is not a peculiar pathology of quantum mechanical calculations: the same problem appears also in classical mechanics, as discussed by Poincaré. Let us continue below to use the anharmonic oscillator as a concrete example.

The reason for the divergence is best explained by a physical argument due to Dyson [Dyson (1952)]. Suppose that we are interested in computing the ground-state energy $E(g)$ for the system

$$H = \frac{1}{2} p^2 + \frac{1}{2} x^2 + \frac{1}{2} g x^4.$$

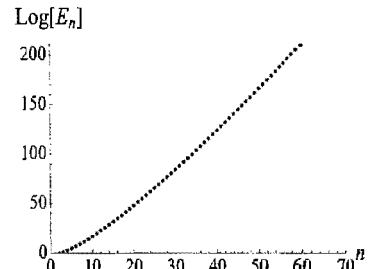


Fig. 21.2 $\log(|E_n|)$ as a function of n , the sign being alternative

The perturbative series for $E(g)$ has the form

$$E(g) = E_0 + \sum_{n=1} E_n g^n.$$

We have seen in the previous subsection that, even if the expansion truncated to some finite order gives a good approximate result for sufficiently small values of g the series is nevertheless divergent, the higher-order terms behaving as $E_n \sim n!$. This means that the function $E(g)$ is not analytic at $g = 0$. The argument by Dyson for the non-analyticity at $g = 0$ is the following. If the function $E(g)$ were analytic at $g = 0$, there must be a domain of convergence around it, $|g| < R$ and there the sum of the series must reproduce the exact function $E(g)$. But for $g < 0$ the Hamiltonian is not limited from below, and we know that the ground state with finite energy does not exist. Therefore the function $E(g)$ cannot be analytic at $g = 0$.

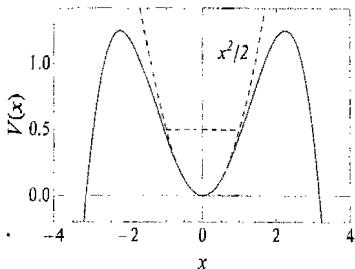


Fig. 21.3 $V(x)$ for $g = -0.1$. For convenience the oscillator potential ($g = 0$) and the value of the ground state for the latter are also shown (dashed curves).

Indeed, for $g < 0$ the potential $V(x) = (x^2 + gx^4)/2$ looks like in Figure 21.3. A particle in the ground state of the unperturbed (harmonic) potential can decay tunneling through the barrier; such a state can only be metastable. Such an effect cannot be explained by any finite-order perturbation theory, which maintains the state in \mathbb{L}^2 , order by order. The tunnel effect for $g < 0$ therefore must be responsible for the non-analyticity of the function $E(g)$. More precisely the imaginary part of $E(g)$ for negative values of g , which gives the line width and the half-lifetime, must be related somehow to the divergent behavior of the perturbative coefficients E_n . Such a relation will be obtained below, through a dispersion relation, see eqn (21.40).

21.4.3 The analyticity domain

From the mathematical point of view the lack of the analyticity can be understood as follows. Consider the unperturbed Hamiltonian H_0 . To this is associated a domain $D(H_0)$, a subset of \mathbb{L}^2 , span by all the functions for which the operator H_0 is self-adjoint. For instance, for any function ψ in such a domain it must be that

$$\int dx |\psi(x)|^2 x^2 < \infty,$$

i.e., the expectation value of the potential exists. Take for instance a function behaving as $\psi_0 \sim 1/x^2$ asymptotically. For such a function

$$\int dx |\psi_0(x)|^2 x^2 < \infty; \quad \int dx |\psi_0(x)|^2 x^4 \sim \int dx \frac{1}{x^4} \cdot x^4 \rightarrow \infty;$$

that is, ψ_0 does not belong to the domain of $H(g)$, $D(H)$. In other words there are states perfectly legitimate from the point of view of the unperturbed operator H_0 for which, however, the perturbation can never be considered small, however small g might be.

The argument can be made more formal in the form of the following theorem.

Theorem 21.1. (Kato–Rellich) Let $H(g)$ be a family of operators, with $g \in S \subset \mathbb{C}$. If

- (A) $D(H(g))$, the domain of $H(g)$, is independent of g ;
- (B) $\forall \psi \in D(H(g))$, $\langle \psi | H(g) | \psi \rangle$ is an analytic function of g in S ,

then $\forall g_0 \in S$ and for each isolated eigenvalue $E(g_0)$ of $H(g_0)$, there exists a neighborhood V_{g_0} such that $H(g)$ has a unique, isolated eigenvalue $E(g)$ in a neighborhood of $E(g_0)$. The function $E(g)$ is analytic in V_{g_0} and a function ψ_g exists which is analytic in g such that

$$H(g)\psi_g = E(g)\psi_g.$$

Furthermore the Taylor series of $E(g)$ coincides with the usual perturbative expansion for $H(g)$. In other words under the conditions of the theorem the perturbative series gives the exact answer.

A sufficient condition for the validity of the conditions A,B has been given by the following criterion:

Theorem 21.2. (Kato) If there exist two numbers a, b such that for any $\psi \in D(H_0), \psi \in D(V)$, the following inequality

$$\|V\psi\| \leq a \|H_0\psi\| + b \|\psi\|,$$

holds, then the conditions A,B of the preceding theorem are satisfied.

As we have already seen, the condition A for Kato–Rellich theorem fails to be satisfied in the case of the anharmonic oscillator. It is clear that the eigenvalues $E(g)$ of the anharmonic oscillator can be expanded around any positive value, but not around $g = 0$. What happens is that as one approaches the origin, the radius of convergence shrinks to zero.

In the case of anharmonic oscillator, many properties concerning the analyticity of $E(g)$ can be obtained from a simple scaling argument due to K. Symanzik. Let us consider the scale transformation

$$U(\lambda)\psi(x) = \lambda^{1/2}\psi(\lambda x). \quad (21.29)$$

It can be readily verified that the transformation (21.29) is a unitary transformation and that for a Hamiltonian of the form

$$H(\alpha, g) = \frac{1}{2} p^2 + \frac{1}{2} \alpha x^2 + \frac{1}{2} g x^4,$$

we have

$$U(\lambda) H(\alpha, g) U(\lambda^{-1}) = \lambda^{-2} H(\alpha \lambda^4, g \lambda^6).$$

As the eigenvalues remain invariant under unitary transformations, it follows that, by setting $\lambda = g^{-1/6}$,

$$E_n(1, g) = g^{1/3} E_n(g^{-2/3}, 1). \quad (21.30)$$

From eqn (21.30) we can deduce that the singularity at $g = 0$ of $E(g)$ must be of a cubic root type; furthermore, by using the criterion of Kato, the “strong-coupling” expansion

$$E_n(g) = g^{1/3} \sum_k a_k g^{-2k/3},$$

is convergent; in particular the asymptotic behavior of the eigenvalues is:

$$E_n(g) \xrightarrow[g \rightarrow \infty]{} g^{1/3}.$$

It can then be shown that the associated Riemann surface is three-sheeted, with a branch point at $g = 0$, as suggested by eqn (21.30). Furthermore one can show [Loeffel and Martin (1972)] that in the first sheet, which corresponds to $|\arg(g)| < \pi$, the function $E(g)$ is analytic. The structure of the singularities of $E(g)$ in the three-fold Riemann surface has been studied by Bender and Wu [Bender and Wu (1973)] in great detail.

21.4.4 Asymptotic series

Given that the perturbative series is divergent, the main question is: what has it to do with the exact result? Can one recover the exact answer from the knowledge of the perturbative (divergent) series? How, concretely? A partial answer to these questions comes from the observation that the perturbative series for the anharmonic oscillator and in many other cases, if not convergent, is an *asymptotic* one.

Asymptotic series: definition

Consider a domain D of the complex plane

$$D : \quad |\arg z| \leq \frac{\alpha}{2}; \quad |z| \leq R, \quad (21.31)$$

and a function analytic in D . The series $\sum f_k z^k$ is said to be *asymptotic* to the function $f(z)$ in D if it is divergent and

$$|f(z) - \sum_{k=0}^N f_k z^k| \leq C_{N+1} |z|^{N+1}, \quad \forall N. \quad (21.32)$$

In practice, eqn (21.32) asserts that a series is asymptotic if for any *finite* N it is possible to choose a small neighborhood of the origin such that the difference between the partial sum and the exact result is $\mathcal{O}(z^{N+1})$. In other words, at fixed order, the exact function can be approximated arbitrarily well, if g is chosen sufficiently small. Vice versa, whatever g may be, the series diverges as can be seen by going to sufficiently high orders.

The characteristic feature of an asymptotic series is thus that whatever it represents can be estimated only by keeping a finite number of terms. As the sum is divergent, it does not pay to try to sum the series literally

to all orders. If the answer is wanted with a given precision ε , given a partial sum, the only thing one can hope to do is to estimate it for sufficiently small values of $|z|$, $C_N|z|^N < \varepsilon$.

Let us consider an explicit form which will appear in the example below: $C_k \sim AB^{-k}k!$. As a function of k , the error will be minimized when the quantity $\delta(k) = B^{-k}k!z^k$ is minimum. By using the expansion

$$k! \sim k^k e^{-k} \sqrt{2\pi k},$$

one finds

$$\log(\delta) \sim k \log(k) - k + \log\left(\frac{B}{z}\right),$$

which has an extremum at $\bar{k} = B/z$ and $\delta(\bar{k}) \sim \exp(-B/z)$. The latter can be made as small as one wishes, by taking sufficiently small z . Going beyond this order, the series starts to grow and the series diverges.

In the absence of other information, an asymptotic expansion alone cannot uniquely determine the function $f(z)$. For consider an addition of a function $g(z) = \exp(-a/z)$. Its Taylor expansion around $z = 0$ is identically null, as

$$\left. \frac{d^n}{dz^n} g(z) \right|_{z=0} = 0,$$

hence $f(z)$ and $f(z) + g(z)$ have the same asymptotic series.

An important result on the possibility of reconstructing the exact function from an asymptotic expansion is the following

Theorem 21.3. (Watson) *If the function $f(z)$ is analytic in a domain $|\arg z| \leq \alpha/2$ with $\alpha > \pi$, that is in a domain larger than the half plane of \mathbb{C} , then the asymptotic expansion $\sum_k f_k z^k$ uniquely determines the function $f(z)$.*

In simple quantum mechanical problems such as the quartic anharmonic oscillator, the situation is exactly as required by Watson's theorem:

- The eigenvalues $E(g)$ are analytic functions in the complex plane of g , with a cut along the negative real axis.
- The usual perturbation series (Rayleigh–Schrödinger series) is an asymptotic series.

The proof of the second point is not difficult and reduces to a counting of all possible terms in perturbative expansion; it is subtler to show the first point; we shall give an intuitive argument in the chapter dedicated to semi-classical approximation.

In systems with infinite degrees of freedom (quantum field theory) such detailed informations are known only in limited cases.

Watson's theorem for the possibility of reconstructing the original function from its asymptotic series, has recently been improved (*Sokal's theorem*) [Sokal (1980)]. The theorem holds actually under a much

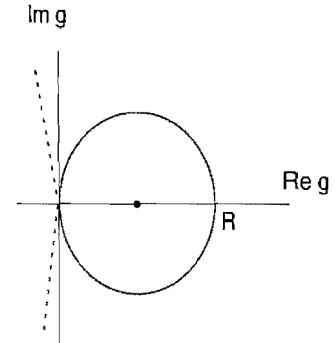


Fig. 21.4 The analyticity domain required for Watson's (on the right of the dashed lines) and Sokal's (inside the circle) theorems.

weaker condition : it is sufficient to have analyticity in a more restricted domain,

$$\operatorname{Re} \left(\frac{1}{g} \right) > \frac{1}{R}$$

i.e., inside a circle tangent to the imaginary axis and centered at $z = (R/2, 0)$), which is entirely contained in the region $\operatorname{Re}(g) > 0$ (See Figure 21.4).

Thus the situation is this: the perturbative series, even though divergent, uniquely determines the exact function in favorable cases covered by Watson's or Sokal's theorem. Vice versa, there are cases such as the double well potential, expanded around one of the minima, in which perturbation theory gives an asymptotic series which *does not* satisfy these criteria. In cases such as this, one finds divergent series with non-alternate sign, $\sim |c|^n n!$: it is essential to take explicit account of non-perturbative effects to get the complete answer.

Let us now go back to those cases in which the above theorems apply. The concrete problem is: *how* to reconstruct the function $f(g)$, given its asymptotic expansion?

The Borel transform

Under the assumption that the conditions for Watson's or Sokal's theorem are satisfied by the function having an asymptotic series, $\sim \sum f_k z^k$, it is possible to define a *convergent* series by

$$B_f(z) = \sum_k \frac{f_k}{k!} z^k; \quad (21.33)$$

called the *Borel transform*. Namely the coefficients of the Borel transformed series are smaller than the original series by factors $1/k!$, and this guarantees the convergence. Once the function $B_f(z)$ is found, the original function can be obtained from the inverse Borel transform:

$$f(z) = \int_0^\infty e^{-t} B(zt) dt = \frac{1}{z} \int_0^\infty e^{-t/z} B(t) dt. \quad (21.34)$$

By substituting eqn (21.33) into (21.34) one finds the original (divergent) series.

A particularly important case is the one in which the coefficients behave as

$$f_k \sim C k^b (-A)^{-k} k!; \quad A > 0. \quad (21.35)$$

The series is of alternate signs, as in the quartic anharmonic oscillator. The Borel transform has the form,

$$B_f(z) = C \sum_k k^b \left(-\frac{z}{A} \right)^k.$$

Note that this function has a singularity at $z = -A < 0$. As it occurs on the negative real axis, the inverse Borel transform is well defined and

Padé	g=1	g=2	g=10
10	0.139 235 162 941	0.160 753 948 765	0.244 712 561 181
20	0.139 235 164 151	0.160 754 129 626	0.244 910 058 400
30	0.139 235 164 153	0.160 754 130 244	0.244 917 070 950
40	0.139 235 164 153	0.160 754 130 247	0.244 917 393 022
50	0.139 235 164 153	0.160 754 130 247	0.244 917 406 959
60	0.139 235 164 153	0.160 754 130 247	0.244 917 407 194
var.	0.139 235 164 153	0.160 754 130 247	0.244 917 407 212

Table 21.6 The reconstruction of the ground-state energy $E_0(g)/2$ by the Borel transformation with Padé's approximants, for $g = 1, 2, 10$. The last line is the result of the variational calculation.

there is no obstruction in reconstructing the original function $f(g)$ in this manner. These series are said to be *Borel-summable*.

Practically, then, we compute some finite number of the perturbative coefficients, say up to the N 'th. Calculate the Borel transform $B(z)$ from such truncated asymptotic series, and continue analytically $B(z)$ and compute the inverse Borel transform, to obtain an approximation for $f(z)$.

The Padé approximation

A standard method to reconstruct an analytic function from a truncated perturbative series, is to approximate the latter by a ratio of two polynomials, having the correct coefficients up to the order given. We call Padé approximant of order $P^{[N,M]}$ the ratio of a polynomial of order N and another of order M . Let us limit ourselves to the diagonal approximants $P^{[N,N]}$. To fix these polynomials we need to assign $(2N+1)$ coefficients. If the series starts at g , that is, if the zeroth-order (the constant) is known, then we must compute the perturbative expansion up to the order $2N$, and by comparing them to the Taylor expansion of $P^{[N,N]}$, the two polynomials can be uniquely determined.

As an illustration we report the results found this way (see the Mathematica notebook, NB-5.5-Divergences.nb in CD) in Table 21.6, for the ground-state energy of the quartic oscillator with $g = 1, 2, 10$. A good agreement is found, with 120 perturbative terms; the error is of the order of 10^{-11} at worst.

Recapitulating what has been said so far:

- (a) For systems such as the anharmonic oscillator, the eigenvalues $E(g)$ are analytic function of g in the complex plane with a cut along the negative real axis.
- (b) In these cases the asymptotic series uniquely determines the function $E(g)$.

In the next subsection we shall see how the various information fits nicely together, and how the perturbative coefficients can be calculated from

the imaginary part of $E(g)$ or vice versa; what type of singularities occur in the Borel transform of $E(g)$, etc.

21.4.5 The dispersion relation

Consider a function analytic in the complex plane \mathbb{C} with a cut along the negative axis. Let us apply Cauchy's theorem to the contour shown in Figure 21.5:

$$f(z) = \frac{1}{2\pi i} \oint_C dz' \frac{f(z')}{z' - z}. \quad (21.36)$$

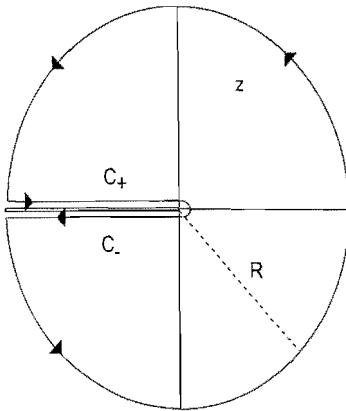


Fig. 21.5 Cauchy integration contour

The contribution of the integral along the large semi-circle of radius R tends to zero as $R \rightarrow \infty$, assuming that the function vanishes sufficiently fast at infinity. By squeezing the contours C_+, C_- on the negative real axis, the two possible values of the function at a negative real value are, for $\varepsilon \rightarrow 0$,

$$f(x + i\varepsilon) \quad \text{on } C_+ ; \quad f(x - i\varepsilon) \quad \text{on } C_- ; \quad x \in [-\infty, 0].$$

Equation (21.36) can be written therefore as

$$f(z) = \lim_{\varepsilon \rightarrow 0} \frac{1}{2\pi i} \int_{-\infty}^0 dx \frac{f(x + i\varepsilon) - f(x - i\varepsilon)}{x' - z} \equiv \frac{1}{\pi} \int_{-\infty}^0 dx \frac{\text{Im}f(x)}{x - z}. \quad (21.37)$$

A relation of this type is known as a *dispersion relation*. The function is determined from its discontinuity along the cut. Suppose now that we consider the asymptotic series

$$f(z) = \sum_k f_k z^k.$$

By expanding the geometric series in eqn (21.37) we find that

$$f_k = \frac{1}{\pi} \int_{-\infty}^0 dx \frac{\text{Im}f(x)}{x^{k+1}}. \quad (21.38)$$

In other words the knowledge of the discontinuity allows us to determine the coefficients of the perturbative expansion. In particular, for $k \rightarrow \infty$ the integral (21.38) is dominated by the contribution from small x : *the large-order coefficients are determined by the small z behavior of $\text{Im}f(z)$.*

Suppose, for instance, that $\text{Im}f(z) \sim z^{-b} e^{a/z}$. Then

$$\begin{aligned} f_k &= \frac{1}{\pi} \int_{-\infty}^0 dx \frac{x^{-b} e^{a/x}}{x^{k+1}} = \frac{1}{\pi} (-1)^{k+b} \int_0^\infty e^{-at} t^{b+k-1} dt = \\ &= \frac{1}{\pi} \Gamma(k+b)(-a)^{-b-k}, \end{aligned} \quad (21.39)$$

therefore we find $k!$ behavior of the large-order coefficients. Applying eqn (21.39) to the function $E(g)$ we get

$$E_k = \frac{1}{\pi} \int_{-\infty}^0 dx \frac{\text{Im}E(x)}{x^{k+1}}. \quad (21.40)$$

Such a relation is consistent with the physical argument of Dyson: as we shall see in more detail in Chapter 11, the system is metastable for $g < 0$ and the eigenvalue $E(g)$ acquires an imaginary part.

An explicit example

$$F(g) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx e^{-x^2/2-gx^4}.$$

This function is evidently singular for real and negative g . Note that $F(g)$ is a perfectly well defined function for $g \geq 0$. If we expand the series around $g = 0$

$$F(g) = \sum_k F_k g^k = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx \frac{1}{k!} e^{-x^2/2} (-x^4)^k.$$

The integral can be done explicitly: it is Γ function, but it is instructive to estimate it by the saddle-point method for large values of k .

Let us briefly recall the method. In calculating the integration of $\exp(-f(x))$ we first determine the stationary point, x_0 , $f'(x_0) = 0$; expanding around this point up to the second-order, one has

$$\frac{1}{\sqrt{2\pi}} \int e^{-f(x)} \sim e^{-f(x_0)} \frac{1}{\sqrt{2\pi}} \int e^{-\frac{1}{2} f''(x_0)(x-x_0)^2} = \frac{1}{\sqrt{f''(x_0)}} e^{-f(x_0)}.$$

In the case under consideration, $f(x) = \frac{x^2}{2} - 4k \log(x)$, the saddle points are: $x_0 = \pm\sqrt{4k}$ and using Stirling's formula for the factorial, we find that

$$f_k \sim (-1)^k 16^k k!. \quad (21.41)$$

Let us now estimate the imaginary part of $F(g)$ for $g < 0$, by using the saddle-point method. In this case the exponent of the integrand is

$$f(x) = \frac{x^2}{2} - |g|x^4.$$

The nontrivial saddle point is at $x_0 = \pm 1/\sqrt{-4|g|}$, where

$$f(x_0) = \frac{1}{16g} \quad f''(x_0) = 1 + 12|g|x_0^2 = -2 < 0.$$

Therefore

$$\text{Im}F(g) \sim e^{-1/16|g|} = e^{1/16g}.$$

By using eqn (21.39) we re-obtain the result (21.41).

Anharmonic oscillator

Let us now apply these methods to the quantum-mechanical anharmonic oscillator. For small negative g the Hamiltonian (we set $m = 1, \omega = 1$)

$$H = \frac{1}{2} p^2 + \frac{1}{2} x^2 - \frac{1}{2} |g|x^4, \quad (21.42)$$

is unstable, see Figure 21.3. The calculation of the probability through the barrier is treated in Chapter 11: the result, apart from a numerical factor, is:

$$\Gamma \propto \exp -2 \int_a^b \sqrt{2m|E - V(x)|} dx ,$$

⁶ In the Euclidean path integral approach, discussed in Chapter 8, eqn (21.43) is the instanton action—the action of a nontrivial classical solution. It gives the contribution of a functional saddle point. These solutions can appear for non-physical value of g (as in the quartic oscillator considered here) or for physical values of the quartic coupling constant as in the case of a double well potential. In the latter case these instantons give indeed non-perturbative corrections in the *real* part of $E(g)$. The essence of the argument does not change, however.

⁷ To be really careful the dispersion relation must be written for the function $[E(g) - E(0)]/g$ to have a better convergence.

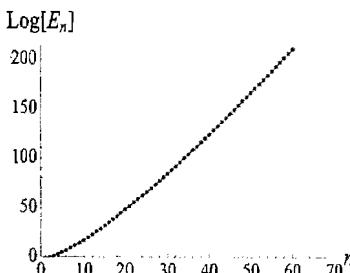


Fig. 21.6 Calculated perturbative coefficients E_k as compared with the asymptotic estimates. $\log(|E_n|)$ is plotted against n , the signs are alternate, as in Figure 21.2. The second figure shows $E_k^{(as)} - E_k$.

where a, b are the zeros of the roots of $E - V(x) = 0$, $V(x)$ is the potential and the integral is over the classically forbidden region, $E < V(x)$.

For small $|g|$ the area under the barrier is large and Γ is a very small quantity. In a first approximation then the energy can be taken to be the unperturbed value, $E = \frac{1}{2}$. The first turning point a is the one close to $x \sim 1$. The second turning point is far from the origin, at $x^2 \sim 1/|g|$. In this region the term E is negligible and we have approximately

$$|E - V(x)| \sim \frac{1}{2} x^2 - \frac{1}{2} |g| x^4 = \frac{1}{2} |g| x^2 \left(\frac{1}{|g|} - x^2 \right) .$$

We could therefore approximate $a \sim 0$, $b = \sqrt{1/|g|}$. Therefore⁶

$$\begin{aligned} -\log(\Gamma) &\simeq 2\sqrt{|g|} \int_0^{1/\sqrt{|g|}} dx x \sqrt{\frac{1}{|g|} - x^2} \\ &= \frac{2}{|g|} \int_0^1 dy y \sqrt{1 - y^2} = \frac{2}{3|g|} , \end{aligned} \quad (21.43)$$

and

$$\Gamma \sim \exp \left(-\frac{2}{3|g|} \right) = \exp \left(\frac{2}{3g} \right) ; \quad \text{Im}E(g) \sim \exp \left(\frac{2}{3g} \right) . \quad (21.44)$$

Recalling eqn (21.39) we get immediately⁷

$$E_k \sim \left(-\frac{3}{2} \right)^k k! . \quad (21.45)$$

Thus the series is indeed of alternate signs: it is divergent but asymptotic and Borel-summable. To get a quantitative prediction on the coefficients we must determine the pre-exponential factor in eqn (21.44). From a semi-classical analysis (see [Bender and Wu (1973)] or Chapter 11) we find

$$\text{Im}E(g) = \frac{2}{\sqrt{\pi}} \frac{e^{2/3g}}{\sqrt{-g}} (1 + \mathcal{O}(g)) , \quad g \rightarrow 0^- .$$

It follows from this and from the dispersion relation that

$$E_k = (-1)^{k+1} \left(\frac{6}{\pi^3} \right)^{1/2} \left(\frac{3}{2} \right)^k \Gamma \left(k + \frac{1}{2} \right) \left[1 + \mathcal{O} \left(\frac{1}{k} \right) \right] . \quad (21.46)$$

In Figure 21.6 the coefficients E_k as calculated directly as in Subsection 21.4.1 and the asymptotic estimates (21.46) are shown. The second figure shows their difference. As can be seen there is a good agreement. The behavior (21.45) or (21.46) of the perturbative coefficients provide for the information on the singularities in the Borel transform, which can be used to elaborate a more sophisticated method of resummation. See for instance [Le Guillou and Zinn-Justin (1990)].

21.4.6 The perturbative–variational approach

There is a method of resummation of divergent series which has characteristics both of perturbation theory and variational approach. In spite of the ease of use, the fact that the method gives a sequence rigorously convergent to the exact result for certain range of g (which can be determined by the detailed study of analyticity domain of the function under consideration) and the fact that it has an intuitive, physical interpretation, make this method very attractive. The method is known under various names: delta expansion, “order-dependent mappings” or simply, the perturbative–variational method.

The basic idea of the method is simple: given a generic Hamiltonian $H = \frac{p^2}{2} + V(q)$ with any potential, we rewrite it as

$$H = \frac{p^2}{2} + V(q) = H_0(\Omega) + \delta \cdot H'|_{\delta=1},$$

where

$$H_0(\Omega) \equiv \frac{p^2}{2} + \frac{\Omega^2}{2}q^2, \quad H' \equiv V(q) - \frac{\Omega^2}{2}q^2,$$

Ω is a *trial frequency*. The theory is now expanded in powers of δ by using standard perturbation theory, with δ set to be unity after the calculation. The partial sum to up to the order N , S_N , will depend on the trial frequency Ω , while the exact result should not depend on such a parameter, artificially introduced in the theory. The approximant to order N is defined as the partial sum S_N , in which $\Omega = \Omega_N$ is determined appropriately, order by order, requiring that S_N be as little dependent on Ω as possible. Ω thus defined depends on N . Concretely, we could impose the criterion of the minimum sensitivity,

$$\left. \frac{\partial S_N}{\partial \Omega} \right|_{\Omega=\Omega_N} = 0,$$

or alternatively we can adopt the criterion of the “fastest convergence”

$$S_N - S_{N-1} = 0.$$

For example take the anharmonic oscillator

$$H = \frac{p^2}{2} + \frac{\omega^2}{2}q^2 + \frac{g}{4}q^4. \quad (21.47)$$

We rewrite it as

$$H = H_0(\Omega) + H', \quad H' \equiv \frac{\omega^2 - \Omega^2}{2}q^2 + \frac{g}{4}q^4,$$

the ground-state energy is given to the first-order in δ by (we set $m = 1$, $\hbar = 1$),

$$S_1 = \frac{\Omega}{4} + \frac{\omega^2}{4\Omega} + \frac{3g}{16\Omega^2}.$$

By extremizing it with respect to Ω , (we set also $\omega = 1$) we have (for $g = 20$)

$$\Omega = 3.21447,$$

and for the energy

$$E^{(0)} \simeq 1.24431\dots$$

to be compared with the exact result

$$E_{es}^{(0)} = 1.22459\dots$$

Such a result is to be compared with the standard perturbation theory, which gives

$$E^{(0)} = \frac{3g}{16} = 7.5,$$

it fails badly for such a large value of g .

To this order, however, this approach can be seen to be equivalent to a variational method, with a particular choice of trial wave functions. Let us therefore go to the third-order in H' . We find (always $g = 20$)

$$E_{es}^{(0)} = 1.22497\dots,$$

which suggests a reasonably fast convergence.

The method indeed possesses several remarkable features. First, as already mentioned, the method uses the apparatus of the standard perturbation theory, and consequently is potentially applicable in much more complex systems such as quantum field theories as well. Second, the method is nevertheless non-perturbative with respect to the coupling constant g , as the order-by-order determination of Ω introduces a non-holomorphic dependence of the result on g . The parameter Ω can be interpreted as a physical parameter describing approximately, e.g., the ground-state wave function. In this sense the method has certain similarity with the variational approach; in fact, as we mentioned already, to first-order the eigenstate of $H_0(\Omega)$ can be regarded as a particular variational trial function. However, beyond the first-order, there is no variational principle involved. In fact, the result can be larger or smaller than the exact one. The method applies equally well to any level, whereas the standard variational method to the excited states requires certain care.

For a quartic oscillator, (21.47), it can be shown rigorously that the sequence S_N converges to the exact answer, if the trial frequency Ω_N is varied with N as

$$x_N \equiv \frac{\Omega_N}{\omega} = C N^\gamma,$$

where either

$$\frac{1}{3} < \gamma < \frac{1}{2}, \quad C > 0,$$

or

$$\gamma = 1/3, \quad C \geq \alpha_c g^{1/3}, \quad \alpha_c \simeq 0.5708751028937741.$$

The convergence of the perturbative-variational approach is a consequence of this fact.

The convergence proof of our sequence goes beyond the scope of this book, but the idea is as follows. For dimensional reasons, the energy eigenvalue of the anharmonic oscillator has the form

$$E(g, \omega) = \omega \tilde{E} \left(\frac{g}{\omega^3} \right).$$

The standard perturbative series

$$E^{(\text{pert})} = \omega \sum_{n=0}^{\infty} c_n \left(\frac{g}{\omega^3} \right)^n, \quad (21.48)$$

has the coefficients c_n (for the K -th level) which behave as

$$c_n \sim -\frac{\sqrt{6} 12^K}{\pi^{3/2} K!} \left(-\frac{3}{4} \right)^n \Gamma \left(n + K + \frac{1}{2} \right).$$

The delta expansion for eqn (21.47), i.e., a perturbative expansion in

$$H' = \frac{\omega^2 - \Omega^2}{2} q^2 + \frac{g}{4} q^4,$$

is equivalent to the following substitution in eqn (21.48)

$$\begin{aligned} \omega &\rightarrow \Omega \left(1 + \delta \frac{\omega^2 - \Omega^2}{\Omega^2} \right)^{1/2} = \omega x [1 - \delta \beta(x)]^{1/2}, \\ g &\rightarrow \delta \cdot g, \end{aligned}$$

where

$$x \equiv \frac{\Omega}{\omega}, \quad \beta(x) \equiv 1 - \frac{1}{x^2},$$

followed by expansion in powers of δ . We arrive at

$$\begin{aligned} E^{(\delta)} &= \omega \lim_{N \rightarrow \infty} S_N(x), \\ S_N(x) &= \sum_{n=0}^N c_n \left(\frac{g}{\omega^3} \right)^n A_n^{(N)}(x), \\ A_n^{(N)}(x) &\equiv \frac{1}{x^{3n-1}} \sum_{k=0}^{N-n} \beta(x)^k \frac{\Gamma(3n/2 + k - \frac{1}{2})}{\Gamma(3n/2 - \frac{1}{2}) \Gamma(k+1)}. \end{aligned}$$

We now see that the approximant $S_N(x)$ has the form of the N -th perturbative approximant, but with the coefficients modified by the factor $A_n^{(N)}(x)$. Except for $A_0^{(N)}(x)$ these coefficients are positive definite and lie between

$$0 < A_n^{(N)}(x) < 1, \quad \text{for } n \geq 1,$$

(we consider $x > 1$). All $A_n^{(N)}(x)$ (including $A_0^{(N)}(x)$) go to 1 for $N \rightarrow \infty$, if x is kept fixed. Vice versa, each $A_n^{(N)}(x)$ approaches zero when $x \rightarrow \infty$ with fixed N (except for $A_0^{(N)}(x)$ which diverges). In other words, $S_N(x)$ can be considered as a sort of *regularized* perturbation series. The idea is then to play with the rate with which N and x are sent to infinity, so as to ensure the convergence. The convergence at the highest ends ($n \sim N$) requires that the condition

$$c_N A_N^{(N)}(x) \sim N! / x^{3N-1} \rightarrow 0,$$

be satisfied, suggesting that x be varied as $x \propto N^\gamma$, $\gamma > 1/3$. On the other hand, to ensure the convergence of $A_0^{(N)}(x)$ in the large N limit, it is necessary that

$$\beta(x)^N = (1 - 1/x^2)^N \rightarrow 0,$$

which implies $\gamma < \frac{1}{2}$.

A detailed analysis [Guida, Konishi and Suzuki (1995)] fully confirms these intuitive ideas (see also [Kleinert (2006), Le Guillou and Zinn-Justin (1990)]) The determination of the domain of g in which the method converges, requires the use of the analyticity of $E(g)$ in the three-sheeted Riemann surface, and in particular the knowledge of the positions of certain singularities which nest in the third Riemann sheet (the so-called Bender-Wu singularities).

Apart from the elegance and the ease of use, it is to be mentioned that this method yields a convergent result, allowing us to reconstruct the value of $E(g)$ from a perturbative series, even in some non-Borel-summable cases (divergent series with non-alternate signs), such as the double-well system as long as the central barrier is not too high.

21.5 The semi-classical approximation in general systems

21.5.1 Introduction

The formulation of semi-classical approximation for systems with more than one degree of freedom is not trivial and a full understanding of the limit $\hbar \rightarrow 0$ is still lacking. The subject has connections with many branches of mathematics and physics, ranging from dynamical systems and chaos to catastrophe theory, from diffraction to asymptotic solutions of partial differential equations. In this Supplement we present some elementary aspects of the problem. In the text we will use mainly a geometrical and intuitive approach, leaving algebraic or analytical proofs of most statements to problems at the end of Chapter 11.

Let us consider as a simple example Schrödinger's equation for a particle in a potential $V(\mathbf{x})$

$$-\frac{\hbar^2}{2m} \Delta \psi + V(\mathbf{x})\psi = i\hbar \frac{\partial}{\partial t} \psi. \quad (21.49)$$

If ψ depends smoothly on \hbar the only solution of eqn (21.49) in the limit $\hbar \rightarrow 0$ would be $\psi = 0$. To balance the explicit factors \hbar a rapidly varying ψ is needed. As in the one-dimensional case we look for solutions in the form

$$\psi(\mathbf{q}, t) = A(\mathbf{q}, t) \exp \left[\frac{i}{\hbar} S(\mathbf{q}, t) \right].$$

By substitution in Schrödinger's equation we have (see also problems)

$$\frac{\partial S}{\partial t} + H(\nabla S, \mathbf{q}) = 0; \quad \frac{\partial A^2}{\partial t} + \nabla(A^2 \mathbf{v}) = 0;$$

with $\mathbf{v} = \partial H / \partial \mathbf{p}$ at $\mathbf{p} = \nabla S$. In particular for stationary states

$$H(\nabla S, \mathbf{q}) = E; \quad \nabla(A^2 \mathbf{v}) = 0. \quad (21.50)$$

The first equation in eqn (21.50) is the well-known Hamilton–Jacobi equation for the classical action S .

There are cases in which the solution of eqn (21.50) can be easily obtained: the separable cases. The Hamilton–Jacobi equation is invariant under coordinate's transformations: a problem is separable if there exists a coordinate's system in which

$$S(\mathbf{q}) = S(q_1) + \dots + S(q_n).$$

In such a case the same monodromy argument used in one dimension works and one can write the quantization condition in the form

$$\frac{1}{2\pi} \oint p_i(q_i) dq_i = \hbar \left(n_i + \frac{\alpha_i}{4} \right). \quad (21.51)$$

In the usual case of oscillatory coordinates $\alpha_i = 2$, for angular coordinates $\alpha_i = 0$ etc. In contrast to what happens in one-dimensional cases the integrals in eqn (21.51) are on cycles in q variables, not on a classical period of motion.

This, very roughly, is the latest development of the old quantum theory (without the fundamental coefficients α_i). It was not clear how to extend (21.51) to non-separable systems, except for classical perturbation theory.

Einstein was the first who pointed out, in a remarkable paper which at that time was not widely appreciated, the lack of *classical* invariance of eqn (21.51) and the geometric structure underlying this kind of semi-classical quantization conditions.

The first point is clear: in (21.51) a special coordinate system is selected. In classical mechanics one asks for invariance under canonical transformations, but eqn (21.51) is not invariant even under a simple coordinate transformation, for a formal proof see the problems.

The geometrical nature of the problem is most clearly seen in the example proposed by Einstein. Consider a motion in a plane, with coordinates and momenta x, y, p_x, p_y . For a generic potential the trajectory fills a region in the x, y plane. Then the problem arises: *when* is it possible to define a function $p(q)$? As was pointed out by Einstein, there can be two possible situations. Consider a small element $dq = dx dy$ in q -space, let p_k the values of momentum when the trajectory passes through this element: either the values p_k repeat themselves and only a finite number of them belong to dq or an infinite number of p_k appear. In the first case one can consider the values as different determinations of the same function defined on a multi-sheeted surface on q space, in the second case it is impossible to associate a definite value of p to a given element dq in a time independent way.

The geometrical object is the surface. It will be shown in the following that the surface is topologically a torus in the phase space of the system,

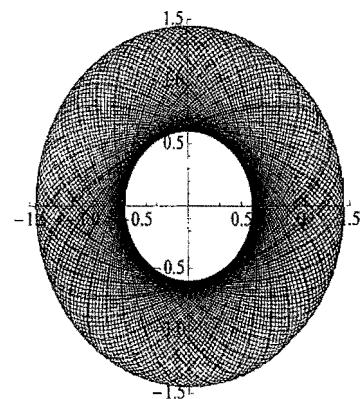


Fig. 21.7 Initial part of an orbit for a central potential. The orbit fills a two dimensional region.

quantization conditions are related to nontrivial topological paths on this torus.

The quantization procedure based on these geometrical ideas is known as *EBK quantization*. B is for Brillouin who shifted the attention from classical momentum to the phase of the wave function, and K stands for Keller, who rediscovered Einstein's procedure in the fifties and extended it to include the essential coefficients α_i in eqn (21.51).

As Einstein noticed the second possibility outlined above corresponds to some form of ergodic motions; this means that a semi-classical quantization procedure for ergodic or chaotic systems must be constructed on entirely different concepts.

21.5.2 Keller quantization

We present here a simplified version of Keller's procedure. It is well known that a solution of the Hamilton–Jacobi equation is formally given by the action integral

$$S(P) = S(P_0) + \int_{P_0}^P \sum_i p_i(\tau) \frac{dq^i}{d\tau} d\tau \quad (21.52)$$

The integral is taken along solutions of equations of motions. In the theory of partial differential equations this method is known as the *method of characteristics*. A given solution is of the form

$$q(\tau) = f(q_0, p_0, \tau).$$

Once the $n + 1$ parameters τ and p_0 are eliminated for the n final coordinates q and the energy E , the function S becomes, at fixed energy, a function of q_0 and q . It is useful to think of the solution as a system of rays (the trajectories) which start from q_0 . Another family of rays, more useful in analyzing wave fronts, is obtained by considering a narrow beam of trajectories originating from a small surface around q_0 .

If these families would cover all the q -region in a regular way, the solution would be regular, but it happens that in the general case these families have natural boundaries beyond which the solution do not exist. This is best understood by considering the equation for the amplitude A in eqn (21.50). Let us consider a small tube of trajectories originating near q_0 , see Figure 21.8. Integrating the equation for A on this tube and using the Gauss' theorem we have

$$A(q_0)^2 \Sigma(q_0) |v_0| = A(q)^2 \Sigma(q) |v(q)|,$$

Σ is the transverse dimension of the tube. The generators of this tube are trajectories, directed along \mathbf{v} , then the lateral flux of vector $A^2 \mathbf{v}$ is zero.

We see that $A(q)$ diverge if $\Sigma(q) = 0$ and/or $|v(q)| = 0$. At these points the flux tube shrinks lowering its transverse dimension and multiple rays concur to the same point, i.e. ∇S is multiple valued. $\Sigma(q) = 0$ define an $n - 1$ -dimensional surface in configuration space, a *caustic*.



Fig. 21.8 A thin tube of trajectories.

This geometrical picture imply that we have several local solutions of the Hamilton-Jacobi equation, A_r and S_r , each one limited by caustic surfaces.

Far from caustic surfaces we look for an asymptotic solution (as $\hbar \rightarrow 0$) of the form

$$\psi = \sum_r A_r \exp\left(\frac{i}{\hbar} S_r\right). \quad (21.53)$$

This form is suggested both by the one-dimensional case, in which the solution is a sum of two exponentials, and from the superposition principle, each term being a local solution of Schrödinger's equation. A *finite* number of determinations for A and ∇S means that these functions can be considered as different branches of the same function defined on a suitable covering space of the configuration space.

The definition of a global vector field $p = \nabla S$ allows a global definition of S , as given in eqn (21.52). On a simply connected space (21.52) in fact defines a function of point P : being p a gradient

$$\oint p dq = 0 \Rightarrow \int_{C_1, q_0}^q p dq = \int_{C_2, q_0}^q p dq \quad (21.54)$$

i.e. the definition is locally independent on the path. The covering surface in general is not simply connected, however; it will be shown in the next section that it has the topology of a torus. On a torus there are non-contractible paths which can be considered as the generators of the first homotopy group (or the fundamental group) of the surface. Let us call γ_i these paths. The integrals

$$\oint_{\gamma_i} p dq \quad (21.55)$$

are not zero, and their value is constant for continuous deformations of γ_i , as it follows from eqn (21.54). Clearly S cannot be a single-valued function, as for example we can add an arbitrary number of closed loops γ_i to a given path $q_0 \rightarrow q$. In classical mechanics this is not a problem as only ∇S has a dynamical significance. In quantum mechanics we need instead S , but only in the form of a phase factor. The request is that ψ is a single valued function, i.e. the phase of ψ along a closed trajectory can change only for a multiple of 2π . If the amplitudes are to be regular functions, this amounts to requiring, for each nontrivial path, the condition

$$\frac{1}{\hbar} \oint_{\gamma_i} p dq = 2\pi n.$$

This is the form of the quantization condition proposed by Einstein, before the formulation of quantum mechanics. A path γ necessarily crosses caustic surfaces, the regions where different sheets of the surface join together. There the amplitudes A_r are singular, and asymptotic approximation (21.53) breaks down. An additional phase shift can be produced by this singularities. Writing the terms in eqn (21.53) as

$$\exp\left[i\left(\frac{1}{\hbar}S - i\log(A)\right)\right]$$

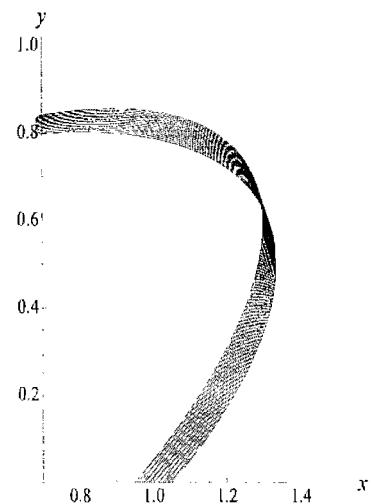


Fig. 21.9 A small pencil of trajectories forms a caustic. The potential is the same as in Figure 21.7, an anharmonic potential.

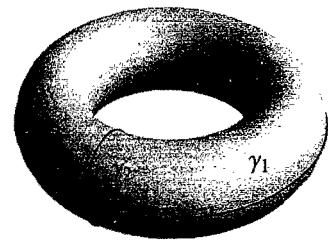


Fig. 21.10 Non-trivial paths on a torus.

it follows that the correct quantization condition is

$$\frac{1}{\hbar} \oint_{\gamma_i} p dq - i \Delta \log(A) = 2\pi n \quad (21.56)$$

where $-i \Delta \log(A)$ is the discontinuity induced by the singular behavior of A . This can be obtained by studying the exact form of the solution near the caustic. The most common case is a reflection point. Let us call x the coordinate perpendicular to caustic surface, $x = 0$ denoting the caustic. The probability density A^2 vanishes like x and $\log(A)$ has a discontinuity of $-i\pi/2$ at the origin. In this case eqn (21.56) takes the form

$$\frac{1}{\hbar} \oint_{\gamma_i} p dq = 2\pi \left(n + \frac{1}{4} \sum_k \alpha_k \right) \quad (21.57)$$

where $\alpha_k = 1$ and the sum runs over the number of caustics crossed by γ_i . In the one-dimensional case the caustics are the two turning points and eqn (21.57) reduces to the known formula

$$\frac{1}{\hbar} \oint p dq = 2\pi \left(n + \frac{1}{2} \right).$$

A more refined deduction uses Airy functions. $x = 0$ is a turning point in x coordinate and we know from the one-dimensional connection formulas that for $x \sim 0$

$$\exp[-|w|] \rightarrow 2 \cos(w - \frac{\pi}{4}) = \exp\left(i w - \frac{\pi}{4}\right) + \exp\left(-i w + \frac{\pi}{4}\right)$$

showing that between the two branches of the exponential there is a phase shift of $\pi/2$, as stated above.

The formula (21.57) is general and covers also different cases.

- If A is not singular, as it happens for purely rotational motions, clearly $\alpha = 0$.
- For boundary with Dirichlet b.c. $\psi = 0$, the wave function vanishes like x , then $\log A \sim \log x$ and the discontinuity is $-i\pi$, i.e. $\alpha = 2$. This is the case for a radial coordinate in S -states, where the quantization condition reads

$$\frac{1}{\hbar} \oint p dq = 2\pi \left(n + \frac{3}{4} \right)$$

corresponding to a usual turning point and to a boundary at $r = 0$.

- For Neumann boundary conditions, with $\psi' = 0$, the function vanishes like x^2 then the discontinuity will be $-2\pi i$ and this shifts simply of one unit of n , i.e. has no effect. This case is interesting for the study of eigenvalues in wave equations for acoustics or electromagnetism.

The general condition (21.57) is due to Keller [Keller (1958)].

21.5.3 Integrable systems

In this section we will define more precisely systems that can be studied with the EBK quantization. We start with some definitions of classical mechanics. The reader can find a complete discussion of the ideas briefly illustrated below in books on analytical mechanics, as [Arnold (1997)].

Let us consider a Hamiltonian system with n degrees of freedom. q_i, p_i , $i = 1, \dots, n$ are coordinates and canonical momenta. A point in the *phase space* of the system is defined by the $2n$ coordinates (q, p) .

Integrals of motion

An integral of motion is a function defined in the phase space, $F(q, p)$, which is conserved under the Hamiltonian evolution

$$0 = \frac{dF}{dt} = \frac{\partial F}{\partial q_i} \dot{q}_i + \frac{\partial F}{\partial p_i} \dot{p}_i = \frac{\partial F}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial F}{\partial p_i} \frac{\partial H}{\partial q_i} \equiv \{F, H\}. \quad (21.58)$$

$\{A, B\}$ is the Poisson bracket of quantities A, B . It is easily shown, see Problem 16 in Chapter 11, there exist at most n independent integrals of motion for a system with n degrees of freedom.

The following theorem (Liouville–Arnold) characterizes an integrable Hamiltonian system.

Theorem 21.4. (Liouville–Arnold) *Let $H(q, p)$ be a Hamiltonian with n degrees of freedom. Let us suppose that:*

- (1) *The system has n integrals of motion F_i independent and in involution, i.e. with*

$$\{F_i, F_j\} = 0$$

- (2) *The surfaces $F_i(\mathbf{p}, \mathbf{q}) = I_i$ are compact manifolds without edges.*

Then

It is possible to associate to each integral F_i an angle action φ such that:

- (a) *Variables (I_i, φ_i) are canonical and are related to the variables (p, q) by a canonical transformation.*
- (b) *The manifold defined by the constraints $F_i = I_i$ is diffeomorphic to a torus.*

Remarks

- The condition $\{F_i, F_j\} = 0$ is the classical analogue of commuting observables.
- All separable systems are integrable, but there are integrable systems which are not separable. The first example has been given in the sixties (Toda lattice).
- The n constraints $F_i = I_i$ can be inverted and define locally a vector field $p = p(q, I)$. It is easily shown (see Problems in Chapter

11) that the involution conditions ensures that this vector field is locally integrable, i.e. there exists S such that $\nabla S = p$, or (locally)

$$\oint p \, dq = 0.$$

- It is often convenient to use different variables as canonical momenta, i.e. F_i are expressed through some parameters, which will be called always I_i in the following, see below.

Action variables and the homotopy group

A torus has a nontrivial first homotopy group, its generators being closed curves which wrap around the surface, see Figure 21.10. Each torus can be characterized by the values taken by the integrals

$$\oint_{\gamma_i} p \, dq = I_i \quad (21.59)$$

These are the variables to be used in the following, i.e. we make the change of variables $F_i \rightarrow I_i$.

21.5.4 Examples

- (1) The simplest example is a one-dimensional system. In this case there is only one constant of motion, the energy, and

$$E \equiv F_1 = \frac{p^2}{2m} + V(x).$$

If a, b are classical inversion points

$$I_1 = \frac{1}{2\pi} \oint p(x) \, dx = \frac{1}{\pi} \int_a^b \sqrt{2m(E - V)} \, dx. \quad (21.60)$$

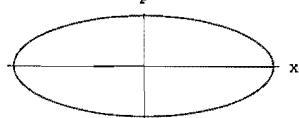


Fig. 21.11 One-dimensional torus.

The motion lies on the one-dimensional torus $E = \text{const}$, inverting eqn (21.60) we can express E in terms of I . This surface is a two sheets covering of q -region of motion, the interval $[a, b]$. On each sheet we have a determination of momentum $p(x)$:

$$p(x) = \pm \sqrt{2m(E - V(x))}.$$

- (2) As a second example consider a motion in a two-dimensional central potential $V(r)$. There are two integrals of motion, the energy and the angular momentum perpendicular to the plane, p_φ , the conjugate variable to the azimuthal angle φ . We have

$$E = \frac{p_r^2}{2m} + \frac{p_\varphi^2}{2mr^2} + V(r).$$

p_r can be obtained from this equation. The motion is oscillatory for r , the inversion points being $r = a, b$ where p_r vanishes, while φ

describes a pure rotation (it has no inversion points). The action variables are

$$I_\varphi = \frac{1}{2\pi} \oint p_\varphi d\varphi = p_\varphi; \quad I_r = \frac{1}{2\pi} \oint p_r dr.$$

From the second relation we can express E in terms of I_r , i.e. both integrals are expressed through the two variables I_r, I_φ . The trajectories fill a two-dimensional region, while in the phase space it wraps around a torus fixed by the values of p_φ and E , as schematically shown in Figure 21.12.

21.5.5 Caustics

In an integrable system the orbit $(q(t), p(t))$ evolves on the invariant torus T fixed by the constants I_i . The trajectory is obtained by projecting this orbit on configuration space, q . The surface T is a regular surface but its projection is singular at points where $\det(\partial p / \partial q) = \infty$, these points form the *caustics* of the projection. To have a geometrical picture of the singularity let us consider p as local coordinates of the surface. The infinitesimal tangent vectors dq span the tangent space, at caustic's points $\det(\partial q / \partial p) = 0$ and these vectors fail to be independent. The reader can verify that at the inversion points of the above examples in effect $\partial p / \partial q = \infty$.

The name caustic comes from optics and reflects a geometrical property of these surfaces. Consider a pencil of rays, i.e. at fixed energy a family of trajectories depending on $n - 1$ parameters. It is easy to show, as illustrated in some of the problems below, that the family has an envelope on caustics. This is a general phenomenon in Hamiltonian dynamics, the simplest example being the caustic formed by trajectories in a uniform gravitational field. Here the parameter is the angle between the starting velocity and the ground plane, see Figure 21.13.

In optics rays play the same role of the particle orbits, on caustics the *intensity* of light grows, becoming formally infinite in geometric optics.

21.5.6 The KAM theorem and quantization

A clue for the semi-classical quantization of *non-integrable systems* comes from KAM theorem, KAM standing for Kolmogorov, Arnold, and Moser.

In general a perturbation applied on a integrable system destroys the invariant tori. The first crucial result in this direction is due to Poincaré who showed that for a perturbed system $H = H_0 + g H_I$ in general there are not analytical integral of motions, apart energy, angular momentum and momentum. Geometrically this imply that it is not possible to define families of tori parametrized with λ , i.e. classical perturbation theory is not convergent. The crucial result obtained in KAM theorem is that *not all* tori are destroyed by perturbation, for small enough λ there is a set of positive measure in the phase space filled with tori. This allows, in principle, a definition of quantization condition via this procedure,

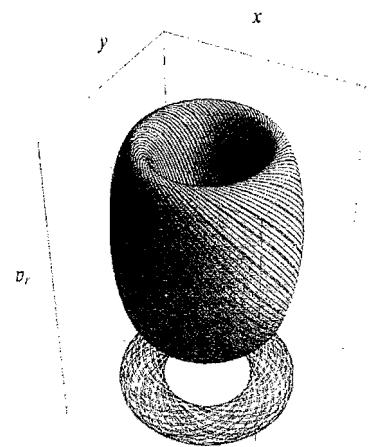


Fig. 21.12 Motion in a two-dimensional central potential. The motion in phase space is shown together with its projection on the x, y plane, the trajectory.

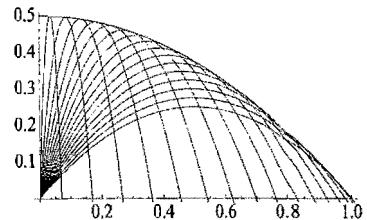


Fig. 21.13 Caustic in a uniform gravitational field.

one has to look for tori on which eqn (21.57) are valid. In this search caustics can be used as a guiding principle. If the motion is chaotic the orbits fill a whole region of the phase space, while in presence of tori they fill an n -dimensional surface, for n degrees of freedom. The projection of these tori appear geometrically as caustics surfaces (or curves) and these curves can be used as cycles in eqn (21.57). For example consider a potential

$$V(x, y) = \frac{1}{2}(\omega_1 x^2 + \omega_2 y^2) + \lambda x(x^2 + \eta y^2).$$

This potential can have metastable states in quantum mechanics and bounded orbits in classical mechanics. For high enough energy the motion is chaotic but for small energy, there exist invariant tori, i.e. orbits fill a two-dimensional surface in phase space. The projection of this surface on (x, p_x) plane or (y, p_y) plane is a curve (Poincaré section). On these closed curves one can compute action integrals. Varying the orbit one can impose the constraints (21.57) and measure the energy, this gives the semi-classical approximation of the full quantum mechanics computation. Some simple examples of the procedure are given in the notebooks.

For a more in-depth analysis of the subject we refer to the literature, for instance, the lectures of Berry [Berry (1983)] or the book by Gutzwiller [Gutzwiller (1990)].

Supplements for Part III

22

22.1 The K^0 - $\overline{K^0}$ system and CP violation

A system of great interest in which the ideas of the mass matrix and decay processes can be studied in detail and which reveals an important fact about the symmetries in Nature, is the K^0 - $\overline{K^0}$ system. This system, and its analogues built with heavier quarks, in fact, are the only instances where a violation of time reversal symmetry (or CP symmetry) has ever been experimentally observed, at the level of fundamental interactions.

The neutral K -mesons, or simply kaons, K^0 and $\overline{K^0}$, are two spin 0 bosons. Their quark content is $\bar{s}d$ and $\bar{d}s$, respectively, where s, d denote the strange and down quarks. To describe the system we recall that at low energies there are three distinct interactions, the strong interactions (nuclear forces) with Hamiltonian H_s , the electromagnetic interactions H_γ and the weak interaction Hamiltonian H_w . The states $|K^0\rangle$ and $|\overline{K^0}\rangle$ are eigenstates of $H_s + H_\gamma$.

The distinction between different terms in the Hamiltonian is related mostly to their behavior under the three fundamental symmetry operations: parity, P , charge conjugation C and time reversal T . Charge conjugation is defined as the operation which exchanges a particle with its anti-particle (see Section 17.2).

The Hamiltonians H_s and H_γ are invariant under all these symmetry operations. Besides these, we shall need another quantum number, the *hypercharge*. In what follows we shall use a related quantity, the *strangeness*, S . The strangeness is carried by the (anti-) “strange quark” \bar{s} , so $S = 1$ for K^0 while $\overline{K^0}$ carries $S = -1$. “Usual” particles made with only u,d quarks like protons and neutrons have no “strangeness”: $S = 0$. A large amount of experimental data confirm that S is rigorously conserved in strong interactions. For example a K^0 is produced in a reaction

$$\pi^- + p \rightarrow K^0 + \Lambda^0. \quad (22.1)$$

Λ^0 is a spin- $\frac{1}{2}$ baryon with $S = -1$. The $\overline{K^0}$ meson is never produced in the reaction (22.1).

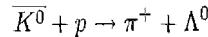
After their production K mesons decay, mainly in two or three π mesons. The very existence of the decay violating the strangeness S suggests that the process is not a strong interaction process (H_s), but is due to the weak interactions, H_w .

The decay of K mesons into pions is a clear example of *parity violating* process. In a two-pion decay, the final particles are in S -wave, as π and K are both spinless. The intrinsic parity of π is negative (and in any case

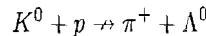
22.1 The K^0 - $\overline{K^0}$ system and CP violation	657
22.2 Level density	661
22.3 Thomas precession	674
22.4 Relativistic corrections in an external field	676
22.5 The Hamiltonian for interacting charged particles	678
22.6 Quantization of electromagnetic fields	687
22.7 Atoms	692
22.8 H_2^+	726
22.9 The Gross-Pitaevski equation	729
22.10 The semi-classical scattering amplitude	731

it is the same for both particles) so the final state has parity +1. The three-pion states have instead negative parity. The fact that the neutral K 's decay both to two and three pions shows that parity is violated. As far as the production process due to H_s is concerned we can assign consistently parity -1 to K 's, with the convention that Λ has parity +1. With parity defined in this standard way, it can be said that parity is grossly violated by $K \rightarrow 2\pi$ days. (See more about this below.)

Actually, there are further subtleties. Let us look again at eqn (22.1). It can be shown that this equation can be read as a chemical reaction; particles can be moved around from one side to the other of the reaction formula, by changing particles with anti-particles. In particular, strangeness conservation implies that the reaction



is allowed, whereas the process



is forbidden.

Now let us consider a K produced inside some materials with the reaction (22.1). This meson can interact again but cannot produce Λ^0 's because of strangeness conservation. But in actual experiments Λ^0 's are produced! The solution of this puzzle (due to Gell-Mann and Pais) is a beautiful application of what we have learned about simple two-level quantum mechanical systems. With respect to the Hamiltonians $H_0 = H_s + H_\gamma$ the two particles $K^0, \overline{K^0}$ are exactly degenerate. We know that in such a situation even an infinitesimal off-diagonal matrix element (perturbation) suffices to produce a complete mixing, just as in the lowest nearly degenerate levels of a deep double well. If such off-diagonal matrix elements are present—and we do know that the weak interaction Hamiltonian H_w in fact contains strangeness changing terms—the eigenstates of the total Hamiltonian would be

$$|K_S\rangle = \frac{|K^0\rangle + |\overline{K^0}\rangle}{\sqrt{2}} ; \quad |K_L\rangle = \frac{|K^0\rangle - |\overline{K^0}\rangle}{\sqrt{2}} . \quad (22.2)$$

This would solve the puzzle as $|K^0\rangle$ produced in a strong interaction process oscillates and can convert to a $|\overline{K^0}\rangle$ state¹ which can then produce Λ^0 .

We know that parity is violated by the weak interactions [Lee and Yang (1956)]. Stated in modern terms, parity is violated because only the left-handed quarks and leptons (see Subsection 17.2.1) are coupled to the W bosons while the right-handed quarks and leptons are not (see Table 24.7). Charge conjugation is also broken by the weak interactions, as C is defined as the symmetry under the exchange of e.g., a left-handed quark with the anti-right-handed quark. As it turned out, the combined symmetry CP is an approximate symmetry of Nature, but not an exact one.

¹In fact it is such an oscillation-regeneration mechanism which allows an experimental determination of an extremely tiny mass difference of K_L and K_S , see below eqn (22.3).

If CP were an exact symmetry, we could classify states with its eigenvalues. We could *define* the anti-particles as $|\bar{K}^0\rangle = CP|K^0\rangle$ and with this choice of phases K_S and K_L would be CP eigenstates with eigenvalues ± 1 . Conservation of CP implies that the same must be true for their decay products. It is easy to see that 2π states in an S-wave have $CP = +1$ while 3π states have $CP = -1$. This means that the only open channels for decays would be

$$K_S \rightarrow 2\pi; \quad K_L \rightarrow 3\pi.$$

The second process occurs just above the threshold; the available phase space being quite small the decay probability is indeed small (i.e. the mean lifetime longer). We expect to observe considerably different mean lives for the two neutral kaons, decaying into the 2π and 3π channel, respectively. This is indeed what is observed:

$$\tau_{K_S} = 0.8923 \times 10^{-10} \text{ s}; \quad \tau_{K_L} = 5.183 \times 10^{-8} \text{ s}.$$

The difference in the mean lifetime explains the suffixes used: S and L are for “short” and “long”.

If the mixing mechanism is correct the Hamiltonian eigenvalues must also be shifted slightly, i.e. the degeneracy removed. Indeed experimentally a tiny mass difference has been observed:²

$$m_{K_L} - m_{K_S} = (3.483 \pm 0.010) \times 10^{-12} \text{ MeV/c}^2; \quad \frac{\Delta m}{m} \sim 10^{-14}. \quad (22.3)$$

As it turns out, both K_S and K_L decay into two-pion and three-pion final states, showing that CP is violated [Christensen, et. al. (1964)]. For example, K_S decays dominantly (with probability of 99.89%) into two-pion final states ($\pi^+\pi^-$, $\pi^0\pi^0$) but decays also into three pions (with the branching ratio of $3.5 \cdot 10^{-7}$). K_L decays dominantly into three pions (with branching ratio of ~ 0.33) but it goes also into two-pion final states, with a branching ratio of about $2 \cdot 10^{-3}$. (We ignore here the semi-leptonic decays.)

These experimental results show that CP is a very good approximate symmetry, the states $|K_S\rangle$ and $|K_L\rangle$ being approximately given by eqn (22.2), but not quite exactly so.

To give a general discussion (see eqn (13.63)): the common intermediate states for both $|K^0\rangle$ and $|\bar{K}^0\rangle$ are precisely the two pion and three pion states) we can choose our phases in such a way that $|\bar{K}^0\rangle = CPT|K^0\rangle$. The mass matrix takes the form

$$\begin{aligned} M_{11} &= m_{K^0} + \langle K^0 | H_w | K^0 \rangle + \mathcal{P} \sum_s \langle K^0 | H_w | s \rangle \frac{1}{m_{K^0} - E_s} \langle s | H_w | K^0 \rangle \\ M_{22} &= m_{K^0} + \langle \bar{K}^0 | H_w | \bar{K}^0 \rangle + \mathcal{P} \sum_s \langle \bar{K}^0 | H_w | s \rangle \frac{1}{m_{K^0} - E_s} \langle s | H_w | \bar{K}^0 \rangle \\ M_{21} &= \mathcal{P} \sum_s \langle \bar{K}^0 | H_w | s \rangle \frac{1}{m_{K^0} - E_s} \langle s | H_w | K^0 \rangle \end{aligned}$$

²The mass difference (22.3) is very small, even by weak interaction standards and calls for an explanation. The fact is that the usual strangeness-changing weak interaction processes satisfy the selection rule $\Delta S = \pm 1$. Indeed, the weak Hamiltonian, now known to be part of the Glashow–Weinberg–Salam electroweak Hamiltonian, contains terms with $\Delta S = 0$ and $\Delta S = \pm 1$, but not $\Delta S = \pm 2$. An effective matrix element which mix K^0 and \bar{K}^0 has $\Delta S = 2$, i.e., it is therefore a second-order effect in H_w .

$$\begin{aligned}\Gamma_{11} &= 2\pi \sum_s \langle K^0 | H_w | s \rangle \langle s | H_w | K^0 \rangle \delta(m_{K^0} - E_s) \\ \Gamma_{22} &= 2\pi \sum_s \langle \bar{K}^0 | H_w | s \rangle \langle s | H_w | \bar{K}^0 \rangle \delta(m_{K^0} - E_s) \\ \Gamma_{21} &= 2\pi \sum_s \langle \bar{K}^0 | H_w | s \rangle \langle s | H_w | K^0 \rangle \delta(m_{K^0} - E_s)\end{aligned}$$

Physical states are obtained by diagonalizing these, or what is the same thing, by diagonalization of $\Gamma/2 + iM$. Following Lee and Wu [Lee and Yang (1966)], we use the parametrization

$$\frac{\Gamma}{2} + iM = D + i\mathbf{E} \cdot \boldsymbol{\sigma} \quad (22.4)$$

where $D, \mathbf{E} = (E_1, E_2, E_3)$ are complex numbers. In polar coordinates

$$E = \sqrt{E_1^2 + E_2^2 + E_3^2};$$

$$E_3 = E \cos \theta; \quad E_1 = E \sin \theta \cos \phi; \quad E_2 = E \sin \theta \sin \phi.$$

The matrix is diagonalized by a rotation. In the basis K^0, \bar{K}^0 the eigenstates are:

$$\begin{aligned}K_S &= \frac{1}{\sqrt{2(1+|\varepsilon_1|^2)}} \begin{pmatrix} 1+\varepsilon_1 \\ 1-\varepsilon_1 \end{pmatrix}, \\ K_L &= \frac{1}{\sqrt{2(1+|\varepsilon_2|^2)}} \begin{pmatrix} 1+\varepsilon_2 \\ -(1-\varepsilon_2) \end{pmatrix},\end{aligned} \quad (22.5)$$

with

$$\frac{1-\varepsilon_1}{1+\varepsilon_1} = \tan \frac{\theta}{2} e^{i\phi}, \quad \frac{1-\varepsilon_2}{1+\varepsilon_2} = \cot \frac{\theta}{2} e^{i\phi}. \quad (22.6)$$

$\varepsilon_1, \varepsilon_2$ measure CP violation.

The eigenvalues $D \pm E$ are easily found using the trace and the determinant of the matrix:

$$\begin{aligned}D &= \frac{1}{4}(\gamma_S + \gamma_L) + \frac{i}{2}(m_S + m_L); \\ iE &= \frac{1}{4}(\gamma_S - \gamma_L) + \frac{i}{2}(m_S - m_L).\end{aligned} \quad (22.7)$$

³This is known as the CPT theorem.

Equation (22.5) is the most general expression for mixing and in principle all parameters can be measured, and have been measured.

Let us call $\Theta = CPT$ the product of all the three discrete transformations. A very general argument shows that in a *local*, relativistic invariant quantum field theory with the standard commutation (for bosons) or anti-commutation relations (for fermions), *CPT* is a symmetry.³ That is, $\Theta^{-1}H_w\Theta = H_w$. This implies, remembering our definition of the transformation Θ on our base, that

$$\Gamma_{11} = \Gamma_{22}; \quad M_{11} = M_{22}. \quad (22.8)$$

To check these equalities it should be remembered that Θ is an *anti-linear* transformation, due to the time-reversal operation. Thus if H_w commutes with Θ , one has for instance

$$\begin{aligned}\Gamma_{11} &= 2\pi \sum_s \langle K^0 | \Theta^\dagger H_w \Theta | s \rangle \langle s | \Theta^\dagger H_w \Theta | K^0 \rangle \delta(m_{K^0} - E_s) = \\ &= 2\pi \sum_s \langle \Theta s | H_w | \bar{K}^0 \rangle \langle \bar{K}^0 | H_w | \Theta s \rangle \delta(m_{K^0} - E_s) = \Gamma_{22}.\end{aligned}$$

It is easy to see that Θ invariance does not give constraints on off-diagonal terms.

Equation (22.8) implies $E_3 = 0$, i.e. $\theta = \pi/2$: in this case from eqn (22.6) it follows that $\varepsilon_1 = \varepsilon_2$.⁴ We see that a measurement of the difference $\varepsilon_1 - \varepsilon_2$ tests one of the deepest aspects of the modern quantum theory: the locality.

CP violation in the B -meson systems

More recently, CP violation has been confirmed (experiments Babar (2002) and Belle (2002)) also in processes involving the so-called B mesons. Just as the K mesons are composites made of s (strange) and d or u quarks (or anti-quarks), the B mesons are made of the bottom (or “beauty”) quarks (b), of mass about 5 GeV, bound together with one of the lighter quarks, u, d, s . Unlike the case of the measurement of CP violation in the kaon systems, the measurement of CP violating parameters in the B meson systems is part of the precision test of the standard model, and in particular, of the Glashow–Weinberg–Salam theory.

⁴ Assuming CPT, the present experimental estimate $\varepsilon_1 = \varepsilon_2 = \varepsilon$ gives

$$\varepsilon \simeq (2.232 \pm 0.007) \times 10^{-3}.$$

More detailed experimental result on the direct CP violation parameters in kaon systems have been obtained more recently (2000) in NA48 (CERN) and KTeV (Fermilab) experiments. Today’s experimental limit on the tests of CPT, (22.8), is $O(10^{-18})$ GeV for $|M_{11} - M_{22}|$, and $|\Gamma_{11} - \Gamma_{22}|$. See Particle Data Group Listings [Yao, et. al. (2006)].

22.2 Level density

One of the most important quantities associated with a Hamiltonian problem is the *level density*, or spectral density. To fix the idea let us consider a Hamiltonian with a discrete spectrum and with $E_n \geq 0$. The number of levels with energy less than E will be a step function which increases by d_n , the degeneracy of the level, when E crosses E_n :

$$N(E) = \sum_n \theta(E - E_n) \equiv \sum_{s \in \text{levels}} d_s \theta(E - E_s).$$

From now on all the sums will be on states, a given factor $\theta(E - E_s)$ will appear d_s times in the sums. The level density is defined as the number of levels per unit energy interval:

$$g(E) \equiv \frac{dN(E)}{dE} = \sum_n \delta(E - E_n).$$

This quantity is directly related to the resolvent of the Hamiltonian. Let us remember that

$$G(E) = \sum_{s \in \text{lev.}} \frac{P_s}{E + i\varepsilon - E_s},$$

and its imaginary part is given by

$$\text{Im } G(E) = -\pi \sum_{s \in \text{lev.}} P_s \delta(E - E_s); \quad (22.9)$$

P_s being the projector on the subspace with energy E_s . Taking the trace in eqn (22.9)

$$g(E) = -\frac{1}{\pi} \text{Im Tr}[G(E)] \equiv \frac{1}{\pi} \text{Im } T(E); \quad T(E) \equiv -\text{Tr}[G(E)]. \quad (22.10)$$

Knowledge of $g(E)$ gives the spectrum of H . The importance of eqn (22.10) lies in the fact that links an approximate knowledge of the propagator $G(E)$ to an estimate of $g(E)$. Let us consider for example the harmonic oscillator in one and two dimensions. We have respectively

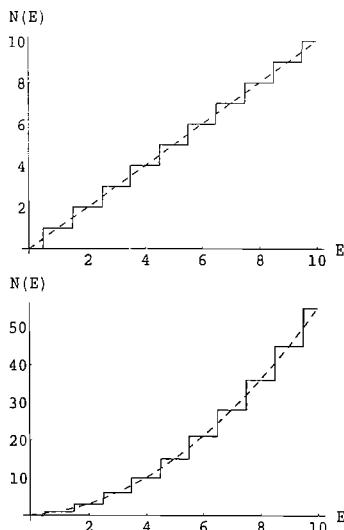


Fig. 22.1 The number of states as a function of E for the one-dimensional and the isotropic two-dimensional harmonic oscillators.

d_k is the degeneracy of the level. A plot of the two functions is shown in Figure 22.1. We can regard $N(E)$ as a smooth curve with a superimposed oscillation. The analogy with a temporal signal $f(t)$ can help. A spectral (Fourier) decomposition of $f(t)$ allows us to distinguish a regular, smooth, part described by low frequency harmonics and a possible discontinuous part related to high frequencies. The smooth part is obtained by filtering high frequency modes, i.e. by averaging on temporal intervals large as compared with the characteristic times of “fast” variations. Here the same analysis can be applied: a smoothing on intervals ΔE will give a coarse description of the spectrum, which can be refined by changing ΔE . We will have a mean spectral density which describe the main features of the spectrum and an oscillating part which describe the details.

The average value of $g(E)$ will be a better approximation as the relative discontinuities $\Delta N/N$ decrease. In usual systems this is the typical regime for high energy. For instance, for a non-degenerate system $\Delta N = 1$ while N grows with energy. We expect that the average description is accurate at high energies. These observations can be translated into properties of the Green function, in the energy or time domain. From eqns (13.7) and (13.10)

$$\mathcal{G}(t) = \frac{i}{2\pi} \int dE e^{-iEt/\hbar} G(E); \quad G(E) = \frac{1}{i} \int_0^\infty \frac{dt}{\hbar} e^{iEt/\hbar} \mathcal{G}(t). \quad (22.11)$$

For large E the oscillating exponential enhances the contribution at small times. The average and high-energy behavior of $g(E)$ is thus related to the short-time behavior of $\mathcal{G}(t)$.

One can be more precise by writing the trace of the propagator $T(E)$

in the form

$$\begin{aligned} T(E) &= \sum_n \frac{1}{E_n - E} = \sum_n \int_0^\infty d\beta e^{-\beta(E_n - E)} \\ &= \text{Tr} \int_0^\infty d\beta e^{\beta E} e^{-\beta H}. \end{aligned} \quad (22.12)$$

$T(E)$ has no poles in $\text{Re}(E) < 0$ (in our conventions $E_n > 0$). As has been seen in the main text it has a positive imaginary part for $E > 0$. As $E \rightarrow -\infty$ eqn (22.12) defines a regular function which, as is clear from the integral representation, has its main contribution in the region $\beta \rightarrow 0$. The imaginary part of the analytic continuation of this function to positive energy is the average density we are looking for.

To write $g(E)$ one can first compute $T(E)$ and then take its imaginary part, or one can work directly with eqn (22.12). The imaginary part of T for $E > 0$ can be computed by

$$T(E + i\varepsilon) - T(E - i\varepsilon) = 2i \text{Im}T,$$

then

$$2\pi i g(E) = \int_0^\infty d\beta \left(\sum_n e^{-E_n \beta} \right) [e^{\beta(E+i\varepsilon)} - e^{\beta(E-i\varepsilon)}].$$

One cannot take the limit $\varepsilon \rightarrow 0$ as the sum over n diverges; but one notes that

$$(E + i\varepsilon)\beta \rightarrow \beta E + i\varepsilon \rightarrow (\beta + i\varepsilon)E.$$

With this observation the first integral is computed on the upper part of the real positive line in the β complex plane, while the second is computed on the lower side of the same axes. The two paths merge at $\beta = 0$. One can now deform our integration path and transform it on a straight line along the imaginary axis in β and write

$$g(E) = \frac{1}{2\pi i} \int_{\varepsilon-i\infty}^{\varepsilon+i\infty} d\beta e^{\beta E} \left(\sum_n e^{-E_n \beta} \right). \quad (22.13)$$

The spectral density is written thus as a *Laplace transform*.

Let us remember a few facts about the Laplace transforms. Given a function $f(E)$, with $f(E) = 0$ for $E < 0$, its Laplace transform is defined by

$$F(\beta) = \mathcal{L}_\beta[f(E)] = \int_0^\infty dE e^{-\beta E} f(E). \quad (22.14)$$

The *inverse Laplace transform* is

$$f(E) = \mathcal{L}_E^{-1}[F(\beta)] = \frac{1}{2\pi i} \int_{\varepsilon-i\infty}^{\varepsilon+i\infty} d\beta e^{\beta E} F(\beta).$$

The Laplace transform of $g(E)$ is

$$\begin{aligned} Z(\beta) &= \int_0^\infty dE e^{-\beta E} \sum_n \delta(E - E_n) = \sum_n e^{-\beta E_n}; \\ g(E) &= \mathcal{L}_E^{-1}[Z(\beta)]; \quad E > 0. \end{aligned}$$

We have shown that the Laplace transform of $g(E)$ is the statistical *partition function* of our system.

In statistical mechanics the partition function for a system with Hamiltonian H is defined by

$$Z(\beta) = \text{Tr} [e^{-\beta H}] ; \quad \beta = 1/kT . \quad (22.15)$$

From eqn (22.12) we see that the trace of the propagator is directly connected to $Z(\beta)$

$$\mathcal{T}(E) = \int_0^\infty d\beta e^{\beta E} Z(\beta) .$$

This integral representation converge for $\text{Re}(E) < 0$. By changing variables in eqn (22.11)

$$\beta = i \frac{t}{\hbar} ; \quad t = -i\hbar\beta ; \quad (22.16)$$

we have, for $E < 0$:

$$\mathcal{T}(E) = \int_0^\infty d\beta e^{\beta E} \text{Tr} [\mathcal{G}(-i\hbar\beta)] \Rightarrow Z(\beta) = \text{Tr} [\mathcal{G}(-i\hbar\beta)] .$$

This is a very important point which has far reaching consequences in quantum theory: *the partition function is the trace of the propagator at imaginary times*.

Let us summarize, in the two different languages of quantum mechanics and statistical mechanics, the picture of asymptotic and average behavior that can be inferred from the above formulas. Consider for example a particle moving in an external potential.

- For small times it is expected that a particle behaves as a free particle, independently of external potentials, then we expect that the leading term as $\beta \rightarrow 0$ (high temperature) of the partition function is universal.
- The leading term in β must reflect the singularity of the free propagator at small times, $\exp(i(x-x')^2/t)$.
- From the relation between statistical mechanics and quantum trace the limiting form of the partition function must be the partition function for a free particle.
- The corrections to this behavior can be computed in statistical mechanics by the high temperature expansion (Wigner–Kirkwood), these corrections must correspond to quantum corrections to the free propagator.
- For a particle in an external potential high energies (small times) correspond to high quantum numbers. In this region the *semi-classical* approximation is accurate. Both the leading behavior as $t \rightarrow 0$ and the quantum corrections to the free propagator must be related to the WKB expansion.

In the following we shall verify these expectations.

22.2.1 The free particle

We consider a free particle confined in a large but finite box of volume V . The divergences hidden in $g(E)$ are easily computed in the Schrödinger picture. The matrix elements of the propagator are

$$\langle \mathbf{x}|G(E)|\mathbf{y}\rangle = \sum_{\alpha} \frac{\psi_{\alpha}(\mathbf{x})\psi_{\alpha}^*(\mathbf{y})}{E + i\varepsilon - E_{\alpha}}; \quad g(E) = -\frac{1}{\pi} \text{Im Tr} G(E).$$

Taking the trace means putting $\mathbf{x} = \mathbf{y}$ and integrate. In the infinite volume limit the eigenfunctions of H are the complete set of momentum eigenvalues $\exp(i\mathbf{p}\mathbf{x}/\hbar)$, here we take the same form in a finite volume. The trace on the quantum numbers \mathbf{p} gives g :

$$g_0(E) = -\frac{1}{\pi} \text{Im} \int \frac{d^d\mathbf{p}}{(2\pi\hbar)^d} \frac{1}{E + i\varepsilon - \frac{\mathbf{p}^2}{2m}} \langle \mathbf{p}|\mathbf{p}\rangle = \int \frac{d^d\mathbf{p}}{(2\pi\hbar)^d} \langle \mathbf{p}|\mathbf{p}\rangle \delta\left(E - \frac{\mathbf{p}^2}{2m}\right).$$

In a finite volume regularization

$$\langle \mathbf{p}|\mathbf{p}\rangle = \int d^d\mathbf{x} e^{-i\mathbf{p}\mathbf{x}/\hbar} e^{+i\mathbf{p}\mathbf{x}/\hbar} = \mathcal{V}_d; \quad g_0(E) = \mathcal{V}_d \int \frac{d^d\mathbf{p}}{(2\pi\hbar)^D} \delta\left(E - \frac{\mathbf{p}^2}{2m}\right)$$

where \mathcal{V}_D is the D -dimensional volume. The integral can be easily performed in radial coordinates

$$g_0(E) = \begin{cases} \frac{\sqrt{m}}{\hbar} \frac{1}{\pi} \frac{\mathcal{V}_1}{\sqrt{2E}} & D = 1 \\ \frac{m}{\hbar^2} \frac{\mathcal{V}_2}{2\pi} & D = 2 \\ \frac{m^{3/2}}{\hbar^3} \frac{\mathcal{V}_3 \sqrt{E}}{\sqrt{2} \pi^2} & D = 3 \end{cases}. \quad (22.17)$$

The same result will be found in different ways below. The number $N_0(E)$ of states up to energy E is the integral of g , then

$$N_0(E) = \mathcal{V}_D \int \frac{d^d\mathbf{p}}{(2\pi\hbar)^d} \theta\left(E - \frac{\mathbf{p}^2}{2m}\right). \quad (22.18)$$

We recognize in eqn (22.18) the well known result that the number of states is given by the number of cells of volume $(\hbar/2\pi)^D$ in the allowed classical phase space.

Weyl expansion

Formulas (22.17) are the large E limit of a general result due to Weyl. The problem is the computation of the asymptotic behavior of the eigenvalues of the Laplacian operator in a finite volume, i.e. a free particle in a finite volume

$$\nabla^2\psi + k^2\psi = 0; \quad k^2 = 2mE/\hbar^2.$$

The Weyl formula which we quote here is for $D = 2, 3$ (in our notations)

$$g_2(E) = \frac{1}{4\pi} \left(\frac{2m}{\hbar^2} \right) \mathcal{A} - \frac{1}{8\pi} \left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{1}{\sqrt{E}} \mathcal{L} + \dots \quad (22.19a)$$

$$\begin{aligned} g_3(E) &= \frac{\mathcal{V}}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E} - \frac{\mathcal{S}}{16\pi} \left(\frac{2m}{\hbar^2} \right) \\ &\quad + \frac{\mathcal{C}}{12\pi^2} \left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{1}{\sqrt{E}} + \dots \end{aligned} \quad (22.19b)$$

Where \mathcal{A} , \mathcal{L} are the area and the perimeter in $D = 2$, \mathcal{V} is the volume in $D = 3$, \mathcal{S} the boundary of \mathcal{V} and \mathcal{C} is defined through the principal curvature radii of \mathcal{S} :

$$\mathcal{C} = \oint_S d\sigma \frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right).$$

The term proportional to \mathcal{C} changes if there are discontinuities in \mathcal{S} . The leading term in eqn (22.19a) is identical to (22.17).

22.2.2 $g(E)$ and the partition function

Let us now consider a particle subjected to an external potential V :

$$H = \frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r}).$$

In this paragraph it is important to distinguish the operator $\hat{\mathbf{p}}$ from its eigenvalues \mathbf{p} . We will compute both the leading behavior of g and its quantum corrections by the corresponding calculation of $Z(\beta)$.

To compute the trace (22.15) we can use a complete set of plane waves

$$Z(\beta) = \text{Tr } e^{-\beta H} = \int \frac{d^D \mathbf{p}}{(2\pi\hbar)^D} \langle \mathbf{p} | e^{-\beta H} | \mathbf{p} \rangle. \quad (22.20)$$

We can use the Schrödinger representation

$$H_S = -\frac{\hbar^2}{2m} \nabla^2 + V, \quad \psi_{\mathbf{p}}(\mathbf{r}) = e^{i\mathbf{p}\mathbf{r}/\hbar},$$

and write

$$Z(\beta) = \int \frac{d^D \mathbf{p}}{(2\pi\hbar)^D} \int d^D \mathbf{r} e^{-i\mathbf{p}\mathbf{r}/\hbar} e^{-\beta H_S} e^{i\mathbf{p}\mathbf{r}/\hbar}. \quad (22.21)$$

D is the dimension.

To compute eqn (22.21) we have to expand the exponential. This can be done by the Baker-Haussdorf formula:

$$e^{A+B} = e^A e^{-\frac{1}{2}[A,B]+\frac{1}{6}[A,[A,B]]-\frac{1}{6}[B,[B,A]]+\dots} e^B.$$

In our case the operators in βH are proportional to β , then each commutator is depressed by a power of β : the Baker-Haussdorf formula provides in fact the high-temperature expansion.

The leading term is the *classical* term and can be computed without commutators. From eqn (22.20)

$$\begin{aligned} Z(\beta) &= \int \frac{d^D p}{(2\pi\hbar)^D} \langle p | e^{-\beta H} | p \rangle \simeq \int \frac{d^D p}{(2\pi\hbar)^D} \langle p | e^{-\beta \hat{p}^2/2m} e^{-\beta V(r)} | p \rangle = \\ &= \int \frac{d^D p}{(2\pi\hbar)^D} e^{-\beta p^2/2m} \int d^D r \langle p | r \rangle e^{-\beta V(r)} \langle r | p \rangle = \\ &= \int \frac{d^D p}{(2\pi\hbar)^D} e^{-\beta p^2/2m} \int d^D r e^{-\beta V(r)}. \end{aligned}$$

This is just the *classical* Boltzmann distribution, the universality of small t (high β) behavior of the propagator in this language means that the Boltzmann distribution is universal, i.e. valid for any potential. The p integral is elementary

$$Z(\beta) = \frac{1}{\lambda^D} \int d^D r e^{-\beta V(r)}, \quad \lambda = (2\pi\hbar^2\beta/m)^{1/2}. \quad (22.22)$$

Equation (22.22) confirms the singularity in the $\beta \rightarrow 0$ limit and that the form of the singularity *do not depend* on V .

Let us verify this point in detail. From the known expression for a free particle propagator

$$\mathcal{G}(t; \mathbf{x}, \mathbf{y}) = \left(\sqrt{\frac{m}{2i\hbar\pi t}} \right)^D e^{im(\mathbf{x}-\mathbf{y})^2/2\hbar t},$$

we can easily compute the trace after performing the substitution (22.16)

$$\sum_{\mathbf{x}} \mathcal{G}(-i\hbar\beta; \mathbf{x}, \mathbf{x}) = \left[\int d^D r \right] \left(\frac{m}{2\hbar^2\pi\beta} \right)^{D/2}.$$

This expression matches eqn (22.22) as $V \rightarrow 0$.

The high-temperature (small t) behavior corresponds to the average behavior of $g(E)$ (we average on the details of the spectrum). Using the elementary properties of the Laplace transform

$$f(E - \alpha) = \mathcal{L}_E^{-1} [e^{-\alpha\beta} F(\beta)] ; \quad \frac{E^{\nu-1}}{\Gamma(\nu)} \theta(E) = \mathcal{L}_E^{-1} [\beta^{-\nu}] ,$$

one has

$$\mathcal{L}_E^{-1} \left[\frac{e^{-\beta V(r)}}{\beta^\nu} \right] = \frac{(E - V(r))^{\nu-1}}{\Gamma(\nu)} \theta(E - V(r)) ,$$

and the mean density approximation for $g(E)$ is

$$g_{TF}(E) = \left(\frac{m}{2\pi\hbar^2} \right)^{D/2} \int d^D r \frac{(E - V(r))^{\frac{D}{2}-1}}{\Gamma(\frac{D}{2})} \theta(E - V(r)). \quad (22.23)$$

The suffix stands for *Thomas-Fermi*, as this is the same distribution one gets in atomic physics in the TF model. One can also consider eqn (22.23) without performing the integral in p . Using the identity

$$\mathcal{L}_E[1] = \delta(E) \Rightarrow \mathcal{L}_E[e^{-\alpha\beta}] = \delta(E - \alpha) .$$

one has

$$g_{\text{TF}}(E) = \int \frac{d^D \mathbf{p} d^D \mathbf{r}}{\hbar^D} \delta \left(E - \frac{p^2}{2m} - V(\mathbf{r}) \right) = \frac{d}{dE} N_{\text{TF}}(E) \quad (22.24a)$$

$$N_{\text{TF}}(E) = \int \frac{d^D \mathbf{p} d^D \mathbf{r}}{\hbar^D} \Theta \left(E - \frac{p^2}{2m} - V(\mathbf{r}) \right). \quad (22.24b)$$

For a free particle we get

$$g_{\text{TF}}(E) = \left(\frac{m}{2\pi\hbar^2} \right)^{\frac{D}{2}} \frac{E^{\frac{D}{2}-1}}{\Gamma(\frac{D}{2})} \mathcal{V}_D, \quad (22.25)$$

which matches our previous result.

In $D = 1$ these formulas give

$$g_{\text{TF}} = \frac{2m}{\hbar} \int dx \frac{1}{p(x)} \Theta(E - V) = \frac{m}{\hbar} \oint \frac{dx}{p(x)} = \frac{T}{\hbar} = \frac{1}{\hbar\omega}; \quad (22.26a)$$

$$N_{\text{TF}} = \frac{1}{\hbar} \int dp dx \Theta(E - \frac{p^2}{2m} - V) = \frac{1}{\hbar} \oint p(x) dx. \quad (22.26b)$$

where $p(x) \equiv \sqrt{2m(E-V)}$, $\omega = 2\pi/T$, T is the classical period of motion.

The result (22.24) is not trivial: the Hamiltonian there is the *classical* Hamiltonian, and the expression for $N(E)$ asserts that the semi-classical counting of states by dividing classical phase space in cells of volume \hbar^D is indeed consistent.

Corrections

The corrections to the previous result can be computed by the explicit use of the Baker-Hausdorff formula. We leave it as an exercise. Here an alternative derivation is given. In eqn (22.21) one must compute

$$u(\mathbf{r}, \mathbf{p}; \beta) = e^{-\beta H_S} e^{i \mathbf{p} \mathbf{r} / \hbar}.$$

u satisfies the equation

$$\frac{\partial u}{\partial \beta} + H_S u = 0. \quad (22.27)$$

One knows the limiting solution as $\beta \rightarrow 0$. One can make the position

$$u(\mathbf{r}, \mathbf{p}; \beta) = e^{-\beta H_{\text{cl}}} e^{i \mathbf{p} \mathbf{r} / \hbar} w(\mathbf{r}, \mathbf{p}; \beta). \quad (22.28)$$

The limiting case is $w = 1$. Substitution in eqn (22.27) gives for w

$$\begin{aligned} \frac{\partial w}{\partial \beta} &= -i\hbar \left[\frac{\beta}{m} (\mathbf{p} \cdot \nabla V) w - \frac{1}{m} (\mathbf{p} \cdot \nabla w) \right] \\ &\quad + \frac{\hbar^2}{2m} [\beta^2 (\nabla V)^2 w - \beta (\nabla^2 V) w + \nabla^2 w - 2\beta (\nabla V \nabla V)]. \end{aligned}$$

The natural expansion parameter is \hbar then by writing

$$w = 1 + \hbar w_1 + \hbar^2 w_2 + \dots,$$

one gets

$$\begin{aligned} w_1 &= -\frac{i\beta^2}{2m} \mathbf{p} \nabla V ; \\ w_2 &= -\frac{\beta^2}{4m} \nabla^2 V + \frac{\beta^3}{6m} (\nabla V)^2 - \frac{\beta^4}{8m^2} (\mathbf{p} \nabla V)^2 + \frac{\beta^3}{6m^2} (\mathbf{p} \cdot \nabla)^2 V . \end{aligned}$$

Substitution in Z and some integration by parts gives

$$\begin{aligned} Z(\beta) &= \left(\frac{1}{\lambda} \right)^D \int d^D \mathbf{r} e^{-\beta V(\mathbf{r})} \left\{ 1 - \frac{\beta^2 \hbar^2}{12 2m} \nabla^2 V \right. \\ &\quad \left. + \frac{\beta^3}{1440} \left(\frac{\hbar^2}{2m} \right)^2 [-7\nabla^4 V + 5\beta(\nabla^2 V)^2 + \beta\nabla^2(\nabla V)^2] \right\} . \end{aligned}$$

By Laplace transform one computes g . In the Laplace transform multiplication by β is equivalent to $\partial/\partial E$ and one gets easily the results, for $D = 2, 3$,

$$\begin{aligned} \bar{g}(E) &= g_{\text{TF}}(E) - \frac{1}{48\pi} \frac{\partial}{\partial E} \int d^2 \mathbf{r} \nabla^2 V \delta(E - V(\mathbf{r})) ; \quad D = 2 \\ \bar{g}(E) &= g_{\text{TF}}(E) - \frac{1}{96\pi^2} \left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{\partial}{\partial E} \int d^3 \mathbf{r} \frac{\Theta(E - V(\mathbf{r})) \nabla^2 V}{(E - V)^{1/2}} ; \quad D = 3 . \end{aligned}$$

For $D = 1$ one finds instead

$$\delta g_{\text{TF}} = -\frac{\hbar}{24\pi} \frac{\partial^2}{\partial E^2} \int dx \frac{\nabla^2 V}{p(x)} \Theta(E - V) .$$

Here $p(x) \equiv \sqrt{2m(E - V)}$. By integration in E

$$\delta N_{\text{TF}} = -\frac{\hbar}{24\pi} \frac{\partial}{\partial E} \int dx \frac{\nabla^2 V}{p(x)} \Theta(E - V) = -\frac{\hbar}{48\pi} \frac{\partial}{\partial E} \oint \frac{\nabla^2 V}{p(x)} dx .$$

This formula corrects eqn (22.26) and is identical to the correction to WKB quantization condition found in the chapter on WKB, as can be easily shown. In the integral we used the existence of two inversion points and transformed the integral in a cyclic integral, as is usual in WKB formulas.

22.2.3 $g(E)$ and short-distance behavior

It is useful to obtain eqn (22.23) directly from the short-distance behavior of the propagator, confirming the connection between high temperatures in $Z(\beta)$ and short times (and distances) in G .

By using the classical momentum $\mathbf{p}(\mathbf{r})$

$$p^2(\mathbf{r}) = 2m(E - V(\mathbf{r})) \equiv \hbar k(\mathbf{r}) ;$$

g_{TF} can be written as

$$g_{\text{TF}}(E) = \frac{2m}{\hbar^2} \frac{1}{2^D \pi^{D/2} \Gamma(\frac{D}{2})} \int d^D \mathbf{r} \left(\frac{p(\mathbf{r})}{\hbar} \right)^{D-2} . \quad (22.29)$$

This is the expression to be proven starting from the propagator. In Schrödinger representation eqn (22.10) is

$$g(E) = -\frac{1}{\pi} \int d^D \mathbf{r} \langle \mathbf{r} | G | \mathbf{r} \rangle . \quad (22.30)$$

The propagator satisfies

$$(E - H)G = 1 \Rightarrow \left(E + \frac{\hbar^2}{2m} \nabla^2 - V(\mathbf{r}) \right) G(\mathbf{r}, \mathbf{r}'; E) = \delta^D(\mathbf{r} - \mathbf{r}') ;$$

or

$$(\nabla^2 + k^2(\mathbf{r})) G(\mathbf{r}, \mathbf{r}') = \frac{2m}{\hbar^2} \delta^D(\mathbf{r} - \mathbf{r}') . \quad (22.31)$$

To compute the trace in eqn (22.30) we need only the behavior of G for $\mathbf{r} \sim \mathbf{r}'$. In this region we can consider \mathbf{k} constant and solve eqn (22.31) directly in Fourier transform

$$G \simeq \frac{2m}{\hbar^2} \int \frac{d^D \mathbf{q}}{(2\pi)^D} \frac{e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}}{k^2 - q^2} .$$

The integral can be done explicitly and one obtains Hankel functions, but it is more instructive to consider its imaginary part as $\mathbf{r} \rightarrow \mathbf{r}'$. With the usual prescription for complex contours for the propagator,

$$k^2 \rightarrow k^2 + i\varepsilon ;$$

and in the limit $\mathbf{r} \rightarrow \mathbf{r}'$

$$\begin{aligned} \text{Im } G(\mathbf{r}, \mathbf{r}') &= -\pi \frac{2m}{\hbar^2} \int \frac{d^D \mathbf{q}}{(2\pi)^D} \delta(q^2 - k^2) \\ &= -\pi \frac{2m}{\hbar^2} \frac{\Omega_D}{(2\pi)^D} \int q^{D-1} dq \delta(q^2 - k^2) = -\pi \frac{m}{\hbar^2} \frac{\Omega_D}{(2\pi)^D} k^{D-2}(\mathbf{r}') . \end{aligned}$$

Ω_D is the solid angle in D dimensions:

$$\Omega_D = 2 \frac{\pi^{D/2}}{\Gamma(\frac{D}{2})} .$$

Substitution in eqn (22.30) gives

$$g(E) = \int d^D \mathbf{r} \frac{m}{\hbar^2} [k(\mathbf{r})]^{D-2} \frac{1}{(2\pi)^D} 2 \frac{\pi^{D/2}}{\Gamma(\frac{D}{2})} ,$$

identical to eqn (22.29). In this new derivation of the result two points emerge clearly:

- (1) The value of $g(E)$ is directly connected to the limit $\mathbf{r} \rightarrow \mathbf{r}'$ in \mathcal{G} . The computed term is the classical analog of a rectilinear motion $\mathbf{r}' \rightarrow \mathbf{r}$, indeed the result is in the form identical to the result for a free-particle.
- (2) Corrections proportional to ∇V are due to non-uniformity of $k(\mathbf{r})$ and are to be interpreted at the classical level as small variations in the trajectory.

22.2.4 Level density and scattering

In a realistic system with a continuous spectrum the level density formally diverges as the eigenstates are not normalizable. In the free particle case this problem has been avoided by putting the system in a finite box. For interacting particles with potentials going sufficiently rapidly to zero at large distances one expects that the same regularization works and that at the large distance the eigenstates approach plane waves. The difference $g(E) - g_0(E)$ is well defined, i.e. it has a limit as $V \rightarrow \infty$. g_0 is the free particle density.

The asymptotic difference between g and g_0 is contained in the scattering phase shifts, so there must be a connection between the phase shifts and $g(E)$.

For definiteness we limit ourselves to a particle moving in a central potential $V(r)$. The scattering eigenstates of the problem will have the form

$$\psi(r, \theta, \varphi) = \frac{1}{r} u_{k,\ell} Y_{\ell m}(\theta, \varphi).$$

The reduced radial wave function with angular momentum ℓ are the regular solutions of the radial equation

$$\frac{d^2}{dr^2} u(r) + k^2 u(r) = \frac{2m}{\hbar^2} \left[V(r) + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} \right]. \quad (22.32)$$

k is the wave number and $E = \hbar^2 k^2 / 2m$.

If $V(r)$ goes to zero sufficiently fast as $r \rightarrow \infty$ the asymptotic solution of (22.32) is a superposition of plane waves

$$u(r) \sim \sin \left(kr - \ell \frac{\pi}{2} + \delta_\ell(k) \right).$$

As discussed in Chapter 16 the constant $\ell\pi/2$ is there also in the free case, the phase shifts δ_ℓ parametrize the scattering.

Let us now put our system in a large sphere of radius R . The boundary condition $\psi = 0$ gives the quantization condition

$$kR - \frac{\ell\pi}{2} + \delta_\ell = n\pi. \quad (22.33)$$

n evidently is the number of states up to momentum k (or up to energy $\hbar^2 k^2 / 2m$). The first term in eqn (22.33) is the free phase δ_ℓ^0 and we can write:

$$\frac{dn}{dE} = \frac{1}{\pi} \frac{d\delta_\ell^0}{dE} + \frac{1}{\pi} \frac{d\delta_\ell}{dE}.$$

If $V = 0$ $\delta_\ell = 0$, then the first term in this relation represent the density of states for a free particle and we have, at fixed ℓ :

$$g(E) - g_0(E) = \frac{1}{\pi} \frac{d\delta_\ell}{dE}. \quad (22.34)$$

The result is clearly valid also in the one-dimensional case, where R represent a one-dimensional cutoff length.

⁵The equation $E(p, r) = E$ has two roots, $\pm k(r)$. The integral in p gives $2k(r)$ which cancel the factor 2 in the denominator of eqn (22.35).

The right-hand side of eqn (22.34) is *finite* and gives us the distortion produced in the level density by the interaction.

The relation (22.34) is mostly evident in the semi-classical approximation. In the effective one-dimensional problem for the ℓ -wave potential (22.32) gives⁵

$$n(E) = \int \frac{dp dr}{2\pi\hbar} \theta(E(p, r) \leq E) = \frac{1}{\hbar\pi} \int p(r) dr \equiv \frac{1}{\pi} \int k(r) dr, \quad (22.35)$$

where

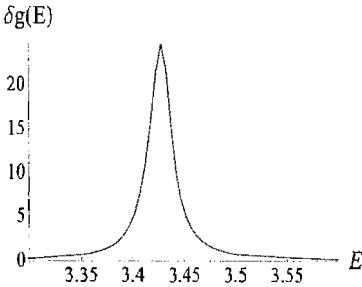
$$k(r) = \sqrt{k^2 - \left(\frac{2m}{\hbar^2} V(r) + \frac{\ell(\ell+1)}{r^2} \right)}.$$

Substituting this value and subtracting the free particle contribution

$$\delta g(E) = \frac{1}{\pi} \frac{d}{dE} \left[\int_b^\infty k(r) dr - \int_{b_0}^\infty k_0(r) dr \right]. \quad (22.36)$$

b and b_0 are the classical inversion points which bound the allowed phase spaces in the two cases. The quantity between parenthesis in eqn (22.36) is exactly the scattering phase shift computed in the WKB approximation, see Chapter 11.

Resonances



We know from Chapter 11, see also Chapter 16, that near a resonance the derivative of the phase shift has a Lorentzian form, centered at the energy of the resonant state, E_0 , and with width Γ , the width of the resonance $\Gamma = \hbar/\tau$:

$$\frac{d}{dE} \delta(E) \simeq \frac{\Gamma/2}{\frac{\Gamma^2}{4} + (E - E_0)^2},$$

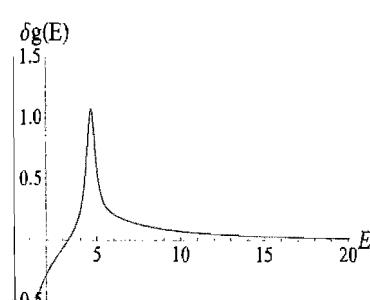
it follows that

$$\delta g(E) \simeq \frac{1}{\pi} \frac{\Gamma/2}{\frac{\Gamma^2}{4} + (E - E_0)^2}.$$

The states accumulate at a resonance.

The computation of phase scattering gives easily the level density, for instance we give in Figure 22.2 $\delta g(E)$ for $\ell = 0, 1$ for a potential

$$V(r) = V_0 r^2 e^{-r}. \quad (22.37)$$



One-dimensional scattering

For completeness we give here the relevant formulas for the one-dimensional scattering, limiting ourselves to even potentials. We remember from Chapter 3 that the asymptotic coefficients for a scattering problem

$$\begin{aligned} x \rightarrow -\infty : \quad \psi &\sim a e^{ikx} + b e^{-ikx} \\ x \rightarrow +\infty : \quad \psi &\sim a' e^{ikx} + b' e^{-ikx} \end{aligned}$$

Fig. 22.2 $\delta g(E)$ for $\ell = 0, 1$ in the potential eqn (22.37).

are related by

$$\begin{pmatrix} a' \\ b' \end{pmatrix} = \Omega \begin{pmatrix} a \\ b \end{pmatrix}; \quad \Omega = \begin{pmatrix} 1/A_T^* & -A_R^*/A_T^* \\ -A_R/A_T & 1/A_T \end{pmatrix}.$$

A_T, A_R are transmission and reflection amplitudes. For even potentials (i.e. parity conserving) the two amplitudes can be written in the form

$$A_T = \cos \theta e^{i\alpha}; \quad A_R = i \sin \theta e^{i\alpha}.$$

The phase shifts in even and odd states are given respectively by

$$\begin{aligned} e^{2i\delta_p} &= A_T + A_R; & 2\delta_p &= \alpha + \theta; \\ e^{2i\delta_d} &= A_T - A_R; & 2\delta_d &= \alpha - \theta. \end{aligned}$$

From (22.34) with $dE/dk = \hbar^2 k/m$ it follows that

$$\begin{aligned} \delta g_p(E) &= -i \frac{m}{2\pi\hbar^2 k} \frac{1}{A_T + A_R} \frac{d}{dk} (A_T + A_R); \\ \delta g_d(E) &= -i \frac{m}{2\pi\hbar^2 k} \frac{1}{A_T - A_R} \frac{d}{dk} (A_T - A_R). \end{aligned}$$

Let us note that the amplitudes A_T, A_R (or the phases) can be computed or by imposing the usual progressive wave boundary condition in the Schrödinger equation or by looking for *regular* solutions. If 0 is the symmetric point of the potential:

$$\begin{aligned} \text{even: } \psi(0) &= 1; \psi'(0) = 0; & \psi &\underset{x \rightarrow \infty}{\sim} \cos(kx + \delta_p); \\ \text{odd: } \psi(0) &= 0; \psi'(0) = 1; & \psi &\underset{x \rightarrow \infty}{\sim} \sin(kx + \delta_d). \end{aligned}$$

22.2.5 The stabilization method

The accumulation of levels near a resonance suggest a different method to detect a resonance on the spectrum, based on a direct construction of $g(E)$. This method is called the stabilization method.

Let us consider for definiteness a one-dimensional system. We use a cutoff L for the “volume” as a regularization. Free-particle eigenvalues can be considered as the eigenmodes of this one-dimensional cavity, the interaction causes an accumulation of these eigenmodes. The eigenvalues of the Hamiltonian depend on the cutoff, $E_n(L)$, and can be easily computed by a numerical solution of Schrödinger’s equation. In this approach L plays a role analogous to a variational parameter, as $L \rightarrow \infty$ we will recover the exact spectrum. For finite L we will have a discretized version of $g(E)$

$$g(E) = \sum \delta(E - E_n(L)).$$

We can regularize the Dirac distribution by averaging on some interval ΔL for the cutoff

$$\begin{aligned}\langle g(E) \rangle &= \frac{1}{\Delta L} \int_{L_{min}}^{L_{max}} dL \sum_j \delta(E - E_j(L)) \\ &= \frac{1}{\Delta L} \sum_j \left| \frac{dE_j(L)}{dL} \right|^{-1}_{E_j=E}.\end{aligned}\quad (22.38)$$

Expression (22.38) can be easily computed if the eigenvalues are known. If a resonance exists we expect a behavior

$$\langle g(E) \rangle \sim \frac{1}{\pi} \frac{\Gamma/2}{(E - E_R)^2 + (\Gamma^2/4)} + \rho_B(E), \quad (22.39)$$

where ρ_B is the background density. Usually this background is approximated by a free spectrum, i.e. by a Thomas-Fermi mean value. For one-dimensional systems (see eqn (22.25)):

$$\rho_B(E) = \frac{\sqrt{m}}{\hbar} \frac{1}{\pi} \frac{\mathcal{V}_1}{\sqrt{2E}}.$$

This method is very simple and efficient, as it is based on the computation of a Hamiltonian with a discrete spectrum for which several methods are at disposal. For instance in Figure 22.3 we show the variation of the eigenvalues with the cutoff and the resulting averaged level density (22.38) for the potential (22.37). The resonance structure is clearly discernible and the parameters E_0, Γ can be extracted by fitting the data with eqn (22.39).

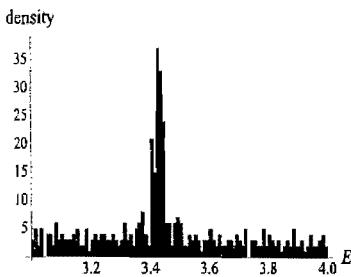
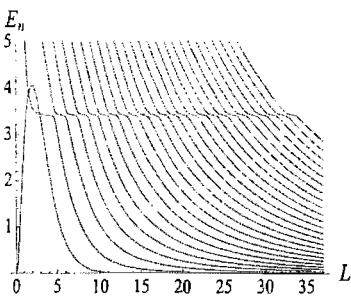


Fig. 22.3 Cutoff dependence of the eigenvalues for the potential eqn (22.37) and averaged level density.

22.3 Thomas precession

We will present a simplified study of the Thomas precession in the $v \rightarrow 0$ limit, a general theory can be found in many textbooks, see for example [Berestetskii, Lifshitz, and Pitaevskii (1980)] (Section 41).

The spin is the angular momentum in the center of mass of a particle. If the particle has a magnetic moment μ we can assume that it is directed in the same direction of the spin. The gyromagnetic factor is defined by

$$\mu = g \frac{e}{2mc} \mathbf{S} \quad (22.40)$$

S is the spin (with factor \hbar included). In classical mechanics the angular momentum of such a particle immersed in a magnetic field \mathbf{B} is subjected to a torque and evolves with

$$\frac{d\mathbf{S}}{dt} = \mu \times \mathbf{B}. \quad (22.41)$$

We pose $\mathbf{S} = S \zeta$, with ζ a unit vector, usually called the polarization of the particle. From (22.41) $d\mathbf{S}/dt = 0$ as $\mathbf{S} \cdot d\mathbf{S}/dt = 0$, then the angular momentum motion is a pure rotation. From (22.40) we have

$$\frac{d\zeta}{dt} = \frac{1}{S} \mu \times \mathbf{B} = g \frac{e}{2mc} \zeta \times \mathbf{B}. \quad (22.42)$$

Our problem is to generalize eqn (22.42) for a particle of charge e in presence of both an electric and a magnetic field.

In relativistic notations the quantity to be studied is a four-vector, reducing to $g\zeta$ in the center of mass of the particle. Let us call a^μ this vector. If the particle moves with momentum \mathbf{p} , and energy E , a simple Lorentz transformation gives

$$\mathbf{a} = \zeta + \frac{\mathbf{p}(\zeta \cdot \mathbf{p})}{m(E + mc^2)} ; \quad a^0 = c \frac{\mathbf{a} \cdot \mathbf{p}}{E} = \frac{\mathbf{p}\zeta}{mc} . \quad (22.43)$$

The equation of motion will be of the form

$$\frac{da^\mu}{d\tau} = X^\mu ,$$

where the vector X will be linear in the external fields. τ is the proper time. We will be interested in the theory up to order v^2/c^2 , in this approximation eqn (22.43) become

$$a^0 = \frac{\mathbf{p}\zeta}{mc} ; \quad \mathbf{a} \simeq \zeta + \frac{\mathbf{p}(\zeta \cdot \mathbf{p})}{2m^2c^2} . \quad (22.44)$$

In (22.44) we retained a v^2 term for \mathbf{a} , and this is crucial to derive the Thomas precession: we want to write equations at first-order in v/c , but the equation of motion in an electromagnetic field

$$\frac{d\mathbf{p}}{dt} = e\mathbf{E} + \frac{e}{c}\mathbf{v} \times \mathbf{B} ,$$

have a term (the first) which is of order 0. The variation of a quantity of order v^2 can give rise to terms of first-order in v , like $\mathbf{v} \cdot \mathbf{E}$, and these will be essential in the following.

Let us now come back to a^μ . The vector part of \mathbf{a} is an axial vector (like the polarization) then the general form for its derivative is

$$\frac{d\mathbf{a}}{dt} = C_0 \mathbf{a} \times \mathbf{B} + C_1 \mathbf{E}(\mathbf{a} \cdot \mathbf{v}) + C_2 \mathbf{v}(\mathbf{a} \cdot \mathbf{E}) + C_3 \mathbf{a}(\mathbf{E} \cdot \mathbf{v}) . \quad (22.45)$$

In general the C 's are function of v , but as we are interested only in the first order in v we can consider them constants. In particular for $v \rightarrow 0$ we must recover (22.42), then $C_0 = ge/2mc$. At first order we can make the substitution $\mathbf{a} \rightarrow \zeta$ in the right-hand side of (22.45). By adding and subtracting terms like $\mathbf{v}(\mathbf{a} \cdot \mathbf{E})$ we can recast this equation in the more convenient form

$$\frac{d\mathbf{a}}{dt} = g \frac{e}{2mc} \zeta \times \mathbf{B} + A_1 \zeta \times (\mathbf{E} \times \mathbf{v}) + A_2 \mathbf{v}(\zeta \cdot \mathbf{E}) + A_3 \mathbf{a}(\mathbf{E} \cdot \mathbf{v}) . \quad (22.46)$$

Let us now perform a Lorentz transformation with a small velocity \mathbf{V}_0 . As $d\mathbf{a}/dt$ is the spatial component of a four-vector its variation must be

$$\begin{aligned} \delta \left(\frac{d\mathbf{a}}{dt} \right) &= \frac{\mathbf{V}_0}{c} \cdot \frac{da^0}{dt} = \frac{1}{mc^2} \mathbf{V}_0 \left[\frac{d\mathbf{p}}{dt} \cdot \zeta \right] + \mathcal{O} \left(\frac{V_0 \cdot p}{c^2} \right) \\ &= \frac{e}{mc^2} \mathbf{V}_0 (\mathbf{E} \cdot \zeta) + \mathcal{O} \left(\frac{v^2}{c^2} \right) . \end{aligned} \quad (22.47)$$

For low velocities

$$\mathbf{B} \rightarrow \mathbf{B} - \mathbf{E} \times \frac{\mathbf{V}_0}{c}; \quad \mathbf{E} \rightarrow \mathbf{E} + \mathbf{B} \times \frac{\mathbf{V}_0}{c}; \quad \mathbf{v} \rightarrow \mathbf{v} + \mathbf{V}_0.$$

By substitution in the right-hand side of eqn (22.46) we see that the variation term linear in \mathbf{V}_0 is

$$-g \frac{e}{2mc} \zeta \times \left(\mathbf{E} \times \frac{\mathbf{V}_0}{c} \right) + A_1 \zeta \times (\mathbf{E} \times \mathbf{V}_0) + A_2 \mathbf{V}_0 (\zeta \cdot \mathbf{E}) + A_3 \zeta (\mathbf{E} \cdot \mathbf{V}_0).$$

Comparison with eqn (22.47) gives

$$A_1 = g \frac{e}{2mc^2}, \quad A_2 = \frac{e}{mc^2}, \quad A_3 = 0,$$

i.e. Lorentz invariance fix all coefficients. By substituting the explicit expression of \mathbf{a} , eqn (22.44), into (22.46) and using the equations of motion, we get, up to order v^2 :

$$\begin{aligned} \frac{d\zeta}{dt} + \frac{e}{2mc^2} [\mathbf{E}(\zeta \cdot \mathbf{v}) + \mathbf{v}(\zeta \cdot \mathbf{E})] = \\ g \frac{e}{2mc} \zeta \times \mathbf{B} + g \frac{e}{2mc^2} \zeta \times (\mathbf{E} \times \mathbf{v}) + \frac{e}{mc^2} \mathbf{v}(\zeta \cdot \mathbf{E}). \end{aligned}$$

With the help of the identity $\mathbf{v}(\zeta \cdot \mathbf{E}) - \mathbf{E}(\zeta \cdot \mathbf{v}) = \zeta \times (\mathbf{v} \times \mathbf{E}) = -\zeta \times (\mathbf{E} \times \mathbf{v})$ we have

$$\frac{d\zeta}{dt} = g \frac{e}{2mc} \zeta \times \mathbf{B} + \frac{e}{2mc} (g-1) \zeta \times \left(\mathbf{E} \times \frac{\mathbf{v}}{c} \right).$$

This formula gives the Thomas precession: the coupling with the effective magnetic field in the rest frame of the electron, $\mathbf{E} \times \frac{\mathbf{v}}{c}$, has an effective gyromagnetic ratio $g-1$.

The physical origin of this effect has to be traced back to the fact that to compute the variation of the polarization it is not sufficient to perform a Lorentz transformation of the external field, as we have to compute the *variation* of ζ in a time dt one has to take into account the fact that an hypothetical rest frame attached to the electron changes in time due to the motion of the particle. The Thomas precession asserts that apart the “usual” precession on the polarization with respect to $\mathbf{E} \times \frac{\mathbf{v}}{c}$, the change of frame produces a change in the components of ζ due to the rotation of the reference frame.

22.4 Relativistic corrections in an external field

We wish to write the effective Hamiltonian for an electron in an external electromagnetic field up to order v^2/c^2 . As compared to the usual Hamiltonian there are two type of corrections: the LS interaction and a term due to the kinetic energy. We treat them separately.

The LS interaction

In the text it has been shown that up to order v/c the effective Hamiltonian for an electron in an external field is

$$H = \frac{1}{2m} \left(\mathbf{p} - \frac{e}{c} \mathbf{A} \right)^2 + e\Phi - g \frac{e}{2mc} \mathbf{s} \cdot \mathbf{B}. \quad (22.48)$$

The second-order corrections, in v^2/c^2 , spin-dependent, have been shown to be (see also Section 22.3)

$$H_{LS} = -(g-1) \frac{e}{2m^2 c^2} \mathbf{s} \cdot (\mathbf{E} \times \mathbf{p}). \quad (22.49)$$

We have to add a small technical clarification. In the general case the external electric field depends on \mathbf{x} , so that we must specify the order in which the operators appear. We will use the Weyl prescription, which turns out to be the correct one if the corrections are derived in a systematic way within a relativistic theory:

$$A_{cl} \rightarrow \frac{1}{2} (A + A^\dagger). \quad (22.50)$$

This prescription is automatically satisfied by the minimal coupling in eqn (22.48). For the spin-dependent interaction (22.49) the Weyl prescription gives

$$\begin{aligned} (\varepsilon_{ijk} E_j p_k)_{class} &\rightarrow \frac{1}{2} [\varepsilon_{ijk} E_j p_k + \varepsilon_{ijk} p_k E_j] = \\ &\varepsilon_{ijk} E_j p_k + \frac{\hbar}{2i} \varepsilon_{ijk} \partial_k E_j = (\mathbf{E} \times \mathbf{p})_i + i \frac{\hbar}{2} (\nabla \times \mathbf{E})_i. \end{aligned}$$

For a static field the last term does not contribute, as Maxwell's equations in this case imply $\text{rot } \mathbf{E} = 0$. The final form of the LS interaction is in general (by setting $g = 2$ for simplicity):

$$H_{LS} = -\frac{e}{2mc^2} \mathbf{s} \cdot (\mathbf{E} \times \mathbf{p}) - i \frac{e\hbar}{4mc^2} \mathbf{s} \cdot (\nabla \times \mathbf{E}). \quad (22.51)$$

Kinetic energy

The kinetic energy of a particle is

$$\sqrt{\mathbf{p}^2 c^2 + m^2 c^4} - mc^2 \sim \frac{\mathbf{p}^2}{2m} - \frac{1}{8} \frac{\mathbf{p}^4}{m^3 c^2}. \quad (22.52)$$

The second term in (22.52) has to be added to the Hamiltonian, up to order v^2/c^2 . In this computation \mathbf{p} can be understood as the canonical momentum as the corrections $e\mathbf{A}/c$ give rise to higher terms in v/c .

This is not the whole story. A more sophisticated computation based on a relativistic generalization of the Schrödinger equation (the Dirac equation) reveals the existence of an additional term, the so-called *Darwin term*

$$H_D = -\frac{e\hbar^2}{8m^2 c^2} \nabla \cdot \mathbf{E}.$$

For a Coulomb external field

$$H_D = -\frac{e\hbar^2}{8m^2c^2} 4\pi Z|e|\delta^3(\mathbf{r}) = +\frac{Ze^2\hbar^2\pi}{2m^2c^2}\delta^3(\mathbf{r}) .$$

This term obviously is relevant only the s -waves in perturbation theory. It is possible to give a semi-classical interpretation of this term. Due to the relativistic effects the electron wave function has short range fluctuations, ξ at wavelengths of the order of Compton radius of the electron, $r_e = \hbar/mc$:

$$\langle \xi_i \rangle = 0 \quad \langle \xi_i \xi_j \rangle = \frac{1}{3}\delta_{ij}r_e^2 .$$

This in turn affects the potential energy, the external Coulomb potential $V_c(\mathbf{x})$ as a fluctuation

$$\langle eV_c(x + \xi) \rangle \simeq eV(x) + \frac{1}{2}\langle \xi_i \xi_j \partial_i \partial_j V_c \rangle = e\frac{1}{6}r_e^2\langle \Delta V_c \rangle = \frac{4\pi}{6}Ze^2r_e^2\delta^3(\mathbf{r}) .$$

Apart a numerical factor this is exactly the Darwin term.

Putting all together the Hamiltonian in a Coulomb field up to order v^2/c^2 is

$$H = \frac{1}{2m} \left(\mathbf{p} - \frac{e}{c} \mathbf{A} \right)^2 + e\Phi - g\frac{e}{2mc} \mathbf{s} \cdot \mathbf{B} - \frac{\mathbf{p}^4}{8m^3c^2} + \frac{e^2}{2m^2c^2} \frac{Z}{r^3} \boldsymbol{\ell} \cdot \mathbf{s} + \frac{Ze^2\hbar^2\pi}{2m^2c^2} \delta^3(\mathbf{r}) .$$

In this formula $\boldsymbol{\ell} = \hbar \mathbf{L}$ and $\mathbf{s} = \hbar \mathbf{S}$.

22.5 The Hamiltonian for interacting charged particles

We wish to write the effective Hamiltonian up to order v^2/c^2 for a system like an atom. In the limit of infinite nuclear mass and at leading order in v/c the Hamiltonian is

$$H = \sum_a \frac{p_a^2}{2m} - \sum_a \frac{Ze^2}{r_a} + \sum_{a < b} \frac{e^2}{r_{ab}} .$$

r_a is the distance between the a -th electron and the nucleus, r_{ab} the distance between electrons a and b . The sum is performed on pairs of electrons. There are several corrections to this Hamiltonian

- The relativistic corrections to the interaction electron–nucleus, which have been studied in Section 22.4 (for an infinite-mass nucleus).
- The relativistic corrections to the electron–electron interaction.
- The corrections due to the finite nuclear mass.

We will study these corrections separately, starting with a short review of the origin of the classical relativistic corrections.

22.5.1 The interaction potentials

Let us consider two spinless particles, particle 1 and 2. If the motion of particle 2 is given, the Lagrangian for particle 1 is

$$L_1 = -m_1 c^2 \sqrt{1 - \frac{v_1^2}{c^2}} - e_1 \varphi + \frac{e_1}{c} \mathbf{v}_1 \cdot \mathbf{A}. \quad (22.53)$$

where φ and \mathbf{A} are respectively the scalar and vector potentials generated by particle 2 at point \mathbf{r}_1 and time t .

For a point particle φ and \mathbf{A} are well known (the Liénard–Wiechert potentials):

$$\varphi(t, \mathbf{r}) = \frac{e_2}{R - \frac{\mathbf{v}_2 \cdot \mathbf{R}}{c}}, \quad \mathbf{A}(t, \mathbf{r}) = \frac{e_2 \mathbf{v}_2}{c \left(R - \frac{\mathbf{v}_2 \cdot \mathbf{R}}{c} \right)}; \quad \mathbf{R} \equiv \mathbf{r} - \mathbf{r}_2.$$

The potentials are time dependent through the trajectory of particle 2, $\mathbf{r}_2(t')$. The time t' is the retarded time, defined by

$$t' = t - \frac{R(t')}{c}. \quad (22.54)$$

In this relation t, \mathbf{r} are the time and the point (the space-time “event”) at which φ, \mathbf{A} are computed and, up to now, they have nothing to do with the coordinates of particle 1. As functions of t we have, at each time:

$$\dot{\mathbf{R}} = -\mathbf{v}_2, \quad (22.55)$$

and in particular at time t'

$$-\mathbf{v}_2 \cdot \dot{\mathbf{R}} = \dot{\mathbf{R}} \cdot \mathbf{R} = \dot{R} R.$$

The potentials can then be written as

$$\varphi(t, \mathbf{r}) = \frac{e_2}{R(t') \left(1 + \frac{\dot{R}(t')}{c} \right)}; \quad \mathbf{A}(t, \mathbf{r}) = \frac{e_2 \mathbf{v}_2}{c R(t') \left(1 + \frac{\dot{R}(t')}{c} \right)}.$$

Using eqn (22.55) the relation (22.54) can be expanded in series of $1/c$ ⁶

$$t' = t - \frac{R(t)}{c} + \frac{R(t) \dot{R}(t)}{c^2} + \mathcal{O}(1/c^3).$$

We can now perform an explicit expansion in $1/c$ for $R(t')$:

$$\begin{aligned} R(t') &= R(t) + (t' - t) \dot{R}(t) + \frac{1}{2} (t' - t)^2 \ddot{R}(t) \\ &= R + \dot{R} \left(-\frac{R}{c} + \frac{R \dot{R}}{c^2} \right) + \frac{1}{2} \frac{R^2}{c^2} \ddot{R}; \\ \frac{\dot{R}(t')}{c} &= \frac{\dot{R}(t)}{c} + (t' - t) \frac{\ddot{R}(t)}{c} = \frac{\dot{R}}{c} - \frac{R \ddot{R}}{c^2}. \end{aligned}$$

⁶ It is sufficient to write $t' = t + a/c + b/c^2$ in eqn (22.55) and match coefficients.

This implies

$$R(t') \left(1 + \frac{\dot{R}(t')}{c} \right) \simeq R - \frac{1}{2} \frac{R^2 \ddot{R}}{c^2};$$

$$\frac{1}{R(t') \left(1 + \frac{\dot{R}(t')}{c} \right)} \simeq \frac{1}{R} + \frac{1}{2} \frac{\ddot{R}}{c^2}.$$

In these formulas R stands for $R(t)$. Expanding the potentials we get up to order $1/c^2$

$$\varphi = \frac{e_2}{R} + \frac{e_2}{2} \frac{\ddot{R}}{c^2} \quad \mathbf{A} = \frac{e_2}{cR} \left(\mathbf{v}_2 - \frac{R}{c} \dot{\mathbf{v}}_2 \right). \quad (22.56)$$

⁷Note that this term would signal a problem: in the Lagrangian would appear the accelerations. In fact the expansion we are doing is inconsistent physically at higher orders, the radiation emission should be taken into account.

As \mathbf{A} has a factor $1/c$ in front in the Lagrangian (22.53) we can omit the last term in (22.56)⁷.

The physics is invariant under the gauge transformations

$$\varphi \rightarrow \varphi - \frac{1}{c} \frac{\partial f}{\partial t}; \quad \mathbf{A} \rightarrow \mathbf{A} + \nabla f.$$

We can use this freedom to put $\varphi = e_2/R$, it is sufficient to use as gauge function $f = -\frac{e_2}{2} \frac{\dot{R}}{c}$. We have for the new potentials

$$\varphi = \frac{e_2}{R}; \quad \mathbf{A} = \frac{e_2}{cR} \mathbf{v}_2 - \frac{e_2}{2} \frac{\nabla \dot{R}}{c};$$

and finally, using again eqn (22.55)

$$\varphi = \frac{e_2}{R}; \quad \mathbf{A} = \frac{e_2}{2c} \frac{\mathbf{v}_2 + (\mathbf{v}_2 \cdot \mathbf{n}) \mathbf{n}}{R}, \quad \mathbf{n} = \mathbf{R}/R \equiv \mathbf{n}_{12}.$$

\mathbf{n}_{12} is the unit vector from particle 2 toward particle 1. These potentials, computed at point \mathbf{r}_1 , have now to be inserted in the Lagrangian. Omitting the constant $m_1 c^2$ we have, up to second order in $1/c$

$$L_1 = \frac{m_1 v_1^2}{2} + \frac{m_1 v_1^4}{8c^2} - \frac{e_1 e_2}{R} + \frac{e_1 e_2}{2c^2 R} [\mathbf{v}_1 \cdot \mathbf{v}_2 + (\mathbf{v}_1 \cdot \mathbf{n})(\mathbf{v}_2 \cdot \mathbf{n})].$$

The first two terms are the usual kinetic energy. The rest is the interaction of the pair of particles.

For N particles it follows easily that

$$L = \sum_a \left[\frac{m_a v_a^2}{2} + \frac{m_a v_a^4}{8c^2} \right] - \sum_{a < b} \frac{e_a e_b}{R_{ab}}$$

$$+ \sum_{a < b} \frac{e_a e_b}{2c^2 R_{ab}} [\mathbf{v}_a \cdot \mathbf{v}_b + (\mathbf{v}_a \cdot \mathbf{n}_{ab})(\mathbf{v}_b \cdot \mathbf{n}_{ab})]. \quad (22.57)$$

A Legendre transformation gives the Hamiltonian, we left the computation as an exercise to the reader:

$$H = \sum_a \left[\frac{p_a^2}{2m_a} - \frac{p_a^4}{8c^2 m_a^3} \right] + \sum_{a < b} \frac{e_a e_b}{R_{ab}}$$

$$- \sum_{a < b} \frac{e_a e_b}{2c^2 m_a m_b R_{ab}} [\mathbf{p}_a \cdot \mathbf{p}_b + (\mathbf{p}_a \cdot \mathbf{n}_{ab})(\mathbf{p}_b \cdot \mathbf{n}_{ab})]. \quad (22.58)$$

22.5.2 Spin-dependent interactions

We know the interaction Hamiltonian for a spin \mathbf{s}_1 in an external electromagnetic field (see Chapter 14 and Supplement 22.3):

$$H_I = -g_1 \frac{e_1}{2m_1 c} \mathbf{s}_1 \cdot \mathbf{B} - (g_1 - 1) \frac{e_1}{2m_1 c} \mathbf{s}_1 \cdot \left(\mathbf{E} \times \frac{\mathbf{v}_1}{c} \right). \quad (22.59)$$

g_1 is the gyromagnetic factor.

This expression is already of order v^2/c^2 (in an atom as we will see $B \sim v/c$), then all relativistic delay effects on \mathbf{E} and \mathbf{B} can be neglected. For the same reason we can neglect in the definition of \mathbf{E} , in this formula, the contribution $\dot{\mathbf{A}}/c$. In this approximation considering a pair of particles 1 and 2, the fields are those created by the particle 2 at the point \mathbf{r}_1 where particle 1 is placed. Using at lowest order in $1/c$ the Liénard-Wiechert potentials

$$\mathbf{E}_2(\mathbf{r}_1) = -\nabla\varphi = \frac{e_2}{R^2} \mathbf{n}_{12}; \quad \mathbf{B}_2(\mathbf{r}_1) = \nabla \times \mathbf{A} = \frac{e_2}{cR^2} \mathbf{v}_2 \times \mathbf{n}_{12}.$$

We used the identities

$$\left[\nabla \times \left(\frac{1}{R} \mathbf{v} \right) \right]_i = \epsilon_{ijk} \partial_j \frac{1}{R} v_k = - \left[\mathbf{v} \times \nabla \frac{1}{R} \right]_i; \quad -\mathbf{v} \times \nabla \frac{1}{R} = \frac{1}{R^2} \mathbf{v} \times \mathbf{n}_{12}.$$

This contribution is due to the charge of the particle 2. If, in addition, the particle 2 has a magnetic moment

$$\boldsymbol{\mu}_2 = g_2 \frac{e_2}{2m_2 c} \mathbf{s}_2,$$

this gives an additional contribution⁸ to \mathbf{B}

$$\mathbf{B}_2(\mathbf{r}_1) = g_2 \frac{e_2}{2m_2 c} \left[\frac{3\mathbf{n}_{12}(\mathbf{s}_2 \cdot \mathbf{n}_{12}) - \mathbf{s}_2}{R^3} + \mathbf{s}_2 \frac{8\pi}{3} \delta^3(\mathbf{R}) \right].$$

Summing both terms the potential energy of the particle 1 in the field of particle 2 is

$$\begin{aligned} E_1 = & - (g_1 - 1) \frac{e_1 e_2}{2m_1^2 c^2 R^2} (\mathbf{n}_{12} \times \mathbf{p}_1) \cdot \mathbf{s}_1 \\ & - g_1 \frac{e_1}{2m_1 c} \mathbf{s}_1 \left\{ \frac{e_2}{m_2 c R^2} \mathbf{p}_2 \times \mathbf{n}_{12} \right. \\ & \left. + g_2 \frac{e_2}{2m_2 c} \left(\frac{3\mathbf{n}_{12}(\mathbf{s}_2 \cdot \mathbf{n}_{12}) - \mathbf{s}_2}{R^3} + \mathbf{s}_2 \frac{8\pi}{3} \delta^3(\mathbf{R}) \right) \right\}. \end{aligned}$$

At this order we are allowed to write momentum \mathbf{p} for $m\mathbf{v}$.

To write the potential energy of the pair (1-2) we have to take care of a trivial point. We have written the energy for the variable \mathbf{s}_1 for fixed \mathbf{s}_2 as

$$E_1 = f(s_1) + g(s_1, s_2),$$

where g is symmetric. Clearly the energy of particle E_2 in the field of particle 1 is obtained by the interchange $1 \leftrightarrow 2$. The energy of the pair is

$$U_{12} = f(s_1) + f(s_2) + g(s_1, s_2),$$

⁸For the origin of the term $\delta^3(\mathbf{r})$ see the analogous computation in Section 14.1.6.

we have *not* to double the function $g(s_1, s_2)$. The reader can convince himself of this point by considering the equation of motion for s_1 and s_2 , treated as canonical variables. Noticing that in the exchange $1 \leftrightarrow 2$ one has $\mathbf{n}_{21} = -\mathbf{n}_{12}$, the interaction term of the pair takes the form

$$\begin{aligned} U_{12} = & -(g_1 - 1) \frac{e_1 e_2}{2m_1^2 c^2 R^2} (\mathbf{n}_{12} \times \mathbf{p}_1) \cdot \mathbf{s}_1 \\ & + (g_2 - 1) \frac{e_1 e_2}{2m_2^2 c^2 R^2} (\mathbf{n}_{12} \times \mathbf{p}_2) \cdot \mathbf{s}_2 \\ & - \frac{e_1 e_2}{2m_1 m_2 c^2 R^2} [g_2(\mathbf{n}_{12} \times \mathbf{p}_1) \cdot \mathbf{s}_2 - g_1(\mathbf{n}_{12} \times \mathbf{p}_2) \cdot \mathbf{s}_1] \\ & + g_1 g_2 \frac{e_1 e_2}{4m_1 m_2 c^2} \left[\frac{\mathbf{s}_1 \cdot \mathbf{s}_2 - 3(\mathbf{s}_1 \cdot \mathbf{n}_{12})(\mathbf{s}_2 \cdot \mathbf{n}_{12})}{R^3} - \mathbf{s}_1 \cdot \mathbf{s}_2 \frac{8\pi}{3} \delta^3(\mathbf{R}) \right]. \end{aligned} \quad (22.60)$$

Here $R \equiv R_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. A sum on all pairs will give the total energy.

22.5.3 The quantum Hamiltonian

The quantum version of U_{12} is obtained by the usual substitution $\mathbf{p} = -i\hbar\nabla$. A possible ordering problem arises in eqn (22.58), the correct order for operators is

$$\frac{1}{R_{ab}} [\mathbf{p}_a \cdot \mathbf{p}_b + \mathbf{n}_{ab}(\mathbf{n}_{ab} \cdot \mathbf{p}_a)\mathbf{p}_b]. \quad (22.61)$$

All differential operators have to be written at the end of the expression. It is possible to show that this ordering gives a self-adjoint operator (as it must be) and, more interesting, this operator is “unique”: indeed the ordering problem is only apparent.

The last point is the addition of the Darwin term

$$-\frac{e_1 e_2 \hbar^2 \pi}{2c^2} \left(\frac{1}{m_1^2} + \frac{1}{m_2^2} \right) \delta^3(\mathbf{r}). \quad (22.62)$$

This form of the Darwin term is correct for spin- $\frac{1}{2}$ particles. A nucleus can have any spin but its contribution proportional to $1/M^2$ will be in any case neglected.

Let us now give the explicit form of the interaction for electron-electron pairs and electron-nucleus pairs.

22.5.4 Electron-electron interactions

Neglecting for the moment the kinetic terms the energy for this pair can be obtained from eqns (22.58), (22.60), and (22.62). With $g = 2$ we have

$$\begin{aligned}
U_{ab} = & \frac{e^2}{R_{ab}} - \frac{e^2}{2m^2c^2R_{ab}} [\mathbf{p}_a \cdot \mathbf{p}_b + \mathbf{n}_{ab}(\mathbf{n}_{ab} \cdot \mathbf{p}_a)\mathbf{p}_b] - \pi \frac{e^2\hbar^2}{m^2c^2} \delta^3(\mathbf{R}_{ab}) \\
& - \frac{e^2}{2m^2c^2R_{ab}^2} (\mathbf{n}_{ab} \times \mathbf{p}_a) \cdot \mathbf{s}_a + \frac{e^2}{2m^2cR_{ab}^2} (\mathbf{n}_{ab} \times \mathbf{p}_b) \cdot \mathbf{s}_b \\
& - \frac{e^2}{m^2c^2R_{ab}^2} [(\mathbf{n}_{ab} \times \mathbf{p}_a) \cdot \mathbf{s}_b - (\mathbf{n}_{ab} \times \mathbf{p}_b) \cdot \mathbf{s}_a] \\
& + \frac{e^2}{m^2c^2} \left[\frac{\mathbf{s}_a \cdot \mathbf{s}_b - 3(\mathbf{s}_a \cdot \mathbf{n}_{ab})(\mathbf{s}_b \cdot \mathbf{n}_{ab})}{R_{ab}^3} - s_1 s_2 \frac{8\pi}{3} \delta^3(\mathbf{R}_{ab}) \right] \\
= & \frac{e^2}{R_{ab}} - \frac{e^2}{2m^2c^2R_{ab}} [\mathbf{p}_a \cdot \mathbf{p}_b + \mathbf{n}_{ab}(\mathbf{n}_{ab} \cdot \mathbf{p}_a)\mathbf{p}_b] - \pi \frac{e^2\hbar^2}{m^2c^2} \delta^3(\mathbf{R}_{ab}) \\
& + \frac{e^2\hbar}{4m^2c^2R_{ab}^2} [-(\sigma_a + 2\sigma_b) \cdot (\mathbf{n}_{ab} \times \mathbf{p}_a) + (\sigma_b + 2\sigma_a) \cdot (\mathbf{n}_{ab} \times \mathbf{p}_b)] \\
& + \frac{e^2\hbar^2}{4m^2c^2} \left[\frac{\sigma_a \cdot \sigma_b - 3(\sigma_a \cdot \mathbf{n}_{ab})(\sigma_b \cdot \mathbf{n}_{ab})}{R_{ab}^3} - \sigma_a \sigma_b \frac{8\pi}{3} \delta^3(\mathbf{R}_{ab}) \right].
\end{aligned} \tag{22.63}$$

This form of the interaction is known as the *Breit equation*. σ_a are Pauli matrices acting on the spinor describing electron a .

It is simple, and important, to estimate the order of magnitude of various terms. Using

$$\frac{e^2}{R} \sim \frac{e^2}{a_B} \sim mc^2\alpha^2; \quad R \sim a_B \sim \frac{\hbar}{mc\alpha}; \quad p \sim \frac{\hbar}{a_B} \sim mc\alpha.$$

one finds that all terms are smaller by a factor α^2 in comparison with the Coulomb energy. As relativistic corrections are given by power series in $v^2/c^2 \sim \alpha^2$, the neglected terms of order v^4/c^4 would give a contribution of order $\alpha^4 \sim 10^{-8}$ times a typical Coulomb energy.

22.5.5 Electron–nucleus interactions

In this case we have two expansion parameters: $1/c$ (or better the fine-structure constant $\alpha = e^2/\hbar c$) and the ratio $m/M \lesssim 10^{-3}$ between electron and nucleus mass. We will consider terms up to order $m/M\alpha^2 \lesssim 10^{-7}$, higher order terms in m/M are of the same order as terms depending on the nuclear structure, as the finite nuclear radius etc. and will be neglected.

The Hamiltonian at this order, including kinetic terms and putting $g = 2$ for the electron follows from eqns (22.58), (22.60), and (22.62). In writing this expression we use for charges $e = -|e|$ and $e_N = Z|e|$. In the following \mathbf{n}_a is the unit vector from the nucleus to the electron a , r_a is the distance between electron a and the nucleus.

$$H = \frac{p_N^2}{2M} + \sum_a \frac{p_a^2}{2m} - \sum_a \frac{p_a^4}{8c^2m^3} + \sum_a U_a. \tag{22.64}$$

$$\begin{aligned}
U_a = & -\frac{Ze^2}{r_a} + \frac{Ze^2}{2mc^2r_a} [\mathbf{p}_a \cdot \mathbf{p}_N + \mathbf{n}_a(\mathbf{n}_a \cdot \mathbf{p}_a)\mathbf{p}_N] \\
& + \pi \frac{Ze^2\hbar^2}{2m^2c^2} \delta^3(\mathbf{r}_a) + \frac{Ze^2}{2m^2c^2r_a^2} (\mathbf{n}_a \times \mathbf{p}_a) \cdot \mathbf{s}_a \\
& + \frac{Ze^2}{2mc^2r_a^2} [g(\mathbf{n}_a \times \mathbf{p}_a) \cdot \mathbf{s}_N - 2(\mathbf{n}_a \times \mathbf{p}_N) \cdot \mathbf{s}_a] \\
& - g \frac{Ze^2}{2mc^2} \left[\frac{\mathbf{s}_a \cdot \mathbf{s}_N - 3(\mathbf{s}_a \cdot \mathbf{n}_a)(\mathbf{s}_N \cdot \mathbf{n}_a)}{r_a^3} - \mathbf{s}_a \mathbf{s}_N \frac{8\pi}{3} \delta^3(\mathbf{r}_a) \right].
\end{aligned} \tag{22.65}$$

Let us note the identity

$$\frac{1}{r_a^2} \mathbf{n}_a \times \mathbf{p}_a = \frac{1}{r_a^3} \boldsymbol{\ell}_a.$$

giving in the limit $M \rightarrow \infty$ the usual $\boldsymbol{\ell} \cdot \mathbf{s}$ coupling.

Center of mass

To compute the spectrum of H one has to disentangle the internal degrees of freedom from the collective motion of the system, this is done by going to the center-of-mass frame.

The conjugate variable to the center-of-mass coordinate is the total momentum of the system. The variables \mathbf{p}_a become the conjugate variables with respect to the relative coordinates $\mathbf{x}_a - \mathbf{x}_N$. We leave to the reader to show explicitly that the change of variables

$$(\mathbf{x}_a, \mathbf{x}_N) \rightarrow \left(\mathbf{R}_{cm} = \frac{m \sum_a \mathbf{x}_a + M \mathbf{x}_N}{\sum m_a + M}, \mathbf{x}_a - \mathbf{x}_N \right)$$

is a canonical (unitary) transformation.

The Hamiltonian becomes

$$H = \frac{P_{cm}^2}{2M_{tot}} + H_{int};$$

where now, in H_{int} , \mathbf{p}_N has to be replaced by

$$\mathbf{p}_N = - \sum_a \mathbf{p}_a, \tag{22.66}$$

i.e. the momentum of the nucleus in the center of mass frame.

From now on we shall neglect the overall motion of the atom.

In the center-of-mass frame the kinetic term in eqn (22.64) takes the form

$$\begin{aligned}
K = & \sum_a \frac{p_a^2}{2m} + \frac{1}{2M} \left(\sum_a \mathbf{p}_a \right)^2 - \sum_a \frac{p_a^4}{8c^2m^3} = \\
& + \left(\frac{1}{m} + \frac{1}{M} \right) \sum_a p_a^2 + \frac{1}{2M} \sum_{a \neq b} \mathbf{p}_a \cdot \mathbf{p}_b - \sum_a \frac{p_a^4}{8c^2m^3}.
\end{aligned}$$

Introducing the reduced mass

$$\frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}; \quad \mu = \frac{mM}{m+M},$$

we have, up to higher orders in m/M

$$K = \sum_a \frac{p_a^2}{2\mu} + \frac{1}{M} \sum_{a < b} \mathbf{p}_a \mathbf{p}_b - \sum_a \frac{p_a^4}{8c^2 \mu^3}.$$

The term of order $1/M$ has been written as a sum on electron pairs and can be included in the electron-electron interaction terms. This term is known as *mass polarization*. Obviously this term is absent in the hydrogen atom.

Let us now consider the interaction part, using (22.66). There are three different order of magnitudes (we put $Z = 1$ in these considerations)

- (1) The Coulomb interaction, of order $e^2/a_B \sim m c^2 \alpha^2$.
- (2) The fine-structure terms: all terms without the $1/M$ factor. Their order of magnitude is $e^2/a_b \cdot \alpha^2$; they give a correction of order $\Delta E/E \sim 10^{-4}$ to the eigenvalues.
- (3) The terms proportional to $1/M$, giving a contribution of order $\Delta E/E \sim \alpha^2 m/M \sim 10^{-7}$. They are interesting if we want to study the *hyperfine structure*, i.e. the influence on the spectrum of nuclear magnetic moment.
- (4) The mass polarization term. This gives a contribution of order $m/M \sim 10^{-3}-10^{-4}$ as important as are fine-structure terms. Being spin independent this term will contribute to the absolute value of energy levels, not to the difference between different fine-structure terms.

The m/M terms will be considered briefly in the next subsection, here we collect the Hamiltonian for nucleus-electron interactions up to order $m/M \alpha^2$

$$H_{eN} = \sum_a \frac{p_a^2}{2\mu} + \frac{1}{M} \sum_{a < b} \mathbf{p}_a \mathbf{p}_b - \sum_a \frac{p_a^4}{8c^2 \mu^3} + \sum_a U_a$$

$$U_a = -\frac{Ze^2}{r_a} + \pi \frac{Ze^2 \hbar^2}{2m^2 c^2} \delta^3(\mathbf{r}_a) + \frac{Ze^2}{2m^2 c^2 r_a^3} \boldsymbol{\ell}_a \cdot \mathbf{s}_a.$$

The total Hamiltonian

Summing all the contributions considered up to now and using the notation

$$\boldsymbol{\ell}_a = \hbar \mathbf{L}_a, \quad \mathbf{s}_a = \hbar \frac{\boldsymbol{\sigma}_a}{2},$$

we have

$$H = H_0 + H_1 + U_{LS} + U_{ee}^{(1)} + U_{ee}^{(2)} + \mathcal{O}(m^2/M^2, m/M\alpha^2). \quad (22.67)$$

$$H_0 = \sum_a \frac{p_a^2}{2\mu} - \sum_a \frac{Ze^2}{r_a}; \quad (22.68)$$

$$H_1 = - \sum_a \frac{p_a^4}{8c^2\mu^3} + \pi \frac{Ze^2\hbar^2}{2m^2c^2} \delta^3(\mathbf{r}_a); \quad (22.69)$$

$$U_{LS} = \sum_a \frac{Ze^2}{2m^2c^2r_a^3} \boldsymbol{\ell}_a \cdot \mathbf{s}_a = \frac{Ze^2\hbar^2}{4m^2c^2r_a^3} \mathbf{L}_a \cdot \boldsymbol{\sigma}_a; \quad (22.70)$$

$$\begin{aligned} U_{ee}^{(1)} &= - \sum_{a < b} \frac{e^2}{2m^2c^2R_{ab}} [\mathbf{p}_a \cdot \mathbf{p}_b + \mathbf{n}_{ab}(\mathbf{n}_{ab} \cdot \mathbf{p}_a)\mathbf{p}_b] \\ &\quad - \sum_{a < b} \pi \frac{e^2\hbar^2}{m^2c^2} \delta^3(\mathbf{R}_{ab}) + \frac{1}{M} \sum_{a < b} \mathbf{p}_a \cdot \mathbf{p}_b; \\ U_{ee}^{(2)} &= \sum_{a < b} \frac{e^2\hbar}{4m^2c^2R_{ab}^2} [(\boldsymbol{\sigma}_b + 2\boldsymbol{\sigma}_a) \cdot (\mathbf{n}_{ab} \times \mathbf{p}_b) - (\boldsymbol{\sigma}_a + 2\boldsymbol{\sigma}_b) \cdot (\mathbf{n}_{ab} \times \mathbf{p}_a)] \\ &\quad + \sum_{a < b} \frac{e^2\hbar^2}{4m^2c^2} \left[\frac{\boldsymbol{\sigma}_a \cdot \boldsymbol{\sigma}_b - 3(\boldsymbol{\sigma}_a \cdot \mathbf{n}_{ab})(\boldsymbol{\sigma}_b \cdot \mathbf{n}_{ab})}{R_{ab}^3} - \boldsymbol{\sigma}_a \cdot \boldsymbol{\sigma}_b \frac{8\pi}{3} \delta^3(\mathbf{R}_{ab}) \right]. \end{aligned}$$

Let us note that within this approximation we can substitute $m \rightarrow \mu$ in terms like U_{ee} . The net effect of nuclear mass has been, up to this order, the polarization mass term and the substitution $m \rightarrow \mu$ which amount to a change in the definition of the Rydberg:

$$\text{Ry}(M) = \frac{M}{m+M} \text{Ry}.$$

22.5.6 The $1/M$ corrections

The corrections to eqn (22.67) are of order m^2/M^2 and $(m/M)\alpha^2$. In fact the correction due to Lamb shift, of order $Z^2\alpha^3 \log(Z\alpha)$ is usually the leading one and is not contained in the effective Hamiltonian. Then only in some particular cases it make sense to treat these corrections. We will review briefly two of such cases, the hydrogen atom and the hyperfine structure.

The hydrogen atom

In this case the substitution $m \rightarrow \mu$ is exact in the non-relativistic approximation, so we have no m^2/M^2 corrections from this side. The center-of-mass Hamiltonian—with a unique electron and $\mathbf{p}_N = -\mathbf{p}$ —is

$$\begin{aligned} H &= \frac{\mathbf{p}^2}{\mu} - \frac{Ze^2}{r} \\ &\quad - \frac{p^4}{8c^2m^3} - \frac{Ze^2}{2mMc^2r} [\mathbf{p} \cdot \mathbf{p} + \mathbf{n}(\mathbf{n} \cdot \mathbf{p})\mathbf{p}] + \pi \frac{Ze^2\hbar^2}{2m^2c^2} \delta^3(\mathbf{r}) \end{aligned} \quad (22.71)$$

$$+ \frac{Ze^2}{2m^2c^2r^3} \ell \cdot s + \frac{Ze^2}{2mMc^2r^3} [g\ell \cdot s_N + 2\ell \cdot s] \\ - g_N \frac{Ze^2}{2mMc^2} \left[\frac{s \cdot s_N - 3(s \cdot n)(s_N \cdot n)}{r^3} - s \cdot s_N \frac{8\pi}{3} \delta^3(r) \right].$$

Up to now everything is exact up to order $1/c^2$. At lowest order in m/M

$$\frac{1}{m^2} = \left(\frac{1}{\mu} - \frac{1}{M} \right)^2 \sim \frac{1}{\mu^2} - 2\frac{1}{\mu M}; \quad \frac{1}{m^3} \simeq \frac{1}{\mu^3} - 3\frac{1}{\mu^2 M};$$

then up to terms of order $(m/M)^2\alpha^2$ the factors $\ell \cdot s$ in (22.71) can be combined together using μ . At the same time we can write the Darwin term and the factor proportional to p^4 using μ . After these changes we have

$$H = H_0 + H_{LS} + H_M + H_{IS}. \quad (22.72)$$

$$H_0 = \frac{p^2}{\mu} - \frac{Ze^2}{r}, \\ H_{LS} = \frac{Ze^2}{2\mu^2c^2r^3} \ell \cdot s - \frac{p^4}{8c^2\mu^3} + \pi \frac{Ze^2\hbar^2}{2\mu^2c^2} \delta^3(r); \\ H_M = \frac{\mu}{M} \left[\frac{3}{8} \frac{p^4}{c^2\mu^3} - 2\pi \frac{Ze^2\hbar^2}{2\mu^2c^2} \delta^3(r) - \frac{Ze^2}{2\mu^2c^2r} [\mathbf{p} \cdot \mathbf{p} + \mathbf{n}(\mathbf{n} \cdot \mathbf{p})\mathbf{p}] \right]; \\ H_{IS} = -g_N \frac{Ze^2}{2mMc^2} \left[\frac{s \cdot s_N - 3(s \cdot n)(s_N \cdot n)}{r^3} - s \cdot s_N \frac{8\pi}{3} \delta^3(r) - \frac{\ell \cdot s_N}{r^3} \right].$$

Apart from radiative corrections this Hamiltonian is exact up to order $\mathcal{O}(\frac{m}{M}\alpha^2)$, the neglected terms being $\mathcal{O}(\frac{m^2}{M^2}\alpha^2)$ and $\mathcal{O}(\frac{m^3}{M^3})$.

Hyperfine structure

In general the terms $\alpha^2 m/M$ have different origins, as an instance from the delay term in the Coloumb interaction, but give no new qualitative effects, except for those terms involving nuclear spin, which imply in general an hyperfine splitting of levels, the Hamiltonian non-commuting with electron angular momentum.

These terms can be read directly from eqn (22.65) and are identical to those of the hydrogen atom

$$H_{IS} = \sum_a -g_N \frac{Ze^2}{2mMc^2} \left[-\frac{\ell_a \cdot s_N}{r_a^3} \right. \\ \left. + \frac{s_a \cdot s_N - 3(s_a \cdot n_a)(s_N \cdot n_a)}{r^3} - s_a \cdot s_N \frac{8\pi}{3} \delta^3(r_a) \right]. \quad (22.73)$$

22.6 Quantization of electromagnetic fields

In this Supplement a simplified treatment of the quantization of the electromagnetic field is given. We have seen already in Section 20.2 that

the energy of the electromagnetic radiation field is given by the sum of the independent oscillators, with angular frequencies $\hbar\omega = \hbar c|\mathbf{k}|$ and with two independent polarizations $\lambda = 1, 2$.

Historically the quantization of such a set of oscillators gave the first example of a *field quantization*. Let us restate the oscillator formalism in a more compact fashion.

A pure radiation field can be described, in the Coulomb gauge, by $\varphi = 0$, $\nabla \cdot \mathbf{A} = 0$, where φ and \mathbf{A} are respectively the scalar and the vector potential. The vector potential satisfies, by Maxwell equations, the wave equation

$$\frac{1}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{A} - \nabla^2 \mathbf{A} = 0 \quad (22.74)$$

The elementary solution of this equation is a plane wave

$$\mathbf{A} = \boldsymbol{\varepsilon} e^{-i(\omega t - \mathbf{k} \cdot \mathbf{x})}$$

$\boldsymbol{\varepsilon}$ is a constant vector. Substitution in eqn (22.74) impose $\omega/c = |\mathbf{k}|$ while the gauge condition gives

$$\nabla \mathbf{A} = 0 \Rightarrow \mathbf{k} \cdot \boldsymbol{\varepsilon} = 0.$$

For each \mathbf{k} we have two independent orthogonal vectors, which we denote by $\boldsymbol{\varepsilon}(\mathbf{k}, \lambda)$, $\lambda = 1, 2$. As any solution can be expanded in plane waves the general form of the vector potential will be

$$\mathbf{A}(x, t) = \int \frac{d^3 k}{(2\pi)^3} \sqrt{\frac{4\pi c^2 \hbar}{2\omega}} [e^{-i(\omega t - \mathbf{k} \cdot \mathbf{x})} \boldsymbol{\varepsilon}_\lambda(\mathbf{k}) a(\mathbf{k}, \lambda) + \text{c.c.}] . \quad (22.75)$$

$a(\mathbf{k}, \lambda)$ are the coefficients of the expansion. We normalize the vectors $\boldsymbol{\varepsilon}$ with

$$\boldsymbol{\varepsilon}^*(\lambda) \boldsymbol{\varepsilon}(\lambda') = \delta_{\lambda, \lambda'} . \quad (22.76)$$

and the factor in front of eqn (22.75) has been chosen for later convenience. Let us now write the energy of the system in terms of these coefficients.

The energy (Hamiltonian) of the electromagnetic field is, in CGS units

$$H = \frac{1}{8\pi} \int d^3 x (\mathbf{E}^2 + \mathbf{B}^2) . \quad (22.77)$$

In the Coulomb gauge

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} ; \quad \mathbf{B} = \nabla \times \mathbf{A} .$$

Using the expansion (22.75) and substituting in eqn (22.77) a tedious but trivial computation gives

$$H = \int \frac{d^3 k}{(2\pi)^3} \hbar \omega a^*(\mathbf{k}, \lambda) a(\mathbf{k}, \lambda) . \quad (22.78)$$

This is exactly the form of the Hamiltonian of set of harmonic oscillators in terms of the (classical analogous) of creation and annihilation operators, i.e. the radiation field has been decomposed in a set of *independent* oscillators, as in Section 20.2.

In a manifestly relativistic formalism, one starts from the action

$$S = -\frac{1}{4} \int d^4x F_{\mu\nu} F^{\mu\nu}, \quad F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu$$

which corresponds to the Lagrangian

$$L = \frac{1}{8\pi} \int d^3x (\mathbf{E}^2 - \mathbf{B}^2).$$

The quantization of such a system is quite obvious: we replace each pair (a, a^*) in eqn (22.75) by the annihilation and creation operators $a(\mathbf{k}, \lambda)$, $a^\dagger(\mathbf{k}, \lambda)$, satisfying the commutators,

$$[a(\mathbf{k}, \lambda), a^\dagger(\mathbf{k}', \lambda')] = (2\pi)^3 \delta^3(\mathbf{k} - \mathbf{k}') \delta_{\lambda, \lambda'}.$$

The Hamiltonian takes the form (disregarding a constant term which depends on the classical ordering of the operators):

$$H = \int \frac{d^3k}{(2\pi)^3} \hbar \omega a^\dagger(\mathbf{k}, \lambda) a(\mathbf{k}, \lambda).$$

As has been explained in Section 20.10 the operator $a^\dagger(\mathbf{k}, \lambda)$ acting on a vacuum state creates a particle (a photon):

$$|\mathbf{k}, \lambda\rangle = a^\dagger(\mathbf{k}, \lambda) |0\rangle.$$

The two values of λ correspond to the two possible value for the polarization.

A useful exercise left for the reader is to show that the Heisenberg equations of motion for \mathbf{E} and \mathbf{B} give the Maxwell equations, i.e.

$$\frac{\partial \mathbf{E}}{\partial t} = \frac{i}{\hbar} [H, \mathbf{E}] = c \nabla \times \mathbf{B}; \quad \frac{\partial \mathbf{B}}{\partial t} = \frac{i}{\hbar} [H, \mathbf{B}] = -c \nabla \times \mathbf{E}.$$

This very short and incomplete version of the quantization of the electromagnetic field is sufficient for all the applications in the realm of elementary quantum physics at low energy, i.e. the subject of our book.

22.6.1 Matrix elements

The Hilbert space of a system composed by matter and radiation is of the form $\mathcal{H}_A \otimes \mathcal{H}_R$. \mathcal{H}_A refers to matter (atoms in our usual applications) while \mathcal{H}_R is the Hilbert space of the radiation, its vectors being a linear superposition of states of the form

$$|\mathbf{k}_1, \lambda_1, \mathbf{k}_2, \lambda_2, \dots\rangle,$$

obtained from the vacuum $|0\rangle$ (the ground state) acting with the creation operators described above.

The computation of matrix elements, transition rates etc. is the standard one in perturbation theory, i.e. Fermi's golden rule, and in fact is simpler than the semi-classical computation presented in the main text.

We will be interested only in first-order effects in the electromagnetic coupling. Using the language of a single particle (one electron) coupled to radiation, the Hamiltonian interaction in Coulomb gauge will be given by

$$H_I = -\frac{e}{c} \mathbf{p} \cdot \mathbf{A}(\mathbf{x}).$$

The generic matrix element will be of the form

$$\mathcal{M} = -\frac{e}{c} \langle a; f | \mathbf{p} \cdot \mathbf{A}(\mathbf{x}) | b; i \rangle.$$

The matter system has a transition $b \rightarrow a$ while the radiation has a change $i \rightarrow f$. In dipole approximation we can neglect variations of \mathbf{A} on size of the system and using the results of Section 9.5

$$\mathcal{M} = -\frac{e}{c} \langle a; f | \mathbf{p} \cdot \mathbf{A}(\mathbf{x}) | b; i \rangle \simeq -i \frac{\omega_{ba}}{c} \mathbf{d}_{ab} \langle f | \mathbf{A}(0) | i \rangle.$$

Decays

This is the simplest case. In the initial state the radiation field is in the ground state (no photons) the final state has a photon in a state $|\mathbf{k}, \lambda\rangle \equiv a^\dagger(\mathbf{k}, \lambda)|0\rangle$. Using commutation relations one gets immediately from eqn (22.75)

$$\langle \mathbf{k}, \lambda | \mathbf{A}(0) | 0 \rangle = \sqrt{\frac{4\pi c^2 \hbar}{2\omega}} \epsilon_\lambda^*. \quad (22.79)$$

Fermi's rule gives the probability of the decay. The initial state has energy E_b , the final state $E_a + \hbar\omega$ then

$$dW = \frac{2\pi}{\hbar} \frac{\omega_{ba}^2}{c^2} |\mathbf{d}_{ab} \epsilon_\lambda^*|^2 \frac{2\pi c^2 \hbar}{\omega} \delta(E_b - E_a - \hbar\omega) \frac{d^3 \mathbf{k}}{(2\pi)^3}.$$

Using $k = \omega/c$ and integrating on ω we get rid of the δ function

$$dW = \frac{\omega_{ba}^3}{2\pi\hbar c^3} |\mathbf{d}_{ab} \epsilon_\lambda^*|^2 d\Omega \equiv P_{\mathbf{k}, \lambda} d\Omega. \quad (22.80)$$

Here $\hbar\omega_{ba} = E_b - E_a$. $d\Omega$ is the infinitesimal solid angle for the emission of the photon.

In general the angular distribution is not isotropic, depending on the initial atomic polarization (we speak of atoms for definiteness).

The simplest case is the one of a unpolarized atom, we do not look at the photon polarization, i.e. we sum on the possible λ . The density matrix for unpolarized photons is

$$\rho_\gamma^{(0)} = \frac{1}{2} (\delta_{ij} - \hat{\mathbf{k}}_i \hat{\mathbf{k}}_j).$$

To sum on final polarizations is the same as using $\rho_\gamma^{(0)}$ and multiply the results by a factor of 2 (the two polarization states), then summing on final photon polarizations the matrix element of the dipole become

$$\mathbf{d}^2 - (\mathbf{d} \cdot \hat{\mathbf{k}})^2.$$

If the initial state is unpolarized everything is rotation invariant and the angular integral is trivial. Using $\overline{\cos^2 \theta} = 1/3$:

$$W = \sum_a \frac{\omega_{ba}^3}{2\pi\hbar c^3} \left(d_{ab}^2 - \frac{1}{3} d_{ab}^2 \right) 4\pi = \frac{4}{3} \frac{\omega_{ba}^3}{\hbar c^3} \sum_a d_{ab}^2 \equiv \frac{4}{3} \frac{\omega_{ba}^3}{\hbar c^3} g_a \overline{d_{ab}^2},$$

identical to the semi-classical result (9.88).

Induced emission and absorption

Let us consider now a state with $N_{k,\lambda}$ photons. To avoid useless complications we remember that the computation of transition probabilities has to be done between normalized states (using the usual form of Fermi's rule). Every additional normalization factor cancel in Fermi's rule (we are saying that the transition probability do not depend on our arbitrary normalization of states). It is simpler to think the system as immersed in a large volume V which will be set equal to 1 (in this way automatically cancel).

The only difference as compared to the previous computation is in the value of matrix elements for \mathbf{A} . For emission and absorption we have respectively

$$\begin{aligned} \langle N_{k,\lambda} + 1 | \mathbf{A}(0) | N_{k,\lambda} \rangle &= \sqrt{N_{k,\lambda} + 1} \varepsilon_\lambda^* ; \\ \langle N_{k,\lambda} - 1 | \mathbf{A}(0) | N_{k,\lambda} \rangle &= \sqrt{N_{k,\lambda}} \varepsilon_\lambda . \end{aligned}$$

We recognize the enhancement factors characteristic of a bosonic system.

Then for the *forward* probability for emission and absorption we have, using eqn (22.80)

$$P_{k,\lambda}^{em} = (N_{k,\lambda} + 1) P_{k,\lambda} , \quad P_{k,\lambda}^{as} = N_{k,\lambda} P_{k,\lambda} .$$

The emitted photon has the same \mathbf{k} of the initial state, this is why we are speaking of "forward" emission. In the emission probability the term proportional to $N_{k,\lambda}$ is the induced emission factor, the rest is the spontaneous emission treated in previous subsection.

To write $N_{k,\lambda}$ in terms of more usual quantities let us note that the number of photons per unit volume with a momentum \mathbf{k} within an interval $d^3\mathbf{k}$ is

$$N_{\mathbf{k}} \frac{d^3\mathbf{k}}{(2\pi)^3} . \quad (22.81)$$

Multiplying eqn (22.81) by the photon energy we get the energy density and by a last multiplication by the velocity of light c we obtain the intensity of the radiation (we remember that $I = uc$). Let the intensity of the radiation coming from a solid angle $d\Omega$ and a frequency between ω and $\omega + d\omega$ and with a polarization λ be

$$I_{\mathbf{n},\lambda}(\omega) d\omega d\Omega ,$$

(\mathbf{n} is the direction of the beam). In the photon variables used above

$$c\hbar\omega N_{\mathbf{k}} \frac{d^3\mathbf{k}}{(2\pi)^3} = I_{\mathbf{n},\lambda}(\omega) d\omega d\Omega .$$

Using $k = \omega/c$ and polar coordinates we finally get

$$N_{\mathbf{k},\lambda} = \frac{8\pi^3 c^2}{\hbar\omega^3} I_{\mathbf{n},\lambda}(\omega);$$

The probability of the transitions can then be written

$$P_{\mathbf{k},\lambda}^{em.ind.} = P_{\mathbf{k},\lambda}^{as} = P_{\mathbf{k},\lambda} \frac{8\pi^3 c^2}{\hbar\omega^3} I_{\mathbf{n},\lambda}(\omega). \quad (22.82)$$

From these relations, in the isotropic case, it is possible to derive the Einstein relations exposed in the main text.

Width of a spectral line

The electromagnetic decay is a particular case of what we have seen in Section 9.4, in this case the unperturbed Hamiltonian H_0 is $H_A + H_R$, while the electromagnetic coupling gives H_I .

Consider a system, let say an atom, in an excited state b . In terms of H_0 we are considering a state $|b\rangle|0\rangle$ (an excited atomic state and the ground state of the radiation field). This is a *normalizable* eigenstate of H_0 with energy E_b . This state is degenerate with each state of the form $|\alpha\rangle = |a\rangle|\mathbf{k}\rangle$, with an atom in the ground state a and a photon with energy $\omega = c|\mathbf{k}| = E_b - E_a$. As the photon direction is arbitrary the subspace spanned by α is a continuous.

To this situation we can apply word by word what was presented in Section 9.4. The energy of the final state has the form $E = E_a + \hbar\omega$ and the probability distribution (9.64) gives the photon spectrum in the decay. Writing eqn (9.64) in term of the photon frequency

$$P_E dE = \frac{1}{\pi} \frac{\Gamma/2}{(E_b + \delta E - E_a - \hbar\omega)^2 + \frac{\Gamma^2}{4}} \hbar d\omega.$$

The width Γ has been given in eqn (9.88):

$$\Gamma = \hbar W_{ab}^{(S)} = g_a \frac{4\omega_{ba}^3}{3c^3} \overline{d_{ab}^2}.$$

Multiplication by $\hbar\omega$ gives the energy distribution of emitted photons

$$dE(\omega) = \frac{1}{2\pi} \frac{\omega \Gamma}{(\omega - \tilde{\omega}_0)^2 + \frac{\Gamma^2}{4\hbar^2}} d\omega.$$

with $\tilde{\omega}_0 = (E_b + \delta E - E_a)/\hbar$.

22.7 Atoms

In this supplement some details of the analysis skipped in the main text are presented.

22.7.1 The Thomas–Fermi approximation

For large Z most electrons are in highly excited states, and it becomes reasonable to use the methods of statistical mechanics to describe the electrons. Each electron will move in an “average” self-consistent potential, as in the Hartree method, but the treatment is simpler. Such a method was introduced independently by Thomas [Thomas (1927)] and Fermi [Fermi (1927)].

A degenerate Fermi gas is a system of (independent) fermions in the state of minimum energy. In a semi-classical framework we can think of a small wavelength λ for the particles. In this situation we can describe the potential in which the electrons move as practically constant over the range large than λ . This is consistent with the condition for the validity of the semi-classical approximation

$$\frac{m\hbar F}{p^3} \ll 1, \quad (22.83)$$

which implies that the spatial variation of the potential (i.e. the force F) is small. In each small volume dV around the point \mathbf{r} we can consider the electrons as moving in a locally constant potential $\Phi(\mathbf{r})$. Φ is the electrostatic potential.

In the ground state the electrons will be distributed by Pauli’s principle in different phase space cells, with increasing momentum up to a certain maximum value p_F , the *Fermi momentum*. If ρ is the number of electrons in a unit of volume, the number of electrons in the volume dV is the double of the number of cells of phase space (the factor 2 is due to spin):

$$\rho dV = dV \cdot 2 \int_{|\mathbf{p}| < p_F} \frac{d^3 p}{(2\pi\hbar)^3} = dV \frac{8\pi}{8\pi^3\hbar^3} \int_0^{p_F} p^2 dp = dV \frac{p_F^3}{3\pi^2\hbar^3},$$

Then the density and the Fermi momentum are related by

$$\rho = \frac{p_F^3}{3\pi^2\hbar^3}. \quad (22.84)$$

The classical energy in a zone around the point \mathbf{r} is $\mathbf{p}^2/2m - |e|\Phi(\mathbf{r})$ and, from what we have just seen, the *maximum* possible energy is given by

$$\frac{p_F^2}{2m} - |e|\Phi(\mathbf{r}) = -|e|\Phi_0(\mathbf{r}).$$

The function Φ_0 must be a constant, for otherwise we will have a flux of electrons from regions with greater Φ_0 to regions with lower Φ_0 . Φ_0 is the chemical potential for this problem: its constancy is in agreement with the general principles of statistical mechanics. We then have the relation

$$\frac{p_F^2}{2m} = |e|(\Phi(\mathbf{r}) - \Phi_0). \quad (22.85)$$

For bound states it must be that $\Phi_0 \geq 0$ so that the total energy is negative. Equation (22.84) implies that for $\Phi(\mathbf{r}) = \Phi_0$ the electronic

density vanishes, i.e. we are at the (semi-classical) boundary of the atom. Outside a sphere which contain all the charge, if the total charge is zero, as in a neutral atom, the potential is zero, with the usual choice of $\Phi = 0$ at infinity. From eqn (22.85) we have $\Phi(\mathbf{r}) \geq \Phi_0$ and as Φ_0 is non-negative and the large r limit of Φ is zero, then for a neutral atom $\Phi_0 = 0$. For ions the situation is different, we will limit ourselves to neutral atoms. Eliminating p_F between eqn (22.84) and eqn (22.85) we get a relation between ρ and Φ , this is in fact the self-consistent constraint:

$$\frac{\hbar^2}{2m} (3\pi^2 \rho)^{2/3} = |e| \Phi. \quad (22.86)$$

The electrostatic potential of a nucleus and of the electron cloud must satisfy Poisson equation

$$\Delta \Phi = -4\pi(-|e|\rho); \quad \Phi \xrightarrow[r \rightarrow 0]{} \frac{Z|e|}{r}. \quad (22.87)$$

end with eqn (22.86)

$$\Delta \Phi = \frac{8\sqrt{2}}{3\pi} \left(\frac{me^{5/3}}{\hbar^2} \right)^{3/2} \Phi^{3/2}. \quad (22.88)$$

We will look for radial symmetric solutions to this equation. Let us use atomic units and perform the change of variables

$$r = xbZ^{-1/3}; \quad b = \frac{1}{2} \left(\frac{3\pi}{4} \right)^{2/3}; \quad \Phi(r) = \frac{Z}{r} F(x) = \frac{Z^{4/3}}{bx} F(x).$$

We obtain for F the *Thomas–Fermi* equation

$$\Delta \Phi = \frac{1}{b^{3/2}} \Phi^{3/2} \Rightarrow x^{1/2} \frac{d^2 F}{dx^2} = F^{3/2}; \quad F(0) = 1. \quad (22.89)$$

For the density we have

$$\rho = \frac{Z^2}{4\pi b^3} \frac{F^{3/2}}{x^{3/2}}. \quad (22.90)$$

Let us point out that this equation is valid for each Z , i.e. is universal. The independence of Z in eqn (22.89) means that r in the solution always appears in the form $r/(bZ^{-1/3})$, i.e. the *characteristic scale* of a Thomas–Fermi atom is $r_Z \sim bZ^{-1/3}$.

In Figure 22.4 we plot the solution $F(x)$, as obtained in one of the notebooks of this chapter.

The boundary conditions $F(0) = 1, F(\infty) = 0$ fix the solutions. An important parameter is the slope of the curve at the origin

$$F'(0) \simeq -1.588 \equiv -B.$$

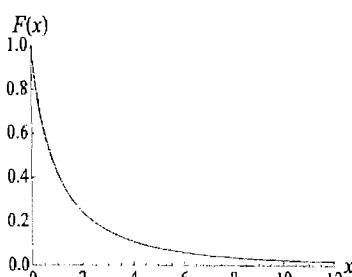


Fig. 22.4 Solution of the Thomas–Fermi equation.

The variational principle

For a Fermi gas the Fermi momentum is connected to the density by eqn (22.84):

$$\frac{p_F^2}{2} = \gamma \rho^{2/3}; \quad \gamma = \frac{1}{2}(3\pi^2)^{2/3} \equiv (4\pi)^{2/3} b.$$

The kinetic energy of the gas is then (the factor 2 is due to spin and we use atomic units)

$$\begin{aligned} E_{\text{kin}} &= \int \frac{p^2}{2} 2 \frac{d^3 p d^3 r}{(2\pi)^3} = \frac{8\pi}{8\pi^3} \int d^3 r \int_0^{p_F} \frac{p^2}{2} p^2 dp \\ &= \frac{3}{5} \gamma \int d^3 x \rho^{5/3}(r). \end{aligned} \quad (22.91)$$

With this form for the kinetic energy it is easy to show the Thomas–Fermi energy follows from a variational principle. With eqn (22.91) we can write the total energy for an atom is a functional of ρ

$$\begin{aligned} E[\rho] &= \frac{3}{5} \gamma \int d^3 r \rho^{5/3}(r) \\ &\quad - \int d^3 r \rho(r) \frac{Z}{|r|} + \frac{1}{2} \int d^3 r d^3 r' \rho(r) \frac{1}{|r - r'|} \rho(r'). \end{aligned} \quad (22.92)$$

The second term is the electron–nucleus interaction, the last term the electron–electron interaction. In a system with N electrons ($N = Z$ for a neutral atom) this quantity must be minimized with the constraint

$$\int d^3 r \rho(r) = N.$$

Using a Lagrange multiplier μ

$$\frac{\delta E}{\delta \rho} + \mu \frac{\delta N}{\delta \rho} = 0, \quad (22.93)$$

or

$$\gamma \rho^{2/3}(r) = \Phi(r) - \mu; \quad \Phi(r) \equiv \frac{Z}{|r|} - \int d^3 r' \frac{1}{|r - r'|} \rho(r'). \quad (22.94)$$

Φ is the electrostatic potential and this equation is the Thomas–Fermi equation in integral form. Using the relation

$$\Delta \frac{1}{|r - r'|} = -4\pi \delta^3(r - r'),$$

one easily gets

$$\Delta \Phi(r) = -Z 4\pi \delta^3(r) + 4\pi \rho(r) = -Z 4\pi \delta^3(r) + 4\pi \gamma^{-3/2} (\Phi - \mu)^{3/2},$$

This is identical with eqn (22.89), together with the boundary conditions, which appear explicitly as a $\delta^3(r)$ term. For a neutral atom we

took $\mu = 0$. In this equation μ play the role of Φ_0 and eqn (22.93) confirms the nature of chemical potential of this parameter:

$$\mu = -\frac{\delta E}{\delta N}.$$

Let us consider in particular the case of a neutral atom. By multiplying eqn (22.94) by $\rho(\mathbf{r})$ and integrating one has

$$\frac{5}{3}E_{\text{kin}} = -U_{\text{en}} - 2U_{\text{ee}}, \quad (22.95)$$

where

$$U_{\text{en}} = - \int d^3\mathbf{r} \frac{Z}{|\mathbf{r}|} \rho(\mathbf{r}); \quad U_{\text{ee}} = \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \rho(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}'),$$

are the electrostatic energy between electrons and nucleus and between electrons. For a motion in a Coulomb field the virial theorem holds

$$E_{\text{kin}} = -\frac{1}{2} (U_{\text{en}} + U_{\text{ee}}).$$

By eliminating E_{kin} one obtains the relations

$$U_{\text{ee}} = -\frac{1}{7}U_{\text{en}} \quad E = E_{\text{kin}} + U_{\text{ee}} + U_{\text{en}} = -E_{\text{kin}}; \quad E = \frac{3}{7}U_{\text{en}}. \quad (22.96)$$

Equation (22.96) explains why the central field approximation works so well: the repulsion energy between electrons is a relatively small fraction of the total energy. This result is not trivial as for a given scale r_0 one expects an electron nucleus interaction of the order Z^2/r_0 while for all pairs a repulsive energy $U_{\text{ee}} \sim Z(Z-1)/2r_0 \sim U_{\text{en}}$. It is in fact the Pauli principle which depresses the $e-e$ energy.

It is a simple matter to compute the total energy as a function of Z

$$\begin{aligned} E &= \frac{3}{7}U_{\text{en}} = -\frac{3}{7} \int d^3\mathbf{r} \frac{Z}{|\mathbf{r}|} \rho(r) = -\frac{3}{7}Z \int dr r^2 4\pi \frac{1}{r} \rho \\ &= -\frac{3}{7}Z \int dr r \Delta \Phi = -\frac{3}{7}Z \int dr \frac{d^2}{dr^2} r \Phi = -\frac{3}{7b}Z^{7/3} \int d\xi F''(\xi). \end{aligned}$$

In the last equality we have changed the variables as $r = b\xi Z^{-1/3} r \Phi = ZF(\xi)$. Finally, using $F'(0) < 0$ one finds

$$E = -\frac{3}{7} \frac{|F'(0)|}{b} Z^{7/3} \simeq -0.7687 Z^{7/3} \text{ a.u.} \quad (22.97)$$

A note on this result: in our study on the variational principle we have found that the virial theorem was a consequence of this principle. We leave it as a problem to verify that this is true also in this formalism; our use of the virial theorem is within the variational procedure.

Validity of the approximation

The semi-classical approximation is valid in regions where eqn (22.83) holds and when λ is smaller than the dimension of the system. For small r electrons move mostly in the nuclear Coulomb potential where

$$|p| \sim \sqrt{2(|E - U|)} \sim \sqrt{2|U|} \sim \sqrt{Z/r} ; \quad F \sim Z/r^2 .$$

From eqn (22.83) one has

$$r \gg 1/Z .$$

The failure of the approximation as $r \rightarrow 0$ could be guessed from eqn (22.86) which implies $\rho \sim r^{-3/2}$ as $r \rightarrow 0$, while from the Schrödinger equation one knows that $\rho(r) \rightarrow \text{const.}$. The wavelength λ becomes of the same order of the dimension of the system for $p \sim 1/r$ and from eqn (22.85) in this region $\Phi \sim 1/r$. Equation (22.88) implies that this limit is reached for

$$\frac{d^2}{dr^2} \Phi \sim \frac{1}{r^3} \sim \frac{1}{r^{3/2}} \Rightarrow r \sim 1 .$$

The conclusion is that the Thomas–Fermi approximation is valid in the “intermediate” region

$$\frac{1}{Z} \ll r \ll 1 \quad (22.98)$$

Most of the electron density is covered by this interval, and this explains the overall validity of the approximation, whereas finer details can be missed in such an approach.

With additional information the wave functions in the region (22.98) can be extrapolated; in particular the general behavior with Z of s -waves functions at the origin can be found. For $r \sim 1/Z$ the potential energy is dominant and $U \sim Z/r$ and semi-classical approximation gives $|p| \sim \sqrt{|U|}$. The radial wave function then behaves as

$$\psi \sim \frac{1}{r|p|^{1/2}} \sim \frac{1}{r|U|^{1/4}} ; \quad \psi\left(\frac{1}{Z}\right) \sim \sqrt{Z} .$$

As for s waves ψ is constant at the origin we have for the probability of finding an electron in a small region of radius $1/Z$ around the origin:

$$P \sim |\psi|^2 r^3 \sim \frac{1}{Z^2} .$$

Order of magnitudes

Let us start with the scaling law $r \sim Z^{-1/3}$. Neglecting the electron interactions we have Z electrons in the Coulomb field of a nucleus of charge Z . The ground state is obtained by filling the shells with increasing principal quantum number n . Each shell has a degeneracy $2n^2$ so that (for closed shell atoms) the maximum n is given by

$$Z = \sum_{i=1}^{n_M} 2n^2 \sim \frac{2}{3} n_M^3 \Rightarrow n_M \sim Z^{1/3} .$$

The corresponding Bohr radius is

$$R \sim \frac{a_B}{Z} n_M^2 \sim a_B Z^{-1/3},$$

which explains the scaling law: the atomic radius, neglecting electrostatic interactions of electrons, behaves as $Z^{-1/3}$. The corrections to the Thomas–Fermi approximation add a “cloud” of charges surrounding the core.

It is important to know the error induced by the inaccurate treatment of the region $r \leq 1/Z$. In this region the number of the electrons is of the order of

$$n_0 \sim \rho r^3 \sim \frac{Z^2}{x^{3/2}} r^3 \sim Z^{3/2} r^{3/2} \sim 1,$$

(see eqn (22.90)). The corresponding interaction with the nucleus is

$$\frac{Z}{r} n_0 \sim Z^2.$$

We expect then that the result $E \sim Z^{7/3}$ suffers from a correction of the order of Z^2 . More important corrections come from the exchange effects which have been neglected, it can be shown that these effects on the total energy are of the order of $Z^{5/3}$. We quote the final result

$$-E(Z) = 0.7687 Z^{7/3} - \frac{1}{2} Z^2 + 0.2699 Z^{5/3} + \mathcal{O}(Z^4/3). \quad (22.99)$$

In Figure 22.5 we illustrate eqn (22.97) and eqn (22.99) and, for comparison, the numerical results obtained with the Hartree–Fock equation. The agreement is excellent. Figure 22.6 shows the “average” accuracy of the Thomas–Fermi approximation.

The onset of type ℓ orbitals

One can use the average potential Φ to write the Schrödinger equation for the reduced radial functions

$$-\frac{1}{2} \frac{d^2}{dr^2} P_{nl}(r) + \frac{\ell(\ell+1)}{2r^2} P_{nl}(r) - \frac{Z}{r} F\left(\frac{rZ^{1/3}}{b}\right) P_{nl} = \varepsilon P_{nl}. \quad (22.100)$$

A modified version will be considered below. For large r the term proportional to F decreases faster than $1/r^2$, so that it is possible that for a fixed ℓ the effective potential

$$V_\ell(r) = -\frac{Z}{r} F\left(\frac{rZ^{1/3}}{b}\right) + \frac{\ell(\ell+1)}{2r^2},$$

is always positive: there is no bound state. Let us note that we are studying the ground state of the system here; the statement does not concern the presence of excited states. As Z grows in eqn (22.100) the attractive part becomes stronger and the potential can become negative: for a fixed ℓ the lowest such values of Z signal the possibility of an ℓ -shell.

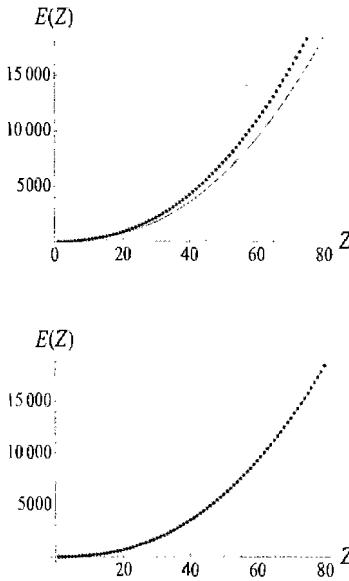


Fig. 22.5 Total energy in the Thomas–Fermi approximation.

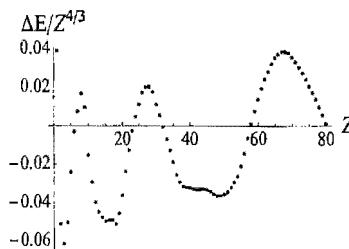


Fig. 22.6 Ratio $(E_{HF} - E_{TF})/Z^{4/3}$.

To determine this point it is necessary to look for a potential tangent to the x axis in the graph (by continuity arguments a tangent point signals the beginning of a negative potential as the parameter Z varies). We must solve the simultaneous equations $V = 0$; $V' = 0$. We find

$$\begin{aligned} Z^{2/3} \frac{F(x)}{x} &= \left(\frac{4}{3\pi}\right)^{2/3} \frac{(\ell + \frac{1}{2})^2}{x^2}; \\ Z^{2/3} \frac{x F'(x) - F(x)}{x} &= -2 \left(\frac{4}{3\pi}\right)^{2/3} \frac{(\ell + \frac{1}{2})^2}{x^2}. \end{aligned}$$

The usual semi-classical substitution $\ell(\ell+1) \rightarrow (\ell + \frac{1}{2})^2$ has been performed. From the ratio of the two equations one gets $F'/F = -1/x$ and by substitution of the numerical solution one finds

$$Z = 0.155(2\ell + 1)^3;$$

which reproduces the observed sequence rather well. The exact results are obtained with

$$Z = 0.17(2\ell + 1)^3; \quad \ell = \{1, 2, 3\} \rightarrow Z = \{5, 21, 58\}.$$

These values correspond to the appearance of the electrons s, p, d respectively. Figure 22.7 reproduces some plots for $V(r)$ with $\ell = 1, 2$, for some values of Z .

Orbitals in the Thomas–Fermi approximation

The Thomas–Fermi equation looks at the atom as a whole; the atomic sequence is analyzed as a function of Z . For individual atoms the approximation is expected to give only an “average” result. An illuminating example is given in Figure 22.8 where the electron density in the Thomas–Fermi approximation is compared with the results of the Hartree–Fock calculations for Hg. The same average accuracy is shown in Figure 22.6 where the deviations of the energy from the asymptotic result (22.99) are reported.

With these points in mind, it is nevertheless interesting to compute the electron wave functions in the Thomas–Fermi approximation. We give here a simple adaptation of a method used by Fermi and Amaldi for this task.

The potential U computed from the Thomas–Fermi equation is the whole potential of the atom, i.e. the potential felt by an external charge, not the potential acting on a single electron inside the atom. For large Z one can neglect this difference and eqn (22.100) was written in this spirit. A better approximation is to consider an atom with Z electrons as “built” from an atom of charge $Z-1$ to which one unit of nuclear charge is added adiabatically. In this process one assumes that the electron potential remains unchanged. The resulting Schrödinger equation is

$$-\frac{1}{2} \Delta \psi + \left(-\frac{1}{r} + \Phi_{Z-1}(r)\right) \psi = E\psi.$$

This approach is developed in the notebooks of Chapter 15 in the main text.

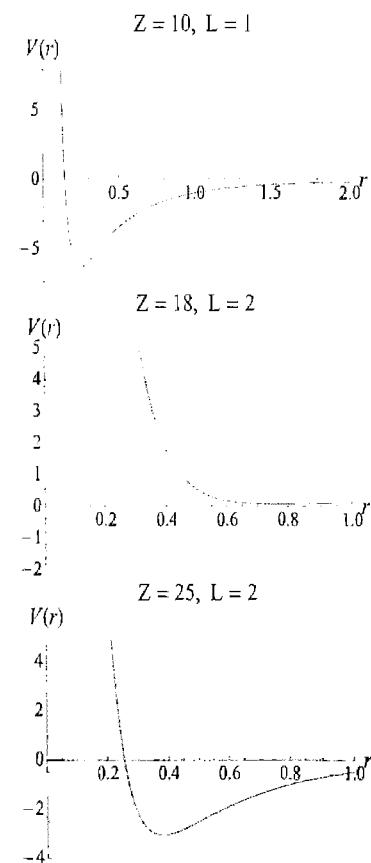


Fig. 22.7 Effective potentials at different Z for p and d electrons.

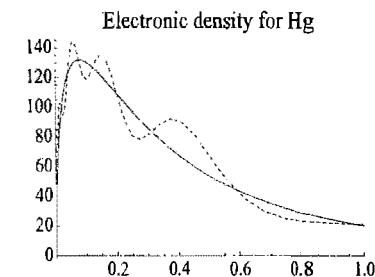


Fig. 22.8 Radial density $4\pi r^2 \rho(r)$ in Thomas–Fermi and Hartree–Fock approximation (dashed).

22.7.2 The Hartree approximation

In the Hartree approximation the Pauli exclusion principle is neglected and the wave function of the system is written in the form $\Psi = \prod_i \psi_i$. The factorized form in terms of single-particle wave functions ψ_i is typical of a mean field approximation. In the main text it has been stressed that the “best” choice for the ψ_i functions can be deduced from the variational principle. In the Hartree approximation a further constraint is added by asking for a radially symmetric effective potential. This is done in two steps:

- (a) The ψ_i functions are assumed in the form

$$\psi(\mathbf{x}) = R_{n\ell}(r)Y_{\ell m}(\Omega), \quad (22.101)$$

$R_{n\ell}$ is the radial wave function and the notation for the quantum numbers (n, ℓ, m) is the usual one for a radial potential.

- (b) We write a variational principle to determine the radial wave functions and, if necessary, we average over directions of angular momentum, enforcing the radial symmetry. The radial wave functions implicitly define the radial potential by the Schrödinger equation they satisfy.

The variational principle is obtained by writing the mean value of the Hamiltonian in the states of the form (22.101)

$$\begin{aligned} \langle \Psi | H | \Psi \rangle &= \sum_i \int_q \psi_i^* \left(-\frac{1}{2} \nabla^2 - \frac{Z}{r_i} \right) \psi_i \\ &\quad + \sum_{i < j} \int_{q,q'} \psi_i^*(q) \psi_j^*(q') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_i(q) \psi_j(q'), \end{aligned} \quad (22.102)$$

and imposing a zero variation with respect to changes in the radial wave functions.

The first term in eqn (22.102) is easily written in radial coordinates

$$\begin{aligned} \int_q \psi_i^* \left(-\frac{1}{2} \nabla^2 - \frac{Z}{r_i} \right) \psi_i &= \int_0^\infty dr P_{n\ell} \left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{Z}{r} + \frac{\ell(\ell+1)}{2r^2} \right) P_{n\ell} \\ &\equiv \int dr P_a(r) \mathcal{L}_a P_a(r) = I(n, \ell). \end{aligned} \quad (22.103)$$

We have defined the reduced radial wave function $P_{n\ell}$ with

$$P_{n\ell}(r) = r R_{n\ell}(r). \quad (22.104)$$

The interaction term in eqn (22.102) is

$$\begin{aligned} &\int dr_1 dr_2 d\Omega_1 d\Omega_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &P_{n_1 \ell_1}^2(r_1) P_{n_2 \ell_2}^2(r_2) |Y_{\ell_1 m_1}(\Omega_1)|^2 |Y_{\ell_2 m_2}(\Omega_2)|^2. \end{aligned} \quad (22.105)$$

Here we impose the radial symmetry performing an average on angular momentum projections. Using the identity

$$\sum_m |Y_{\ell m}|^2 = \frac{2\ell+1}{4\pi}, \quad \Rightarrow \quad \overline{|Y_{\ell m}|^2} \equiv \frac{1}{2\ell+1} \sum_m |Y_{\ell m}|^2 = \frac{1}{4\pi}, \quad (22.106)$$

the angular dependence in eqn (22.104) is confined in

$$\int \frac{d\Omega_1}{4\pi} \frac{d\Omega_2}{4\pi} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (22.107)$$

Let us now consider the multipoles expansion

$$\begin{aligned} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} &= \frac{1}{r_>} \sum_{k=0}^{\infty} \left(\frac{r_<}{r_>} \right)^k P_k(\cos \gamma) = \\ &= \frac{1}{r_>} \sum_{k=0}^{\infty} \left(\frac{r_<}{r_>} \right)^k \frac{4\pi}{2k+1} \sum_{m=-k}^k Y_{km}(\Omega_1) Y_{km}^*(\Omega_2), \end{aligned} \quad (22.108)$$

where $r_> = \max(r_1, r_2)$, $r_< = \min(r_1, r_2)$; γ is the angle between $\mathbf{r}_1, \mathbf{r}_2$. The last equality in eqn (22.108) follows from

$$P_k(\cos \gamma) = \frac{4\pi}{2k+1} \sum_{m=-k}^k Y_{km}(\Omega_1) Y_{km}^*(\Omega_2). \quad (22.109)$$

Using the orthogonality of the spherical harmonics one has

$$\int \frac{d\Omega_1}{4\pi} Y_{km}(\Omega_1) = \frac{1}{\sqrt{4\pi}} \int d\Omega_1 Y_{km}(\Omega_1) Y_{00}(\Omega_1) = \delta_{k0} \delta_{m0} \frac{1}{\sqrt{4\pi}},$$

and eqn (22.107) can be written as

$$\int \frac{d\Omega_1}{4\pi} \frac{d\Omega_2}{4\pi} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{r_>},$$

The interaction term (22.105) becomes

$$\int dr_1 dr_2 \frac{1}{r_>} P_{n_1 \ell_1}^2(r_1) P_{n_2 \ell_2}^2(r_2).$$

Let us note that the integral is symmetric:

$$\frac{1}{r_>} = \frac{1}{r_1} \theta(r_1 - r_2) + \frac{1}{r_2} \theta(r_2 - r_1).$$

The mean value of H , averaged over the angular momentum projections is

$$\langle \Psi | H | \Psi \rangle = \sum_{el} I(n\ell) + \sum_{pairs} \int dr_1 dr_2 \frac{1}{r_>} P_{n_1 \ell_1}^2(r_1) P_{n_2 \ell_2}^2(r_2).$$

It is convenient to simplify this expression by enumerating orbital functions instead of particles.

First introduce the function:

$$Y^0(n_1\ell_1, n_2\ell_2; r) = \int_0^r ds P_{n_1\ell_1}(s)P_{n_2\ell_2}(s) + \int_r^\infty ds \frac{r}{s} P_{n_1\ell_1}(s)P_{n_2\ell_2}(s). \quad (22.110)$$

One writes

$$\int \frac{1}{\max(r, r')} P_b^2(r') = \int_0^r dr' \frac{1}{r} P_b^2(r') + \int_r^\infty dr' \frac{1}{r'} P_b^2(r') = \frac{1}{r} Y^0(b, b; r).$$

Finally by using the identity

$$\sum_{pairs} X_{ij} = \sum_{i < j} X_{ij} = \frac{1}{2} \sum_{i,j} X_{ij} - \frac{1}{2} \sum_i X_{ii},$$

valid for any symmetric quantity, one finds for the Hamiltonian:

$$\begin{aligned} \langle \Psi | H | \Psi \rangle &= \sum_a q_a I(a) + \sum_{a,b} \frac{1}{2} q_a q_b \int dr P_a^2(r) \frac{1}{r} Y^0(b, b; r) - \\ &\quad - \frac{1}{2} \sum_a q_a \int dr P_a^2(r) \frac{1}{r} Y^0(a, a; r). \end{aligned} \quad (22.111)$$

The indices a, b now run over the *orbital* (i.e. over the quantum numbers (n, ℓ)). q_a stands for the multiplicity of the orbital. Introducing the function $F^0(a, b)$ representing the classical electrostatic energy:

$$F^0(a, b) = \int_r P_a^2(r) \frac{1}{r} Y^0(b, b; r) = \int dr_1 dr_2 P_a^2(r_1) \frac{1}{r_>} P_b^2(r_2).$$

Equation (22.111) can be written as

$$\begin{aligned} \langle \Psi | H | \Psi \rangle &= \sum_a q_a I(a) + \sum_{a,b} \frac{1}{2} q_a q_b F^0(a, b) - \sum_a \frac{1}{2} q_a F^0(a, a) \\ &= \sum_a q_a I(a) + \sum_{a \neq b} \frac{1}{2} q_a q_b F^0(a, b) + \frac{1}{2} \sum_a q_a (q_a - 1) F^0(a, a). \end{aligned}$$

This equation is identical to eqn (15.13) and eqn (15.14) of the main text. The radial functions must be normalized: it can be done in the variational approach with a Lagrange multiplier

$$\sum_i \varepsilon_i \left(\int dr P_i(r)^2 - 1 \right) = \sum_a q_a \varepsilon_a \left(\int dr P_a(r)^2 - 1 \right).$$

The Hartree equation follows from the variational principle

$$\frac{\delta}{\delta P_a(r)} \left[\overline{H} - \sum_b \varepsilon_b (\|P_b\|^2 - 1) \right] = 0.$$

An easy computation gives

$$\begin{aligned} \mathcal{L}_a P_a(r) + (q_a - 1) \frac{1}{r} Y^0(a, a; r) P_a(r) \\ + \sum_{b \neq a} q_b \frac{1}{r} Y^0(b, b; r) P_a(r) = \varepsilon_a P_a(r). \end{aligned}$$

where \mathcal{L}_a is the single-particle operator defined in eqn (22.103). These equations can be solved by an iterative procedure; some examples are given in the notebooks.

A subtle point is the following. The average on the angular quantum numbers, (22.106), in general destroys the orthogonality of the radial wave functions with the same ℓ . The result is thus incorrect due to a small superposition of these wave functions. To perform a consistent computation an additional set of Lagrange multipliers must be added to enforce the orthogonality: this will be discussed in the case of the Hartree–Fock equation.

22.7.3 Slater determinants and matrix elements

In a mean field approach, like the Hartree and the Hartree–Fock approximations, multiparticle wave functions are constructed starting from the single-particle eigenfunctions in effective fields. Pauli's principle requires a complete antisymmetric function, therefore these single particle functions must be anti-symmetrized, i.e. in the Slater determinants. An introduction to this subject is presented in the main text.

For atomic problems the single-particle functions are taken of the form (22.101) and equipped with a spinor

$$\psi_i = R_{n_i \ell_i}(r_i) Y_{\ell_i m_i}(\Omega_i) \chi_{s_i}(\sigma_i). \quad (22.112)$$

Determinants are constructed in the form given in the text, see eqn (15.25). We look for an effective radial potential, thus the quantum numbers for a single particle have the usual form (n, ℓ, m) , where n is the principal quantum numbers and (ℓ, m, s) describe angular momentum and spin states. With this choice it makes sense to speak about *shell* structure, with complete shells of the form $(1s^2, 2s^2, 2p^6, \dots)$, as in every central potentials. In this context a given shell structure, or *electronic term* will correspond to a fixed set of (n, ℓ) orbitals.

The Slater determinants constructed in this way have some general transformation properties under rotation which will be useful in the construction of the Hamiltonian eigenstates and which have been enumerated in the main text, see Section 15.4.

In the case of complete shells (nobel gases) only one Slater determinant is possible, and the variational principle will determine the radial wave functions by minimizing $\langle \Psi | H | \Psi \rangle$. For incomplete shells several determinant $|\Psi_a\rangle$ are possible for a given electronic configuration, and before the minimization process we must diagonalize the matrix $\langle \Psi_a | H | \Psi_b \rangle$. In the following we discuss the simplest kind of Hartree–Fock computation, in which *only one* electronic configuration is used, then the above determinants differ at most by azimuthal quantum numbers m, s (s stands for the eigenvalue of s_z).

In most cases the diagonalization procedure is avoided as the eigenstates of L, S are non-degenerate and therefore are automatically eigenstates of H , which commute with the total orbital momentum L and total spin S . This give rise to the usual structure of (L, S) multiplets.

To compute effectively the matrix elements of the Hamiltonian let us write H in the form

$$H = \sum_i f_i + \sum_{i < j} g_{ij} \equiv f + g ;$$

$$f_i = -\frac{1}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} ; \quad g_{ij} = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} .$$

In the following we assume that single-particle states (22.112) are orthogonal to each other.

One-particle operators

The operators f_i act on the coordinates of a single particle; they can have non-vanishing matrix elements only between the states which differ at most for one particle, the others being left unaffected by the operator.

Diagonal matrix elements (i.e. between the same Slater determinant) are trivially given by

$$\langle \Psi | \sum_i f_i | \Psi \rangle = \sum_i \langle i | f_i | i \rangle .$$

$|i\rangle$ stands for a wave function shown in eqn (22.112). Both kinetic terms and electron–nucleus interaction are rotationally invariant and spin independent, thus by using orthogonality of spherical harmonics one can write

$$\langle i | f_i | i \rangle = \int d\mathbf{r} r^2 R_{n_i \ell_i} R_{n_i \ell_i} \equiv I(n_i, \ell_i) . \quad (22.113)$$

We note explicitly that eqn (22.113) does not depend on the azimuthal quantum numbers (m_ℓ, m_s) therefore are the same for all Slater determinants within a given electronic configuration. As the dependence is restricted to the quantum numbers (n, ℓ) we have simply

$$\langle \Psi | f | \Psi \rangle = \sum_{el} I(n, \ell) \equiv \sum_a q_a I(n_a, \ell_a) \quad (22.114)$$

where again a stands for the orbital and q_a is its multiplicity. For example, for carbon, with a configuration $1s^2 2s^2 2p^2$ we have

$$\langle \Psi | f | \Psi \rangle = 2I(1s) + 2I(2s) + 2I(2p) .$$

The off-diagonal matrix elements of f are zero, within a given electronic configuration. In fact, two states can differ at most in their quantum numbers (m_ℓ, m_s), but the selection rules on the angular momentum and spin imply

$$\langle i | f | j \rangle \propto \delta_{m_i m_j} \delta_{s_i s_j} .$$

Two-particle operators

A generic matrix elements has the form

$$\langle \Psi_2 | g_{ij} | \Psi_1 \rangle = \int_{q_i, q_j} \psi_a^*(q_i) \psi_b^*(q_j) g_{ij} \psi_c(q_i) \psi_d(q_j) \prod_{k \neq i, j} \int_{q_k} \psi_{a_k}^*(q_k) \psi_{b_k}(q_k) .$$

As the ψ_a functions are assumed to be orthogonal at most two orbitals can be different between Ψ_1 and Ψ_2 .

(1) *Diagonal matrix elements.*

In this case, as all other orbitals are left unaffected, the pair (a, b) must coincide with the pair (c, d) and do the antisymmetry it follows

$$\langle \Psi | g | \Psi \rangle = \sum_{i < j} \left[(\langle i, j | g | i, j \rangle - \langle i, j | g | j, i \rangle) \right]; \quad (22.115)$$

Here $|i, j\rangle$ stands for single particle states and denoting with q space and spin variables:

$$\begin{aligned} \langle i, j | g | i, j \rangle &= \int_{q, q'} \psi_i^*(q) \psi_j^*(q') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_i(q) \psi_j(q'); \\ \langle i, j | g | j, i \rangle &= \int_{q, q'} \psi_i^*(q) \psi_j^*(q') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_j(q) \psi_i(q'). \end{aligned}$$

The second term is called *exchange integral*.

(2) *Off diagonal matrix elements. One orbital change $i' \rightarrow i$.*

It is easy to see that:

$$\langle \Psi | g | \Psi' \rangle = \sum_{j \neq i} \left[(\langle i, j | g | i', j \rangle - \langle i, j | g | j, i' \rangle) \right].$$

(3) *Off diagonal matrix elements. Two orbital changes $(i', j') \rightarrow (i, j)$.*

$$\langle \Psi | g | \Psi' \rangle = \left[(\langle i, j | g | i', j' \rangle - \langle i, j | g | j', i' \rangle) \right]. \quad (22.116)$$

We see that the most general matrix element is $\langle i, j | g | r, t \rangle$. Using the previous definitions its explicit form is

$$\begin{aligned} \langle i, j | g | r, t \rangle &= \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \sum_{\sigma, \sigma'} \chi_{s_i}(\sigma) \chi_{s_r}(\sigma) \chi_{s_j}(\sigma') \chi_{s_t}(\sigma') \\ &\quad R_{n_i \ell_i}(r_1) Y_{\ell_i m_i}^*(\Omega_1) R_{n_j \ell_j}(r_2) Y_{\ell_j m_j}^*(\Omega_2) \\ &\quad \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} R_{n_r \ell_r}(r_1) Y_{\ell_r m_r}(\Omega_1) R_{n_t \ell_t}(r_2) Y_{\ell_t m_t}(\Omega_2). \end{aligned} \quad (22.117)$$

Orthogonality of spin functions gives

$$\sum_{\sigma, \sigma'} \chi_{s_i}(\sigma) \chi_{s_r}(\sigma) \chi_{s_j}(\sigma') \chi_{s_t}(\sigma') = \delta_{s_i s_r} \delta_{s_j s_t},$$

in agreement with the spin independence of g .

The angular integration can be performed by using the multipole expansion, (22.108). Inserting this expansion the angular integral becomes

$$\begin{aligned} \frac{4\pi}{2k+1} \int d\Omega_1 Y_{\ell_i m_i}^*(\Omega_1) Y_{\ell_r m_r}(\Omega_1) Y_{km}(\Omega_1) \cdot \\ \int d\Omega_2 Y_{\ell_j m_j}^*(\Omega_2) Y_{\ell_t m_t}(\Omega_2) Y_{km}^*(\Omega_2). \end{aligned}$$

The index k is bounded by angular momentum composition rules

$$|\ell_i - \ell_r| \leq k \leq |\ell_i + \ell_r|; \quad |\ell_j - \ell_t| \leq k \leq |\ell_j + \ell_t|; \quad (22.118)$$

while the integration over the azimuthal angles φ_1, φ_2 gives

$$m = m_i - m_r; \quad m = m_t - m_j, \quad (22.119)$$

Defining

$$c^k(\ell_i, m_i; \ell_r, m_r) = \sqrt{\frac{4\pi}{2k+1}} \int d\Omega_1 Y_{\ell_i m_i}^*(\Omega_1) Y_{\ell_r m_r}(\Omega_1) Y_{km}(\Omega_1), \quad (22.120)$$

the angular integration gives

$$c^k(\ell_i, m_i; \ell_r, m_r) \cdot c^k(\ell_t, m_t; \ell_j, m_j).$$

We note that with our phase convention all imaginary parts contained in the spherical harmonics cancel. The coefficients c^k are related to the Clebsh–Gordan coefficients by

$$\begin{aligned} c^k(\ell_i, m_i; \ell_r, m_r) &= (-1)^{m_r} \sqrt{\frac{(2\ell_i+1)(2\ell_r+1)}{(2k+1)^2}} \\ &\quad C(\ell_i - m_i, \ell_r m_r | k m_r - m_i) C(\ell_i 0, \ell_r 0 | k 0), \end{aligned} \quad (22.121)$$

and can be listed, see also the notebooks. The above formulas can be made more symmetric by introducing Wigner's $3j$ -symbols, which are related to the Clebsh–Gordan coefficients by

$$\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix} = \frac{(-1)^{j_1-j_2+M}}{\sqrt{2J+1}} \langle j_1 m_1, j_2 m_2 | JM \rangle. \quad (22.122)$$

In this notation

$$\begin{aligned} c^k(\ell_i, m_i; \ell_r, m_r) &= (-1)^{m_i} \sqrt{(2\ell_i+1)(2\ell_r+1)} \\ &\quad \begin{pmatrix} \ell_i & \ell_r & k \\ -m_i & m_r & -(m_r - m_i) \end{pmatrix} \begin{pmatrix} \ell_i & \ell_r & k \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned}$$

while the integrals of spherical harmonics are written as

$$\int Y_{\ell_1 m_1} Y_{\ell_2 m_2} Y_{\ell_3 m_3} d\Omega = \left[\frac{(2\ell_1+1)(2\ell_2+1)(2\ell_3+1)}{4\pi} \right]^{1/2} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix}.$$

For later use we note that by using eqn (22.122) and orthogonality of spherical functions one can show

$$\begin{pmatrix} \ell & \ell & 0 \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{1}{(2\ell+1)}. \quad (22.123)$$

Substitution of the multipole expansion in eqn (22.117) gives rise to the radial integrals

$$R^k(ij; rt) = \int_0^\infty dr_1 dr_2 r_1^2 r_2^2 R_{n_i \ell_i} R_{n_j \ell_j} \frac{r_-^k}{r_+^{k+1}} R_{n_r \ell_r} R_{n_t \ell_t}, \quad (22.124)$$

and finally to

$$\langle ij | g | rt \rangle = \delta_{s_i s_r} \delta_{s_j s_t} \sum_k c^k(\ell_i, m_i; \ell_r, m_r) \cdot c^k(\ell_t, m_t; \ell_j, m_j) R^k(ij; rt). \quad (22.125)$$

The sum over k has only a finite number of terms due to eqn (22.118).

An important consequence of our selection rules for single configuration states is that the off-diagonal matrix elements differing by a single orbital vanish. Indeed suppose that $i = r$, $j \neq t$ in eqn (22.125). Spin conservation implies $s_j = s_t$. From eqn (22.119) one has $m_i = 0$, as $i = r$, and this implies $m_j = m_t$. As the two states j, t refer to the same electronic configuration they must have the same radial wave function (all other states being unaffected in the matrix element). Then the states j, t have the same radial function, the same angular momentum and the same spin, i.e. are equal contrary to the hypothesis.

Now one can write the matrix elements for H , starting from the simplest case, a closed shell structure.

22.7.4 Hamiltonians for closed shells

For an atom with only complete shells there is only one Slater determinant and one must compute

$$\langle \Psi | H | \Psi \rangle.$$

For single-particle operators one gets eqn (22.114):

$$\langle \Psi | f | \Psi \rangle = \sum_{el} I(n, \ell) \equiv \sum_a q_a I(n_a, \ell_a).$$

For closed shells, $q_a = 2(2\ell_a + 1)$.

The sum over the pairs of particles in eqn (22.115) can be split as a sum on particles in the same shell and a sum over pairs in different shells:

$$\langle \Psi | g | \Psi \rangle = \sum_a \left[(\langle i, j | g | i, j \rangle - \langle i, j | g | j, i \rangle) \right] + \sum_{a < b} \left[(\langle i, j | g | i, j \rangle - \langle i, j | g | j, i \rangle) \right]$$

As the shells are complete there appear in the sum all allowed combinations compatible with Pauli's principle for the quantum numbers $(m_i, s_i), (m_j, s_j)$. One can rewrite this sum as the *average* times the number of terms, i.e.

$$\binom{q_a}{2} = \frac{q_a(q_a - 1)}{2} = (2\ell_a + 1)(4\ell_a + 1); \quad q_a q_b$$

for particles in the same shell or in different shells, respectively. Then

$$\langle \Psi | g | \Psi \rangle = \sum_a \frac{q_a(q_a - 1)}{2} \bar{U}_{aa} + \sum_{a < b} q_a q_b \bar{U}_{ab}.$$

\bar{U} is the mean energy. Let us consider the two terms separately.

Equivalent electrons (same shell)

The average over pairs of different quantum numbers can be written as

$$\binom{q_a}{2} \bar{U}_{aa} = \sum_{\text{pairs}} g_{ij} = \frac{1}{2} \sum_{i \neq j} g_{ij} = \frac{1}{2} \sum_{i,j} g_{ij}.$$

We used the fact that for $i = j$ the exchange term cancel the direct term. The direct term in the sum can be written as

$$\begin{aligned} \frac{1}{2} \sum_{i,j} \langle ij | g | ij \rangle &= \frac{1}{2} \sum_{m_i s_i m_j s_j} \sum_{\sigma, \sigma'} \int_{\mathbf{r}_1, \mathbf{r}_2} \chi_{s_i}^*(\sigma) \chi_{s_j}^*(\sigma') \chi_{s_i}(\sigma) \chi_{s_j}(\sigma') \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &\quad R_{n\ell}(r_1) R_{n\ell}(r_2) Y_{\ell m_i}^*(\Omega_1) Y_{\ell m_j}^*(\Omega_2) R_{n\ell}(r_1) R_{n\ell}(r_2) Y_{\ell m_i}(\Omega_1) Y_{\ell m_j}(\Omega_2). \end{aligned}$$

The sum over spin variables gives a factor of 4, due to the normalization of spinors. Using eqn (22.109) and that for Legendre polynomials $P(\cos 0) = P_k(1) = 1$ one has the identity

$$\sum_{m=-\ell}^{\ell} Y_{\ell m}(\Omega_1) Y_{\ell m}^*(\Omega_1) = \frac{2\ell + 1}{4\pi} P_\ell(1) = \frac{2\ell + 1}{4\pi}$$

Substituting the multipole expansion one gets

$$\begin{aligned} \frac{1}{2} \sum_{i,j} \langle ij | g | ij \rangle &= \frac{1}{2} 4 \left(\frac{2\ell + 1}{4\pi} \right)^2 \int r_1^2 dr_1 r_2^2 dr_2 d\Omega_1 d\Omega_2 \\ &\quad R_{n\ell}^2(r_1) R_{n\ell}^2(r_2) \frac{1}{r_>} \sum_k P_k(\cos \gamma). \end{aligned}$$

where γ is the relative direction 1–2. The angular integration can be done by fixing the direction 1 and integrating over the relative angle, i.e. $d\Omega_1 d\Omega_2 = d\Omega_1 d\Omega_\gamma$. Finally, by using

$$P_k(\cos \gamma) = \sqrt{\frac{4\pi}{2k+1}} Y_{k0}(\Omega_\gamma),$$

the angular integral becomes

$$\int d\Omega_1 d\Omega_\gamma \sqrt{\frac{4\pi}{2k+1}} Y_{k0}(\Omega_\gamma) = \frac{(4\pi)^2}{\sqrt{2k+1}} \int d\Omega_\gamma Y_{k0} Y_{00} = (4\pi)^2 \delta_{k0}.$$

Using the reduced wave functions $P_{n\ell} = r R_{n\ell}$ we have then

$$\frac{1}{2} \sum_{i,j} \langle ij | g | ij \rangle = 2(2\ell + 1)^2 F^0(n, \ell; n, \ell).$$

The functions F^0 are a particular case of the more general functions

$$F^k(n_1, \ell_1; n_2, \ell_2) = \int dr_1 dr_2 |P_{n_1 \ell_1}(r_1)|^2 \frac{1}{r_>} \left(\frac{r_<}{r_>} \right)^k |P_{n_2 \ell_2}(r_2)|^2 ;$$

to be used below. F^k are an example of eqn (22.124).

Consider now the exchange term.

$$\begin{aligned} \frac{1}{2} \sum_{i,j} \langle ij|g|ji\rangle &= \frac{1}{2} \sum_{m_i s_i m_j s_j} \sum_{\sigma, \sigma'} \int_{\mathbf{r}_1, \mathbf{r}_2} \chi_{s_i}^*(\sigma) \chi_{s_j}^*(\sigma') \chi_{s_j}(\sigma) \chi_{s_i}(\sigma') \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ R_{n\ell}(r_1) R_{n\ell}(r_2) Y_{\ell m_i}^*(\Omega_1) Y_{\ell m_j}^*(\Omega_2) R_{n\ell}(r_1) R_{n\ell}(r_2) Y_{\ell m_j}(\Omega_1) Y_{\ell m_i}(\Omega_2) . \end{aligned}$$

The sum over spin variables now gives a factor 2, due to the fact that the exchange integral is different from zero only for equal spin:

$$\sum_{s_i s_j} \sum_{\sigma, \sigma'} \chi_{s_i}^*(\sigma) \chi_{s_j}^*(\sigma') \chi_{s_j}(\sigma) \chi_{s_i}(\sigma') = \sum_{s_i s_j} \delta_{s_i s_j} \delta_{s_i s_j} = 2 .$$

Using eqn (22.109) and the multipole expansion the angular integration reduces to

$$\begin{aligned} &\int d\Omega_1 d\Omega_\gamma \left(\frac{2\ell+1}{4\pi} \right)^2 P_\ell(\cos \gamma) P_\ell(\cos \gamma) P_k(\cos \gamma) \\ &= 4\pi \frac{2\ell+1}{4\pi} \int d\Omega_\gamma Y_{\ell 0}(\Omega_\gamma) Y_{\ell 0}(\Omega_\gamma) \sqrt{\frac{4\pi}{2k+1}} Y_{k 0}(\Omega_\gamma) \\ &= (2\ell+1) c^k(\ell, 0, \ell, 0; k, 0) . \end{aligned}$$

The coefficients c^k have been defined in eqn (22.120). The radial integrations are similar to those for the direct term and putting all together

$$\begin{aligned} \frac{1}{2} \sum_{i,j} \langle ij|g|ji\rangle &= (2\ell+1) \sum_k c^k(\ell, 0, \ell, 0; k, 0) F^k(n, \ell; n, \ell) \\ &= (2\ell+1) F^0(n, \ell; n, \ell) + (2\ell+1) \sum_{k>1} c^k(\ell, 0, \ell, 0; k, 0) F^k(n, \ell; n, \ell) . \end{aligned}$$

In the last equation we have used $c^0(\ell, 0, \ell, 0; 0, 0) = 1$. The factors F^0 combine in the two terms giving

$$2(2\ell+1)^2 - (2\ell+1) = (2\ell+1)(4\ell+1) ,$$

therefore

$$\begin{aligned} \frac{1}{2} \sum_{i,j} [\langle ij|g|ij\rangle - \langle ij|g|ji\rangle] &= (2\ell+1)(4\ell+1) F^0(n, \ell; n, \ell) \\ &\quad - (2\ell+1) \sum_{k>1} c^k(\ell, 0, \ell, 0; k, 0) F^k(n, \ell; n, \ell) \end{aligned}$$

The mean energy is finally

$$\overline{U}_{aa} = F^0(a; a) - \frac{1}{4\ell_a + 1} \sum_k c^k(\ell_a, 0, \ell_a, 0; k, 0) F^k(a; a) . \quad (22.126)$$

From parity invariance the sum over k runs over even integers between $k = 0$ e $k = 2\ell_a$ only. Using 3-j coefficients this can be written as

$$\frac{1}{4\ell_a + 1} c^k(\ell_a, 0, \ell_a, 0; k, 0) = \frac{(2\ell_a + 1)}{4\ell_a + 1} \begin{pmatrix} \ell_a & k & \ell_a \\ 0 & 0 & 0 \end{pmatrix}^2.$$

Non-equivalent electrons

The computation is similar to the previous one; we sketch the main points only. The number of states is

$$q_a q_b = 4(2\ell_a + 1)(2\ell_b + 1),$$

and the mean energy is given by

$$q_a q_b \bar{U}_{ab} = \sum_{i,j} [\langle ij|g|ij\rangle - \langle ij|g|ji\rangle]. \quad (22.127)$$

The direct term is given by

$$\begin{aligned} \sum_{i,j} \langle ij|g|ij\rangle &= \sum_{m_i s_i m_j s_j} \sum_{\sigma, \sigma'} \int_{\mathbf{r}_1, \mathbf{r}_2} \chi_{s_i}^*(\sigma) \chi_{s_j}^*(\sigma') \chi_{s_i}(\sigma) \chi_{s_j}(\sigma') \quad (22.128) \\ &\cdot R_{n_a \ell_a}(r_1) R_{n_b \ell_b}(r_2) Y_{\ell_a m_i}^*(\Omega_1) Y_{\ell_b m_j}^*(\Omega_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &\cdot R_{n_a \ell_a}(r_1) R_{n_b \ell_b}(r_2) Y_{\ell_a m_i}(\Omega_1) Y_{\ell_b m_j}(\Omega_2). \end{aligned}$$

The spin and angular momentum are summed as in the previous case, producing

$$\sum_{i,j} \langle ij|g|ij\rangle = 4(2\ell_a + 1)(2\ell_b + 1) F^0(n_a, \ell_a; n_b, \ell_b).$$

For the exchange term the spin part gives a factor 2 while the angular part is

$$\begin{aligned} &\int d\Omega_1 d\Omega_\gamma \left(\frac{2\ell_a + 1}{4\pi} \right) \left(\frac{2\ell_b + 1}{4\pi} \right) P_{\ell_a}(\cos \gamma) P_{\ell_b}(\cos \gamma) P_k(\cos \gamma) = \\ &4\pi \frac{\sqrt{(2\ell_a + 1)(2\ell_b + 1)}}{4\pi} \int d\Omega_\gamma Y_{\ell_a 0}(\Omega_\gamma) Y_{\ell_b 0}(\Omega_\gamma) \sqrt{\frac{4\pi}{2k + 1}} Y_{k0}(\Omega_\gamma) = \\ &= \sqrt{(2\ell_a + 1)(2\ell_b + 1)} c^k(\ell_a, 0, \ell_b, 0; k, 0). \end{aligned}$$

The radial part of the exchange term involves a new kind of integral:

$$G^k(n_a \ell_a; n_b \ell_b) = \int_{\mathbf{r}_1, \mathbf{r}_2} P_{n_a \ell_a}(r_1) P_{n_b \ell_b}(r_2) \frac{1}{r_>} \left(\frac{r_<}{r_>} \right)^k P_{n_b \ell_b}(r_1) P_{n_a \ell_a}(r_2).$$

Collecting the various contributions one has

$$\sum_{i,j} \langle ij|g|ji\rangle = 2\sqrt{(2\ell_a + 1)(2\ell_b + 1)} \sum_k c^k(\ell_a, 0, \ell_b, 0; k, 0) G^k(n_a \ell_a; n_b \ell_b).$$

Summing the direct and exchange terms the mean energy becomes

$$\begin{aligned}\bar{U}_{ab} &= F^0(n_a, \ell_a; n_b, \ell_b) \\ &\quad - \frac{1}{2} \frac{1}{\sqrt{(2\ell_a + 1)(2\ell_b + 1)}} \sum_k c^k(\ell_a, 0, \ell_b, 0; k, 0) G^k(n_a \ell_a; n_b \ell_b).\end{aligned}\quad (22.129)$$

Using 3-j coefficients

$$\frac{1}{\sqrt{(2\ell_a + 1)(2\ell_b + 1)}} c^k(\ell_a, 0, \ell_b, 0; k, 0) = \begin{pmatrix} \ell_a & k & \ell_b \\ 0 & 0 & 0 \end{pmatrix}^2.$$

Equations (22.126) and (22.129) solve our problem. Summing the two terms we find

$$\langle \Psi | H | \Psi \rangle = \sum_a q_a I(a) + \sum_a \frac{q_a(q_a - 1)}{2} \bar{U}_{aa} + \sum_{a < b} q_a q_b \bar{U}_{ab}. \quad (22.130)$$

or

$$\begin{aligned}E &= \sum_a q_a I(a) + \sum_a \frac{q_a(q_a - 1)}{2} \sum_{k=0} f_k(a) F^k(a, a) + \\ &\quad + \sum_{a < b} q_a q_b \left[F^0(a, b) + \sum_{k=0} g_k(a, b) G^k(a, b) \right]\end{aligned}\quad (22.131)$$

$$f_0(a) = 1; \quad f_k(a) = -\frac{(2\ell_a + 1)}{4\ell_a + 1} \begin{pmatrix} \ell_a & k & \ell_a \\ 0 & 0 & 0 \end{pmatrix}^2;$$

$$g_k(a, b) = -\frac{1}{2} \begin{pmatrix} \ell_a & k & \ell_b \\ 0 & 0 & 0 \end{pmatrix}^2;$$

$$F^k(a, b) = \int dr dr' P_a(r) P_a(r) U^k(r, r') P_b(r') P_b(r');$$

$$G^k(a, b) = \int dr dr' P_a(r) P_b(r) U^k(r, r') P_a(r') P_b(r');$$

$$U^{(k)}(r, s) = \frac{1}{r} \left(\frac{s}{r}\right)^k \theta(r - s) + \frac{1}{s} \left(\frac{r}{s}\right)^k \theta(s - r).$$

From these equations it is easy to compute the contribution to the energy of each pair:

$$\begin{aligned}s &\quad s \quad F^0[s, s] \\ p &\quad p \quad F^0[p, p] - \frac{2}{25} F^2[p, p] \\ d &\quad d \quad F^0[d, d] - \frac{2}{63} F^2[d, d] - \frac{2}{63} F^4[d, d]\end{aligned}$$

$$\begin{aligned}s &\quad s' \quad F^0[s, s'] - \frac{1}{2} G^0[s, s'] \\ s &\quad p \quad F^0[s, p] - \frac{1}{6} G^1[s, p] \\ s &\quad d \quad F^0[s, d] - \frac{1}{10} G^2[s, d] \\ p &\quad p' \quad F^0[p, p'] - \frac{1}{6} G^0[p, p'] - \frac{1}{15} G^2[p, p'] \\ p &\quad d \quad F^0[p, d] - \frac{1}{15} G^1[p, d] - \frac{3}{70} G^3[p, d] \\ d &\quad d' \quad F^0[d, d'] - \frac{1}{10} G^0[d, d'] - \frac{1}{35} G^2[d, d'] - \frac{1}{35} G^4[d, d']\end{aligned}\quad (22.132)$$

22.7.5 Mean energy

A quantity defined by Shortley and Slater, the *mean energy*, simplifies the analysis of energy levels in atoms with incomplete shells. We know that for a given electronic configuration the energy level is split in multiplets with eigenvalues $E(\lambda, L, S)$, where L, S are the total angular momentum and spin (commuting with the electrostatic electron interaction) and λ is some additional quantum number, eventually needed to distinguish the degenerate levels.

Let d_g be the degree of degeneracy of the electronic configuration, i.e. the number of independent Slater determinants. The eigenvalues $E(\lambda, L, S)$ are computed by diagonalizing H in the d_g -dimensional linear subspace generated by these states. The *unitary* transformation which diagonalizes H leaves invariant the trace of the operator and also the mean $1/d_g \text{Tr}(H)$. The trace can be computed in two different ways: either in the base of original Slater determinants or in the final base which diagonalizes H . Each level, after diagonalization, has a degree of degeneracy $(2L+1)(2S+1)$ so that we can write

$$\overline{E}_{\text{mean}} \equiv \frac{1}{d_g} \sum_{\alpha} \langle \Psi_{\alpha} | H | \Psi_{\alpha} \rangle = \frac{1}{d_g} \sum_{L,S} (2L+1)(2S+1) E(L, S). \quad (22.133)$$

The first representation of the mean energy amounts to a sum over all possible quantum numbers for the electrons, in particular for those in the incomplete shells. This summation is exactly what has been done in the previous section to compute the energy of complete shells. This means that for every electronic configuration (22.130) is *always* valid.

For instance, the reader can check that for carbon, with a configuration $1s^2, 2s^2, 2p^2$ one gets, from eqn (22.132)

$$\begin{aligned} \overline{E}_{\text{mean}} &= 2I(1s) + 2I(2s) + 2I(2p) + \sum_a \overline{U}_a + \sum_{a < b} \overline{U}_{ab}; \quad (22.134) \\ \sum_a \overline{U}_a &= \left[F^0(1s, 1s) + F^0(2s, 2s) + F^0(2p, 2p) - \frac{2}{25} F^2(2p, 2p) \right]; \\ \sum_{a < b} \overline{U}_{ab} &= 4 \left\{ F^0(1s, 2s) - \frac{1}{2} G^0(1s, 2s) \right. \\ &\quad \left. + F^0(1s, 2p) - \frac{1}{6} G^1(1s, 2p) + F^0(2s, 2p) - \frac{1}{6} G^1(2s, 2p) \right\}. \end{aligned}$$

The mean energy is useful because it gives a first easy approximation to the energy levels and allows to write the general form of energy by enumerating the *differences* of eigenvalues from the mean.

22.7.6 Hamiltonians for incomplete shells

We shall limit to those states built on a single-electronic configuration. Let $\Psi_{\alpha}, \Psi_{\beta}$ be the Slater determinants. We must compute and diagonalize

$$\langle \Psi_{\alpha} | H | \Psi_{\beta} \rangle, \quad \alpha, \beta = 1, \dots, d_g. \quad (22.135)$$

d_g is the degree of degeneracy of the configuration. The Slater determinants Ψ_α have a fixed “core” (the wave functions of the closed shells) and a variable part due to electrons in the incomplete shell. We write separately the off-diagonal and the diagonal matrix elements.

Off-diagonal matrix elements

We have already seen that if Ψ_α, Ψ_β refer to the same electronic configuration the matrix element (22.135) vanishes between states differing by a single particle. Off-diagonal elements are due to a change of two particles only. As both states share the same structure of closed shells the only orbitals which can change are those in the incomplete shells, relatively few in general. The only variation from i_α, j_α to i_β, j_β is in the azimuthal quantum numbers, the quantum numbers (n, ℓ) remaining unchanged. From general formulas one has eqn (22.116) and eqn (22.125)

$$\langle \Psi_\alpha | g | \Psi_\beta \rangle = \left[(\langle i_\alpha, j_\alpha | g | i_\beta, j_\beta \rangle - \langle i_\alpha, j_\alpha | g | j_\beta, i_\beta \rangle) \right].$$

$$\langle ij | g | rt \rangle = \delta_{s_i s_r} \delta_{s_j s_t} \sum_k c^k(\ell_i, m_i; \ell_r, m_r) \cdot c^k(\ell_t, m_t; \ell_j, m_j) R^k(ij; rt).$$

As the radial functions remain the same the only kind of R^k functions are the functions F^k and G^k already met, therefore

$$\langle i_\alpha, j_\alpha | g | i_\beta, j_\beta \rangle = \delta_{s_{i_\alpha} s_{i_\beta}} \delta_{s_{j_\alpha} s_{j_\beta}} \quad (22.136a)$$

$$\sum_k c^k(\ell_i, m_{i_\alpha}; \ell_i, m_{i_\beta}) c^k(\ell_j, m_{j_\beta}; \ell_j, m_{j_\alpha}) F^k(\ell_i, \ell_j);$$

$$\langle i_\alpha, j_\alpha | g | j_\beta, i_\beta \rangle = \delta_{s_{i_\alpha} s_{j_\beta}} \delta_{s_{j_\alpha} s_{i_\beta}} \quad (22.136b)$$

$$\sum_k c^k(\ell_i, m_{i_\alpha}; \ell_j, m_{j_\beta}) c^k(\ell_i, m_{i_\beta}; \ell_j, m_{j_\alpha}) G^k(\ell_i, \ell_j).$$

These matrix elements are easily written down once the coefficients c^k are computed.

Diagonal matrix elements

The single-particle matrix elements do not depend on the azimuthal quantum numbers. For each determinant one has the same contribution

$$\sum_a q_a I(a).$$

In the interaction part one can split the sum on pairs of particle in three terms

- (a) The sum over pairs belonging to complete shells.
- (b) The sum over pairs belonging to incomplete shells.
- (c) The sum on pairs with one particle in a complete shell and one in a incomplete shell.

In the following $i', j' \dots$ indicate states in the closed shells, $i'', j'' \dots$ states refer to the incomplete shells. For each state Ψ_α , using the cancellation between direct and exchange term in g_{ii} one has

$$\begin{aligned} \sum_{i < j} [\langle ij|g|ij\rangle - \langle ij|g|ji\rangle] &= \frac{1}{2} \sum_{ij} [\langle ij|g|ij\rangle - \langle ij|g|ji\rangle] = \quad (22.137) \\ \frac{1}{2} \sum_{i'j'} [\langle i'j'|g|i'j'\rangle - \langle i'j'|g|j'i'\rangle] + \sum_{i''j''} [\langle i''j''|g|i''j''\rangle - \langle i''j''|g|j''i''\rangle] + \\ \frac{1}{2} \sum_{i''j''} [\langle i''j''|g|i''j''\rangle - \langle i''j''|g|j''i''\rangle] . \end{aligned}$$

The first term clearly does not depend on the particular determinant. It is the “core” contribution to electrostatic energy. The main point is that also the second term, describing the interaction of an electron with a closed shell, is *independent* of the particular state Ψ_α . We shall prove this point below. This means that the difference between various matrix elements is related to the mutual interaction of electrons in the incomplete shells. We can say more: the mean energy of the first and second term in eqn (22.137) gives the *exact* result, as this contribution does not depend on the state. The third term has a common part, that contained in the mean energy, and a variable part, describing the deviation from the mean energy. Thus all matrix elements have the form

$$\langle \Psi_\alpha | H | \Psi_\alpha \rangle = E_{\text{mean}} + \delta U_\alpha , \quad (22.138)$$

where δU_α depends only on the electrons in the incomplete shells.

The explicit expression for matrix elements is always given by eqn (22.136), with $\alpha = \beta$. Thus

$$\langle ij|g|ij\rangle = \sum_k c^k(\ell_i, m_i; \ell_i, m_i) c^k(\ell_j, m_j; \ell_j, m_j) F^k(\ell_i, \ell_j) ; \quad (22.139a)$$

$$\langle ij|g|ji\rangle = \sum_k [c^k(\ell_i, m_i; \ell_j, m_j)]^2 G^k(\ell_i, \ell_j) . \quad (22.139b)$$

Example

Consider carbon $1s^2 2s^2 2p^2$. The $2p$ shell is incomplete. There exists three multiplets ${}^3P, {}^1D, {}^1S$. To compute the energies one can limit ourselves to the three dimensional subspace $L_z = 0, S_z = 0$ (the dimension being equal to the number of multiplets). Using the notation $v[\ell_z^1, s_z^1, \ell_z^2, s_z^2]$ the three independent states are given by

$$v[-1, -\frac{1}{2}, 1, \frac{1}{2}], v[-1, \frac{1}{2}, 1, -\frac{1}{2}], v[0, -\frac{1}{2}, 0, \frac{1}{2}]$$

On these states one can compute, with the above rules, the interaction matrix

$$U_{2p^2} = \begin{pmatrix} F^0[p] + \frac{1}{25}F^2[p] & -\frac{6}{25}F^2[p] & -\frac{3}{25}F^2[p] \\ -\frac{6}{25}F^2[p] & F^0[p] + \frac{1}{25}F^2[p] & \frac{3}{25}F^2[p] \\ -\frac{3}{25}F^2[p] & \frac{3}{25}F^2[p] & F^0[p] + \frac{4}{25}F^2[p] \end{pmatrix}$$

From eqn (22.130) one obtains the mean energy for the incomplete shell:

$$U_{\text{mean}} = F^0[p] - \frac{2}{25} F^2[p] \quad (22.140)$$

This can be subtracted from the eigenvalues of the above matrices to get the deviation from the mean energy. Let us stress that the mean energy is *not* the arithmetic mean of the matrix written above, one must take into account the multiplicities of the levels before computing the trace. The full expression for the mean energy, taking into account the closed shells, is given in eqn (22.134).

Proof for the interaction energy

Let us show that

$$\sum_{i''} [\langle i' j'' | g | i' j'' \rangle - \langle i' j'' | g | j'' i' \rangle] , \quad (22.141)$$

does not depend on the state Ψ_α considered. If so, the independence for the sum on j'' which appear in eqn (22.137) holds a fortiori.

Various states differ by the azimuthal quantum numbers of the orbital j'' ; we must show that eqn (22.141) does not depend on these quantum numbers. As far as s_z is concerned this is trivial, one must sum over indexes for complete shells then one will find the same numbers of terms with the spin parallel or anti-parallel to $s_{j''}$, keeping fixed all other variables. This means that the two projections $s_{j''} = \pm \frac{1}{2}$ have exactly the same expression. The only problem is the quantum number m_j (we omit apices).

For the direct term the dependence on m_j is in eqn (22.128):

$$Y_{\ell_i m_i}^*(\Omega_1) Y_{\ell_j m_j}^*(\Omega_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} Y_{\ell_i m_i}(\Omega_1) Y_{\ell_j m_j}(\Omega_2) :$$

it cancels between the two spherical harmonics depending on Ω_2 .

For the exchange term the general expression (22.125) gives

$$\langle ij | g | ji \rangle = \delta_{s_i s_j} \sum_k c^k(\ell_i, m_i; \ell_j, m_j) \cdot c^k(\ell_i, m_i; \ell_j, m_j) R^k(ij; ji). \quad (22.142)$$

Using eqn (22.121) the dependence on azimuthal numbers is

$$\langle \ell_i, -m_i; \ell_j, m_j | k, M \rangle^2, \quad M = m_j - m_i .$$

Using the symmetry property

$$\langle j_1, m_1; j_2, m_2 | JM \rangle = (-1)^{j_2 - J - m_1} \sqrt{\frac{2J+1}{2j_2+1}} \langle j_1, -m_1; J, M | j_2 m_2 \rangle ,$$

one can rewrite this expression as

$$\frac{2k+1}{2\ell_j+1} \langle \ell_i, m_i; k, M | \ell_j m_j \rangle^2 .$$

For fixed m_j, m_i only one index M contributes to this expression. One can sum over M and, using the orthogonality properties of Clebsh–Gordan coefficients, getting

$$\sum_{m_i, M} \langle \ell_i, m_i; k, M | \ell_j m_j \rangle^2 = 1$$

This means that there is no dependence on m_j in the exchange term either, q.e.d.

22.7.7 Eigenvalues of H

We can adopt several strategies for diagonalizing H . The first possibility is just to proceed by “brute force”; this is neither clever nor illuminating. A better choice is to note that L and S , the total angular momentum and spin, commute with H . This means that eigenstates can be organized in L -multiplets and S -multiplets, the so called fine-structure terms. Each multiplet contains the state $(L_z = 0, S_z = 0)$ for an even number of electrons, or the state $(L_z = 0, S_z = \frac{1}{2})$ for an odd number of electrons. The subspace of Slater determinants corresponding to this subspace is easily selected, as each determinant contains explicitly the azimuthal quantum numbers. A possible procedure can now be then:

- Choose a labeling for the Slater determinants, for instance

$$v[\{m_1, s_1, m_2, s_2 \dots\}], \quad (22.143)$$

where the quantum numbers refer to electrons in incomplete shells, and it is understood that the vectors are completely antisymmetric in the labels. Select the vectors with $(L_z = 0, S_z = 0)$ or $(L_z = 0, S_z = \frac{1}{2})$. These will span a subspace of dimension d_M , equal to the number of possible fine-structure terms.

- Define on these vectors the angular momentum operators and diagonalize it in this subspace.
- Write the matrix elements of H on this subspace and diagonalize it.

In most cases step (c) can be avoided as the eigenstates of L^2, S^2 are non-degenerate: H is diagonal in this basis. If some non-diagonal submatrices are left we must do step (c). The first case in which this occurs is for some excited levels with 3 d -electrons.

The angular momentum operators are defined by the usual formulas on the Slater determinants. For instance

$$L_+ v[\ell_1 m_1 \dots] = \sum_i \sqrt{\ell_i(\ell_i + 1) - m_i(m_i + 1)} v[\dots, m_i + 1, \dots].$$

The operators L^2, S^2 are given by

$$L^2 = L_+ L_- + L_z^2 - L_z; \quad S^2 = S_+ S_- + S_z^2 - S_z.$$

The computation of eigenstates is straightforward. In the example discussed above of carbon the subspace $(L_z = 0, S_z = 0)$ is generated by

$$v[-1, -\frac{1}{2}, 1, \frac{1}{2}], v[-1, \frac{1}{2}, 1, -\frac{1}{2}], v[0, -\frac{1}{2}, 0, \frac{1}{2}]$$

The eigenvalues of L^2, S^2 are easily seen to be

$$(L, S) = (1, 1); (0, 0); (0, 2)$$

and on this basis the H matrix is written as

$$E_{\text{mean}} + \begin{pmatrix} {}^3P & {}^1S & {}^1D \\ {}^3P & -\frac{3}{25}F^2[p] & 0 \\ {}^1S & 0 & \frac{12}{25}F^2[p] \\ {}^1D & 0 & 0 \end{pmatrix} \quad (22.144)$$

It is easily seen that for p^4 shells we obtain the same matrix and in general the difference between the mean energy and eigenvalues for a configuration is the same for the electrons and for the holes.

An interesting point is related to Hund's rule: the ground state of an atomic system is given by the term with the maximum S and, among them, the term with the maximum compatible L . This rule will be confirmed by explicit computation of the eigenvalues. It is easy to see in fact that this term is always isolated, i.e. belong to a non-degenerate subspace of H (apart from angular momentum orientations). The unique representative of the state can be constructed by putting all the spin "up" and assigning the L_z quantum numbers according to Pauli's principle, i.e.

$$v[\ell_z, \frac{1}{2}, (\ell_z - 1), \frac{1}{2}, \dots].$$

For more-than-half-filled shells, the vacancies (holes) take the place of the electrons. For instance, the ground state of a shell with 4 d -electrons has $S = 4 \cdot \frac{1}{2} = 2$ and from $L_z = 2, 1, 0, -1$ we deduce that $L = 2$, i.e. the ground state is 5D .

For one or two electrons an alternative procedure is to use the Clebsch-Gordan series to construct angular momentum eigenstates. Both cases are studied in the notebooks of this chapter.

Whichever approach is used to diagonalize H one obtains for the eigenvalues an expression of the form

$$\begin{aligned} E = \sum_a q_a I(a) + \sum_a \frac{q_a(q_a - 1)}{2} \sum_{k=0} f_k(a) F^k(a, a) + \\ + \sum_{a < b} q_a q_b \left[\sum_k f_k(a, b) F^k(a, b) + \sum_{k=0} g_k(a, b) G^k(a, b) \right], \end{aligned} \quad (22.145)$$

where the coefficients f_k, g_k are obtained from their mean energy values adding a shift depending on the particular term (i.e. (L, S)) considered. These deviations depend only on the structure of incomplete shells and can be computed once and for all.

22.7.8 The elementary theory of multiplets

The results obtained in the previous section allow a preliminary comparison with the experimental data. Suppose that we have a given set of radial wave functions, obtained for instance by solving the Hartree equations. We can compute the radial integrals F^k, G^k and obtain an approximation for the energy levels.

Some predictions are even *independent* of the particular value of the wave functions. This is apparent in example (22.144). The number of

independent integrals appearing in the deviation from the mean energy is lower than the number of the eigenvalues. This implies a relation between the energy levels. For instance, it is seen from eqn (22.144) that for configuration p^2 and p^4 the following relations hold:

$$\frac{E(^1S) - E(^1D)}{E(^1D) - E(^3P)} = \frac{3}{2}; \quad \frac{E(^2P) - E(^2D)}{E(^2D) - E(^4S)} = \frac{2}{3}. \quad (22.146)$$

A comparison between the prediction and the experimental values (we take a mean on the fine-structure splitting) is given in Table 22.1.

Atom	Config.	$\frac{^1S - ^1D}{^1D - ^3P}$	Atom	Config.	$\frac{^2P - ^2D}{^2D - ^4S}$
theory		1.50	theory:		0.667
C	$2p^2$	1.13	N	$2p^3$	0.500
Si	$3p^2$	1.48	P	$3p^3$	0.648
Ge	$4p^2$	1.50	As	$4p^3$	0.715
Sn	$5p^2$	1.39	Sb	$5p^3$	0.908
O	$2p^4$	1.14	Bi	$6p^3$	1.121
S	$3p^4$	1.43			
Te	$5p^4$	1.50			

Table 22.1 The ratios between the energy differences between different terms for p^2 and p^4 shells.

More detailed statements can be given using the explicit form of radial functions. For example in Figure 22.9 we report the calculated ionization potentials I compared with the experimental data. The agreement is qualitatively good, in particular the increasing shape of I and its small discontinuity at the half-filled shells. The agreement is better for complete shells, where the radial approximation used in the Hartree equation is exact.

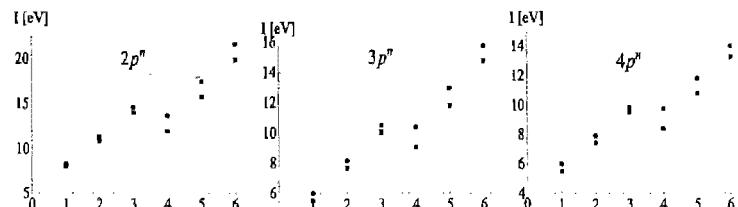


Fig. 22.9 Ionization potentials for the shells $2p^n$, $3p^n$, $4p^n$. The circles are experimental data, the squares the results obtained with Hartree-Fock approximation.

We stress that the agreement is not trivial, for instance the ionization potential for Kr is obtained from the difference of two quite large numbers:

$$E(Kr^+) - E(Kr) = [-74\,792.4 - (-74\,806.3)] \text{ eV} \simeq 13.9 \text{ eV},$$

showing that the precision on the eigenvalues is of the order of a fraction of percent. More precise predictions must avoid the assumption of identity of wave functions for each term. This can be done using a more sophisticated approach of the Hartree–Fock equation.

22.7.9 The Hartree–Fock equations

The basic idea behind this approximation is to choose the “best” radial functions which minimize the Hamiltonian for each (L, S) value, the choice is dictated by the variational principle. There exist several types of Hartree–Fock approximation varying by the choice of possible wave functions. We make the simplest assumptions:

- (1) The single-particle wave functions are taken in the form

$$\psi_{n\ell m\sigma}(\mathbf{r}, \tilde{\sigma}) = R_{n\ell}(r) Y_{\ell m}(\Omega) \chi_{\sigma}(\tilde{\sigma}), \quad (22.147)$$

with orthogonal functions. Equation (22.147) contains two implicit assumptions:

- The central field approximation used in the variational principle.
 - The assumption that the radial wave function is the same for both spin components.
- (2) We shall assume that the wave function of the system can be written as a linear combination of Slater determinants built with wave functions of a *single electronic configuration*, i.e. with a fixed set of quantum numbers (n, ℓ) . For instance for carbon the unknown quantities are the three radial functions R_{1s}, R_{2s}, R_{2p} . This approximation is usually known as SCHF (single configuration Hartree–Fock). A possible generalization is give by a MCHF scheme (multi configuration Hartree–Fock).
 - (3) Russell–Saunders coupling. We have constructed the eigenstates of H diagonalizing L and S , neglecting the spin–orbit interactions. This is a reasonable approximation for light atoms.

One must minimize the energy functional (22.131)

$$E = \sum_a q_a I(a) + \sum_a \frac{q_a(q_a - 1)}{2} \sum_{k=0} f_k(a) F^k(a, a) + \sum_{a < b} q_a q_b \left[\sum_k f_k(a, b) F^k(a, b) + \sum_k g_k(a, b) G^k(a, b) \right]. \quad (22.148)$$

under the constraint of orthogonal and normalized radial functions. At a pedagogical level one can start with a simpler problem of the minimization of mean energy functional, but as the formulas differ only in the values of the coefficients f_k, g_k we shall treat the more general problem directly.

The constraints can be introduced by the Lagrange multipliers in the variational principle:

$$V_L = \sum_i \varepsilon_i [(P_i, P_i) - 1] + \sum_{i \neq j} \delta_{\ell_i \ell_j} \varepsilon_{ij} (P_i, P_j). \quad (22.149)$$

Here P_i stands for the reduced radial wave functions and

$$(P_i, P_j) \equiv \int_0^\infty P_i(r) P_j(r) dr.$$

In the following we will suppress the factors $\delta_{\ell_a \ell_b}$ by putting $\varepsilon_{ab} = 0$ for $\ell_a \neq \ell_b$. It is convenient to rewrite eqn (22.149) as a sum over the orbitals occupied by the electrons:

$$V_L = \sum_a q_a \varepsilon_a [(P_a, P_a) - 1] + 2 \sum_{a < b} \delta_{\ell_a \ell_b} q_a q_b \varepsilon_{ab} (P_a, P_b). \quad (22.150)$$

Let us note that the Lagrange multipliers ε_{ab} are symmetric.

The Hartree–Fock equations are obtained with

$$\frac{\delta}{\delta P_a(r)} [E - V_L] = 0.$$

It is easy to check that

$$\begin{aligned} \frac{\delta}{\delta P_a(r)} F^k(a, a) &= 4 \left[\int ds P_a(s) P_a(s) U(s, r) \right] P_a(r) = \frac{4}{r} Y^k(a, a; r) P_a(r); \\ \frac{\delta}{\delta P_a(r)} F^k(a, b) &= 2 \left[\int ds P_b(s) P_b(s) U(s, r) \right] P_a(r) = \frac{2}{r} Y^k(b, b; r) P_a(r); \\ \frac{\delta}{\delta P_a(r)} G^k(a, b) &= 2 \left[\int ds P_a(s) P_b(s) U(s, r) \right] P_b(r) = \frac{2}{r} Y^k(a, b; r) P_b(r), \end{aligned}$$

where the potential functions Y^k are the generalization of those used in the Hartree approximation:

$$\begin{aligned} \frac{1}{r} Y^k(n_1 \ell_1, n_2 \ell_2; r) &= \int_0^r ds \frac{1}{r} \left(\frac{s}{r} \right)^k P_{n_1 \ell_1}(s) P_{n_2 \ell_2}(s) \\ &\quad + \int_r^\infty ds \frac{1}{s} \left(\frac{r}{s} \right)^k P_{n_1 \ell_1}(s) P_{n_2 \ell_2}(s). \end{aligned} \quad (22.151)$$

Let us note that the variation of the exchange integral introduces a term in which the unknown function, P_a , is part of an integral. Using eqn (22.150) a short computation gives

$$\begin{aligned} \mathcal{L}_a P_a + (q_a - 1) \sum_{k=0} f_k(a) \frac{1}{r} Y^k(a, a; r) P_a \\ + \sum_{b \neq a} q_b \left[\frac{1}{r} Y^0(b, b; r) P_a + \sum_{k=0} g_k(a, b) \frac{1}{r} Y^k(a, b; r) P_b(r) \right] \\ = \varepsilon_a P_a + \sum_b q_b \varepsilon_{ab} P_b, \end{aligned} \quad (22.152)$$

where

$$\mathcal{L}_a = \left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell_a(\ell_a+1)}{2r^2} - \frac{Z}{r} \right). \quad (22.153)$$

We have a set of integro-differential equations which can be solved by an iterative procedure. The diagonal parameters ε_a play the role of eigenvalues. To start an actual computation it is necessary to understand the role of the “off diagonal” parameters ε_{ab} and their relation to the uniqueness of the solution.

22.7.10 The role of Lagrange multipliers

In general we expect that the parameters ε_{ab} are small. Indeed if we multiply eqn (22.152) by P_b and integrate ε_{ab} can be expressed as an integral of an overlap of different wave functions, expected to be small. To effectively compute these parameters let us consider two orbitals with the same ℓ . The differential operator \mathcal{L} is the same and it is self-adjoint, i.e.

$$(P_b, \mathcal{L}_a P_a) - (P_a, \mathcal{L}_b P_b) = 0. \quad (22.154)$$

Substituting the equations for P_a e P_b in this relation one obtains after some tedious but trivial calculation

$$\begin{aligned} q_b \varepsilon_{ab} - q_a \varepsilon_{ba} &= \sum_{k=0} \sum_{c \neq a, b} q_c R^k(ac, bc) [g_k(a, c) - g_k(b, c)] \\ &\quad - R^0(aa, ab) [1 + q_a g_0(a, b)] + R^0(bb, ab) [1 + q_b g_0(a, b)] + \\ &\quad \sum_{k>0} R^k(aa, ab) [(q_a - 1)f_k(a) - q_a g_k(a, b)] \\ &\quad - \sum_{k>0} R^k(bb, ab) [(q_b - 1)f_k(b) - q_b g_k(a, b)]. \end{aligned} \quad (22.155)$$

The relations $f_0(a) = 1$ and $g_k(a, b) = g_k(b, a)$ have been used. The integrals R^k are those introduced in eqn (22.124):

$$R^k(ab, cd) = \int ds dt P_a(s) P_b(s) U^k(s, t) P_c(t) P_d(t). \quad (22.156)$$

We recall that the parameter ε_{ab} is symmetric. One has the following alternatives

(C1) $q_a \neq q_b$. In this case eqn (22.155) gives the value of ε_{ab} .

(C2) $q_a = q_b$. There are two possibilities:

(C2a) The combination on the right-hand side of eqn (22.155) is identically zero. In this case the coefficients are not fixed. We shall see in the next section the meaning of this result. We anticipate that in this case the coefficients can be set to zero (see Koopman's theorem in the next section).

(C2b) The right-hand side of eqn (22.155) is not identically zero. In this case eqn (22.155) puts a strong constraint on the solution and the coefficients ε_{ab} can be found with a technique similar

to the one used in a similar situation for a linear differential equation. Let us multiply by P_b the equation for P_a and sum the result to the same expression with (a, b) exchanged. Denoting by \mathcal{F} the operator in the left hand side of eqn (22.152) we obtain (with $q_a = q_b$):

$$2q_a \varepsilon_{ab} = (P_b, \mathcal{F}_a P_a) + (P_a, \mathcal{F}_b P_b). \quad (22.157)$$

To distinguish between the different cases we shall limit ourselves to the cases of the atoms with at most two incomplete shells.

Only complete shells

It has been shown, see page 715, that the interaction of an electron with a closed shell does not depend on the azimuthal quantum numbers but only on the moduli of the angular momentum. This means in particular that if at least one of the orbitals in the coefficient $g_k(c, d)$ in the formula above belongs to a closed shell, then this coefficient is independent on the azimuthal numbers and in particular it is equal to the coefficient computed for the mean energy, see eqn (22.131). This implies that the sum over c in the first term of eqn (22.155) is identically zero (we remember that a and b have the same angular momentum ℓ). For $k = 0$ the coefficient of the second term in eqn (22.155) is zero. This can be checked by using eqn (22.131) and eqn (22.123):

$$-1 + 2(2\ell+1)\frac{1}{2} \begin{pmatrix} \ell & 0 & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 = 0.$$

As for the other terms we note that for a closed shell $q_a = 2(2\ell_a + 1)$, thus also the last term vanishes

$$-(4\ell - 1)\frac{(2\ell + 1)}{4\ell + 1} \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 + 2(2\ell + 1)\frac{1}{2} \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 = 0.$$

This means that for closed shells we have the case (C2a) above, and $\varepsilon_{ab} = 0$.

One incomplete shell

This case and the previous one cover almost all atomic configurations in the ground state. If between the three orbitals a, b, c in the first term of eqn (22.155) at least two are complete, then this term vanishes as before. If a, b are closed shells also the remaining two terms vanish. The only nontrivial case is with a in a complete shell while b is in an incomplete shell (or viceversa). As a is complete the first terms in eqn (22.155) are zero and one is left with

$$(q_b - q_a) \varepsilon_{ab} = R^0(bb, ab) [1 + q_b g_0(a, b)] - \sum_{k>0} R^k(bb, ab) [(q_b - 1)f_k(b) - q_b g_k(a, b)].$$

Then for single incomplete shells the only coupling relevant for ε_{ab} is the one between the orbital in the incomplete shell and the electrons in the complete shells with the same angular momentum. In this case the above relation gives ε_{ab} as obviously $q_a \neq q_b$.

The first case which this appears is lithium, where the $2s$ electron pairs with the $1s^2$ shell. For carbon there is no coupling as there is a single p -orbital, with two electrons.

Two incomplete shells

If a, b are orbitals of complete shells, again the coefficients of eqn (22.155) vanish, and the relative Lagrange multipliers can be set to zero. If a belongs to a complete shell and b to an incomplete shell we have $q_a \neq q_b$ and the parameter ε_{ab} can be computed by using eqn (22.155) or eqn (22.157). If the both orbitals belong to incomplete shells, the situation is more complicated. One must distinguish between the options (C2a) and (C2b) listed above. In the present case, where a and b are both incomplete, the orbital c in eqn (22.155) belongs to a complete shell and the first term in this expression vanishes. One must compute the last two terms. If they identically vanish then one can put $\varepsilon_{ab} = 0$; otherwise one must determine ε_{ab} by using eqn (22.157).

This case happens, for instance, for excited helium with $1s2s$. There are two terms in the spectrum, ${}^3S, {}^1S$. Using the known techniques one shows easily that

$$\begin{aligned} {}^3S : \quad g_0(1s, 2s) &= -1 \Rightarrow 1 + g_0(1s, 2s) = 0 \\ {}^1S : \quad g_0(1s, 2s) &= +1 \Rightarrow 1 + g_0(1s, 2s) = 2 \end{aligned}$$

In the first case one can put $\varepsilon_{ab} = 0$ while in the second case (22.157) must be computed. This case of the excited helium is one of the worst cases as far as the convergence properties for the Hartree–Fock equations are concerned.

22.7.11 Koopman's theorem

A central problem in the solution of Hartree–Fock equations is the determination of energy parameters ε_{ij} which appear in the form of Lagrange multipliers. This problem is also related to the uniqueness of the solution of the equations. Koopman's theorem states that for closed-shell atoms (or for configurations satisfying the more general condition obtained from eqn (22.159) below) the off-diagonal coefficients can be set to zero and the resulting diagonal matrix can be interpreted as the set of ionization energy for the single orbitals. This covers almost all configurations of interest for low-excited atoms; in the remaining cases the off-diagonal matrix elements must be found as part of the solution, as explained below and in the numerical problems of the book.

In the usual radial Schrödinger equation for a single particle the uniqueness of the solution for a bound state is determined by two conditions, $R_{nl} \in \mathbb{L}^2$ and a choice of phase, for instance, $R_{nl}(r) > 0$ as $r \rightarrow 0$.

Let us consider now the Slater determinants and suppose that they are built of \mathbb{L}^2 functions. It remains to be seen what the analogue of the choice of phase is. The generic form is

$$\Psi = \det(\psi_i(q_j)),$$

and this is invariant under a general unitary transformation of the rows

$$\psi_j(q_j) \rightarrow U_{ik} \psi_k(q_j), \quad (22.158)$$

or in general, under any linear combination of them. The transformations (22.158) leave invariant the orthogonality relations $\langle \psi_i | \psi_j \rangle = \delta_{ij}$. Generalizing the one-dimensional case, the uniqueness of the solution can be obtained by fixing this arbitrariness. In the Hartree–Fock case the freedom is somewhat limited: we have assumed the form (22.147) for single-particle states, i.e. the radial part of the wave function must be the same for both components of the spin. Only the transformations which change the two spin components in the same way are allowed. For example, for Li in the configuration $1s^2 2s$ with Slater determinant

$$\begin{vmatrix} R_{10}(r_1)\chi_+(\sigma_1) & R_{10}(r_2)\chi_+(\sigma_2) & R_{10}(r_3)\chi_+(\sigma_3) \\ R_{10}(r_1)\chi_-(\sigma_1) & R_{10}(r_2)\chi_-(\sigma_2) & R_{10}(r_3)\chi_-(\sigma_3) \\ R_{20}(r_1)\chi_+(\sigma_1) & R_{20}(r_2)\chi_+(\sigma_2) & R_{20}(r_3)\chi_+(\sigma_3) \end{vmatrix}.$$

a transformation which mixes the first and the third row is not allowed, as the two spinor components (first and second row) would acquire a different radial part. The same considerations can be made for angular parts, i.e. spherical harmonics. This means that the only allowed transformations are those between radial functions, and if the phases are fixed in such a way that the functions P_a are real, only orthogonal transformations between the functions with the same ℓ are allowed.

For the Hartree–Fock equations the situation is a little worse for two reasons:

- (a) The solution is in general a sum of several Slater determinants.
- (b) In the Hartree–Fock equations the orthogonality is a *result*, obtained through Lagrange multipliers. If we perform an orthogonal transformation on the P_a 's the equations change. Let us put $\lambda_{ab} = q_a \epsilon_{ab}$. It is easy to see that the matrix λ changes as $U^\dagger \lambda U$. The value of the multipliers depends on the transformation matrix. How can one find it by solving the HF equations?

The variational principle helps in clarifying the problem. The uniqueness of the minimum for the Hamiltonian clearly does not depend on the value of Lagrange multipliers, therefore the correct question is: are there orthogonal transformations which leave invariant the minimum? If there are such transformation it is necessary to impose additional constraints to solve the Hartree–Fock equation, and this condition will fix the undefined Lagrange parameters.

Let us consider an infinitesimal orthogonal transformation between two orbitals a, b , with the same angular momentum

$$P_a \rightarrow P_a + \theta P_b; \quad P_b \rightarrow P_b - \theta P_a; \quad \theta \ll 1.$$

The general case can be recovered by successive small transformations so we are not limiting ourselves. Let us consider in eqn (22.148) the term which depends on these orbitals

$$\begin{aligned} E(a, b) &= q_a I(a) + q_b I(b) \\ &+ \frac{q_a(q_a - 1)}{2} \sum_{k=0} f_k(a) F^k(a, a) + \frac{q_b(q_b - 1)}{2} \sum_{k=0} f_k(b) F^k(b, b) \\ &+ q_a q_b \left[F^0(a, b) + \sum_{k=0} g_k(a, b) G^k(a, b) \right] \\ &+ \sum_c q_a q_c \left[F^0(a, c) + \sum_{k=0} g_k(a, c) G^k(a, c) \right] \\ &+ \sum_c q_b q_c \left[F^0(b, c) + \sum_{k=0} g_k(b, c) G^k(b, c) \right]. \end{aligned}$$

Using the variations

$$\begin{aligned} \delta_\theta F^k(a, a) &= 4\theta R^k(aa, ab); \quad \delta_\theta F^k(b, b) = -4\theta R^k(bb, ab); \\ \delta_\theta F^k(a, b) &= 2\theta [R^k(ab, bb) - R^k(aa, ab)]; \\ \delta_\theta G^k(a, b) &= 2\theta [R^k(bb, ab) - R^k(aa, ab)]; \\ \delta_\theta F^0(a, c) &= 2\theta R^0(ab, cc); \quad \delta_\theta F^0(b, c) = -2\theta R^0(ab, cc); \\ \delta_\theta G^k(a, c) &= 2\theta R^k(ac, bc); \quad \delta_\theta G^k(b, c) = -2\theta R^k(ac, bc), \end{aligned}$$

one gets

$$\begin{aligned} \delta_\theta E(a, b) &= 2\theta (q_a - q_b) (a, Lb) \\ &+ 2\theta q_a R^k(aa, ab) [(q_a - 1)f_k(a) - q_b \delta_{k0} - q_b g_k(a, b)] \\ &- 2\theta q_b R^k(bb, ab) [(q_b - 1)f_k(b) - q_a \delta_{k0} - q_a g_k(a, b)] \\ &+ 2\theta \sum_c q_c (q_a - q_b) \left[R^0(ab, cc) + \sum_k (g_k(a, c) - g_k(b, c)) R^k(ac, bc) \right]. \end{aligned} \tag{22.159}$$

We see that we have invariance if $q_a = q_b$ and if the coefficients in eqn (22.159) are identically vanishing. This happens in particular if a, b are orbitals of closed shells. In this case the conditions in eqn (22.159) reduce to those considered in eqn (22.155) and the HF *does not* fix the solution, as an arbitrary orthogonal transformation of the type considered above leaves E invariant. We have seen that the matrix $\lambda_{ab} = q_b \epsilon_{ab}$ transforms as $U^\dagger \lambda U$. For $q_a = q_b$ the matrix λ is symmetric: it can be diagonalized by an orthogonal transformation. We can choose the transformation U as the diagonalizing matrix. With this transformation

we see that by fixing $\varepsilon_{ab} = 0$ in the HF equation is equivalent to fixing the phase in the usual Schrödinger equation.

The physical meaning of all this is quite clear: the eigenvalues of the inatrix λ_{ab} have the value $q_a \varepsilon_a$, as usual are the extrema of the matrix (as for every symmetric matrix). As the values $\lambda_{aa} = q_a \varepsilon_a$ appear in the equation as the energy of the electron in the orbital a , the extremization of the matrix corresponds to applying the variational principle to the single orbital. This interpretation can be translated into a computation similar to the one exposed in the text for the Hartree equation (we leave it as an exercise).

This is the content of Koopman's theorem: for closed shells or in general for systems in which the coefficients in eqn (22.159) vanish, the terms ε_{ab} with $a \neq b$ can be set to zero and the diagonal Lagrange parameters can be interpreted as the energy of the orbital.

This theorem solves the problem raised in the study of eqn (22.155): as stated all non-diagonal parameters can be set to zero with the only exception of case (C2b) where one must use eqn (22.157).

This machinery is used in the numerical notebooks of the chapter to effectively solve the Hartree-Fock equation.

22.8 H_2^+

Just as the hydrogen atom is the simplest atomic system, the H_2^+ ion represents the simplest of molecular binding. It is a bound state of two protons and an electron. A brief account of the nature of this molecular binding (which is the basis for understanding the chemical bonds) will be given here. The molecular binding, though caused by the same electrostatic Coulomb interactions as in the case of the atomic binding, exhibits considerably different features from the latter, which was studied in the main text and in the preceding Section 22.7 in some detail.

Neglecting the center-of-mass motion the Hamiltonian of H_2^+ is given by

$$H = \frac{\mathbf{p}_R^2}{2\mu} + \frac{e^2}{R} - \frac{\mathbf{p}^2}{2m} - \frac{e^2}{r_1} - \frac{e^2}{r_2},$$

where \mathbf{R} is the relative position of the two protons, \mathbf{p}_R the conjugate momentum, \mathbf{p} the momentum operator of the electron.

The proton mass is about 2000 times larger than the electron mass, so mechanically we can think of the H_2^+ molecule as a bound state of two protons, surrounded by the cloud of the electron wave function. Of course, in the absence of the electron the rest of the system—two protons—will repel each other by the Coulomb repulsion, without the possibility of forming a bound state. It is known that even a short-distance attraction due to the nuclear interactions is not sufficient to bind two protons (even though in the case of a proton and a neutron, a nuclear bound state—the deuteron—exists.) In other words, it is the electron cloud which causes an effective attraction between the two pro-

tons.

As the proton mass is relatively enormous, the frequency of the electron motion is much higher than the characteristic frequency associated with the proton motion. The latter can therefore be treated adiabatically in considering the electron motion. Such a treatment is known as the *Born–Oppenheimer approximation*. We thus consider the quantization of the electron motion for fixed R , to begin with. Let us first consider the case $R \gg r_B$, where $r_B = \frac{\hbar^2}{m e^2}$ is the Bohr radius. In such a condition the electron moves in the two Coulomb potential wells, far distant from each other. In a first approximation, the ground state of such a system will be the electron in the ground state of the hydrogen atom formed around one of the protons. Of course the electron can be bound to one proton or to the other, so the system is doubly degenerate. It is similar to the one-dimensional double-well problem. Consider for instance, the state in which the electron is bound to the proton 1. In the reduced Hamiltonian, neglecting the proton kinetic terms,

$$H = \frac{\mathbf{p}^2}{2m} - \frac{e^2}{r_1} + \frac{e^2}{R} - \frac{e^2}{r_2},$$

the last two terms due to the other proton can be regarded as a small perturbation. For $R \gg r_B$ we can expand:

$$H' = \frac{e^2}{R} - \frac{e^2}{r_2} = \frac{e^2}{R} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{R}|} = -\frac{e^2}{R} \sum_{\ell=1}^{\infty} \left(\frac{r_1}{R}\right)^\ell P_\ell(\cos \theta),$$

where $\mathbf{r}_1 \cdot \mathbf{R} = r_1 R \cos \theta$. To the first-order in $\frac{1}{R}$ we have

$$H' \simeq -\frac{e^2}{R^2} r_1 \cos \theta = -\frac{e^2}{R^2} z$$

and the problem is reduced to the polarizability of the hydrogen atom in an external static electric field, $\mathcal{E} = \frac{e}{R^2}$. This problem has been studied in Chapter 9 of the main text, see Subsections 9.1.3, and 21.1.4. The correction to the first-order vanishes obviously; the result to the second order is:

$$\Delta E = \sum_{n,\ell,m} \frac{|\langle n\ell m | z | 100 \rangle|^2}{E_{100} - E_{n\ell m}} = -\frac{9e^4}{4R^4}.$$

Actually, such a perturbative analysis does not capture an important “non-perturbative” effect, due to the tunneling of the electron from the one Coulomb well to the other. The situation is analogous to that of a one-dimensional double well (see Section 11.3.1). The doubly degenerate ground state actually splits into two closely lying levels, with the energy splitting due to the tunnel effect given by

$$\Delta E = c e^{-\frac{1}{\hbar} \int dr \sqrt{2m(V-E)}} = c e^{-R/r_B}, \quad c = 1.47 \frac{R e^2}{r_B^2},$$

(the determination of the constant c is given in [Landau and Lifshitz (1976 c)], §81). The ground state corresponds to the symmetric combination

$$\psi_0 \simeq \frac{1}{\sqrt{2}}(\psi_0(\mathbf{r}_1) + \psi_0(\mathbf{r}_2)); \quad (22.160)$$

the ground-state energy is therefore

$$E_0 \simeq -\frac{e^2}{2\tau_B} - \frac{9}{4} \frac{e^4}{R^4} - \frac{c}{2} e^{-R/\tau_B}.$$

Both the perturbative effect (polarization of the electron cloud) and non-perturbative one (tunnel effect) are attractive, and tend to reduce the inter-proton distance R .

Let us note that to all orders of perturbation in H' , the double degeneracy mentioned above remains exact: only the non-perturbative effect is able to eliminate it. In other words, although the effects of powers in $\frac{1}{R}$ are certainly dominant over the exponentially suppressed tunneling amplitude, the latter is the dominant contribution in the difference between the ground-state energy and that of the excited state.

To understand the qualitative features of the H_2^+ molecule, however, it is necessary to consider the region $R \sim \tau_B$ which, we shall find out *a posteriori*, will be the most relevant regime. In those ranges of R the approximation sketched above is no longer valid. Nevertheless, the weakness of the molecular binding suggests that a wave function of the type (22.160) might not be too far from a realistic wave function. As a simple variational Ansatz we may choose a form

$$\Psi = c_1 \psi_1 + c_2 \psi_2, \quad (22.161)$$

$$\psi_1(\mathbf{r}) = \psi_{100}(r_1); \quad \psi_2(\mathbf{r}) = \psi_{100}(r_2);$$

where R , c_1 e c_2 are the variational parameters, and where $\psi_{100}(r_1)$ is the ground-state wave function of a hydrogen atom (near the first proton), and similarly for $\psi_{100}(r_2)$. The solution of the eigenvalue problem with a trial function of such a form requires some care, as the functions $\psi_{100}(r_1)$ and $\psi_{100}(r_2)$ are not orthogonal to each other. In fact, at fixed R the equations to be solved reduce to the eigenvalue problem:

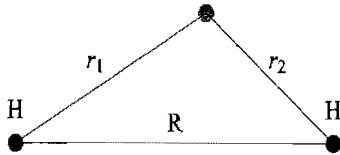


Fig. 22.10 Elliptic coordinates for H_2^+ .

that is,

$$(H_{11} - E S_{11}) c_1 + (H_{12} - E S_{12}) c_2 = 0, \quad (22.162)$$

$$(H_{21} - E S_{21}) c_1 + (H_{22} - E S_{22}) c_2 = 0,$$

where $S_{ij} = \langle \psi_i | \psi_j \rangle$; $H_{ij} = \langle \psi_i | H | \psi_j \rangle$, which determine $c_{1,2}$ apart from the normalization, and E as a function of R . With the choice of the independent variational parameters (r_1, r_2, ϕ) , see Figure 22.10, $\mathbf{R}_1 = (0, 0, R/2)$, $\mathbf{R}_2 = (0, 0, -R/2)$,

$$r_1 = |\mathbf{r} - \mathbf{R}_1| = \sqrt{x^2 + y^2 + (z - R/2)^2},$$

$$r_2 = |\mathbf{r} - \mathbf{R}_2| = \sqrt{x^2 + y^2 + (z + R/2)^2},$$

$$\tan \phi = \frac{y}{x},$$

$$d^3r = \frac{1}{R} dr_1 r_1 dr_2 r_2 d\phi, \quad |R - r_1| \leq r_2 \leq R + r_1, \quad 0 < r_1 < \infty.$$

Evaluation of the various integrals appearing in H_{ij} and S_{ij} is elementary. For example, the “exchange integral” $S \equiv S_{12} = \langle \psi_1 | \psi_2 \rangle = \langle \psi_2 | \psi_1 \rangle$ gives (setting $r_B = 1$)

$$S_{12} = e^{-R} \left(1 + R + \frac{R^2}{3} \right).$$

The orthonormal eigenstates of H are symmetric and antisymmetric combinations,

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2(1 \pm S)}} (|\psi_1\rangle \pm |\psi_2\rangle),$$

with the corresponding eigenvalues (in the atomic unit):

$$\begin{aligned} E_{\pm}(R) = & \quad (22.163) \\ & \frac{1}{2} \left[-1 + \frac{2}{R} \mp \frac{2e^{-R}(1+R) \pm \frac{2}{R} \{1 - e^{-2R}(1+R)\}}{1 \pm e^{-R}(1+R+R^2/3)} \right]. \end{aligned}$$

Only in the symmetric state (ψ_+) the two protons attract each other and form a bound state, with the effective distance of the order of $R \sim 2r_B$. At $R \rightarrow \infty$ the energy tends to that of the hydrogen atom, naturally. In the antisymmetric states the protons repel each other: no bound states can be formed. See Figure 22.11.

The energy $E_+(R)$ should then be treated as a potential for the relative motion of the two protons,

$$V(R) = E_+(R) = E_{min} + \frac{1}{2}\Omega^2(R - R_{min})^2 + \dots, \quad (22.164)$$

which introduces, after quantization, various vibrational levels. In more general molecules, the attraction due to the electrons gives rise to the positions of the atomic nuclei in a three-dimensional structure. For instance, the ammonia ($N-H_3$) molecule has a well-known tetrahedral structure, with the base formed by the three hydrogen atoms. Quantization of the oscillations around the equilibrium positions of the atoms will give rise to a complicated vibrational levels. Also, there are various rotational levels (like the rotations of the proton–proton axis in the case of H_2^+) to be taken into account. See [Davydov (1965), Landau and Lifshitz (1976 c)] for an introductory discussion on the molecular levels.

Quantitatively the approximation (22.161) is not of the highest precision. A more precise calculation requires a better variational evaluation. The difference between them is reported in Figure 22.12. Details of the calculation are given in the Mathematica notebook, H2piu.nb, of the accompanying CD.

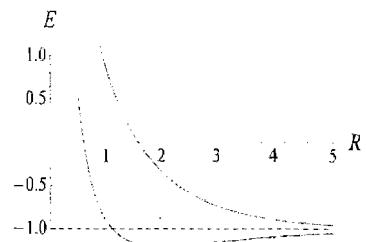


Fig. 22.11 The energy (in Rydberg) of the ground state and of the first excited state of H_2^+ .

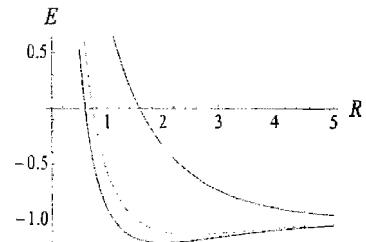


Fig. 22.12 A better variational calculation for the ground-state energy (full curve) is compared to the approximate one obtained from eqn (22.163) (dashed curve).

22.9 The Gross–Pitaevski equation

The Hartree–Fock equation can be written also for the bosons. An example of this sort can be written for an ensemble of atoms of spin

zero. The equation in this case has an application in the so-called Bose-Einstein condensation phenomenon.

Consider for simplicity only the ground state of a system of a Hamiltonian of the type:

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_{i < j} U(\mathbf{r}_i - \mathbf{r}_j) + \sum_i V(\mathbf{r}_i). \quad (22.165)$$

V is a possible external potential. For simplicity, we consider the case of spinless atoms; otherwise it is necessary consider wave functions $\varphi_\alpha(\mathbf{r})$ where α indicates the spin components, and to take into account spin-dependent interactions in general.

In the independent-particle approximation the ground state of the system is described by

$$\Psi = \prod_{i=1}^N \varphi(\mathbf{r}_i),$$

in which all the particles occupy the same state, φ .

To determine φ we use the variational principle. The expectation value of H in the state Ψ can be written in a very simple way, as the single-particle matrix elements are all equal:

$$\begin{aligned} E[\varphi] &= \langle \Psi | H | \Psi \rangle = \\ &= N \int d^3\mathbf{r} \varphi^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \varphi(\mathbf{r}) + N \int d^3\mathbf{r} \varphi^*(\mathbf{r}) V(\mathbf{r}) \varphi(\mathbf{r}) \\ &\quad + \frac{N(N-1)}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \varphi^*(\mathbf{r}) \varphi^*(\mathbf{r}') U(\mathbf{r} - \mathbf{r}') \varphi(\mathbf{r}) \varphi(\mathbf{r}'). \end{aligned}$$

$N(N-1)/2$ is the number of the pairs. In the most cases of interest, $N \gg 1$, so this number can be approximated by $N^2/2$. The functional E depends then only on $\Phi = \sqrt{N} \varphi$:

$$\begin{aligned} E[\Phi] &= \langle \Psi | H | \Psi \rangle = \int d^3\mathbf{r} \Phi^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) \Phi(\mathbf{r}) \\ &\quad + \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \Phi^*(\mathbf{r}) \Phi^*(\mathbf{r}') U(\mathbf{r} - \mathbf{r}') \Phi(\mathbf{r}) \Phi(\mathbf{r}'). \end{aligned}$$

The variational principle requires the normalization condition, which in the new variables take the form $\langle \Phi | \Phi \rangle = N$:

$$\frac{\delta}{\delta \Phi^*(\mathbf{r})} \left(E[\Phi] - \mu \left(\int |\Phi|^2 - N \right) \right) = 0;$$

it follows then that

$$\begin{aligned} &- \frac{\hbar^2}{2m} \nabla^2 \Phi + V(\mathbf{r}) \Phi + \int_{\mathbf{r}'} U(\mathbf{r} - \mathbf{r}') |\Phi(\mathbf{r}')|^2 \Phi(\mathbf{r}) = \mu \Phi; \\ &\int |\Phi|^2 = N. \end{aligned} \quad (22.166)$$

At low energies, i.e., at large wavelengths, it is usual to approximate⁹

⁹The scattering length at low energies between two particles of mass m is given by

$$\alpha = \frac{m}{4\pi\hbar^2} \int d^3\mathbf{r} U(\mathbf{r}) = \frac{m}{4\pi\hbar^2} g;$$

therefore the parameter g is directly related to a physical parameter.

the interactions with

$$U(\mathbf{r} - \mathbf{r}') = g \delta^3(\mathbf{r} - \mathbf{r}'),$$

and eqn (22.166) becomes

$$-\frac{\hbar^2}{2m} \nabla^2 \Phi + V(\mathbf{r})\Phi + g|\Phi(\mathbf{r})|^2 \Phi(\mathbf{r}) = \mu \Phi; \quad \int |\Phi|^2 = N, \quad (22.167)$$

which is the Gross-Pitaevskii equation. See e.g. [Dalfovo, et. al. (1999)] for more details. Let us note that eqn (22.167) is very general and has, not accidentally, the same form as that used in the description of the “macroscopic” wave function of systems such as superconductivity (the Landau-Ginzburg equation), if the interactions with the electromagnetic field are taken into account via the minimal coupling $\mathbf{p} \rightarrow \mathbf{p} - (q/c)\mathbf{A}$.

22.10 The semi-classical scattering amplitude

The general formula for the scattering amplitude in a central potential is eqn (16.16):

$$f(\theta) = \sum_{\ell=0}^{\infty} \frac{2\ell+1}{2k} P_\ell(\cos \theta) (e^{2i\delta_\ell} - 1). \quad (22.168)$$

The semi-classical limit is expected to hold for large ℓ and we expect also large δ_ℓ , as phases are related to the classical action which by definition is much larger than \hbar in the semi-classical domain. This allows an asymptotic estimate of eqn (22.168). For large ℓ Legendre polynomials can be approximated by (see eqn (11.41))

$$P_\ell(\cos(\theta)) \simeq -\frac{i}{\sqrt{2\pi\ell \sin \theta}} \left[e^{i(\ell+\frac{1}{2})\theta+i\frac{\pi}{4}} - e^{-i(\ell+\frac{1}{2})\theta-i\frac{\pi}{4}} \right]. \quad (22.169)$$

We are interested in $\theta > 0$ angles so we can drop the term -1 in eqn (22.168) and using eqn (22.169) for large ℓ we have

$$f(\theta) \simeq \frac{1}{k} \sum_{\ell} \sqrt{\frac{\ell}{2\pi \sin \theta}} \left[e^{i\{2\delta_\ell - (\ell+\frac{1}{2})\theta - \frac{\pi}{4}\}} - e^{i\{2\delta_\ell + (\ell+\frac{1}{2})\theta + \frac{\pi}{4}\}} \right]. \quad (22.170)$$

For large ℓ the sum can be approximated by an integral and this can be evaluated by the saddle-point technique. Stationary points are at

$$\frac{d\delta_\ell}{d\ell} \pm \theta = 0. \quad (22.171)$$

The semi-classical phase shifts are (see eqn (16.20))

$$\delta_\ell = \int_{r_0}^{\infty} \left\{ \sqrt{k^2 - \frac{2mV(r)}{\hbar^2} - \frac{(\ell + \frac{1}{2})^2}{r^2}} - k \right\} dr + \frac{\pi}{2}(\ell + \frac{1}{2}) - kr_0. \quad (22.172)$$

r_0 is the classical inversion point. It is a common convention in this approximation to express the angular momentum through the classical “impact parameter” b with

$$\ell = mvb. \quad (22.173)$$

¹⁰In deriving eqn (22.174) the reader must note that the $dr_0/d\ell$ term coming from the variation of the integral cancels with the explicit r_0 term in eqn (22.172).

With this substitution the saddle-point equations (22.171) take the form¹⁰

$$\int_{r_0}^{\infty} \frac{b dr}{r^2 \sqrt{1 - \frac{U}{E} - \frac{b^2}{r^2}}} = \frac{\pi \mp \theta}{2}. \quad (22.174)$$

It can be easily seen that for repulsive (attractive) fields the sign must be $- (+)$. This equation gives the saddle point angular momentum ℓ_0 as a function of θ and conversely.

The saddle point

Let us fix our notation by taking the lower sign in eqn (22.171) (attractive case). Near the stationary point

$$\delta_\ell \simeq \delta_{\ell_0} + \frac{1}{2} \frac{d^2 \delta_\ell}{d\ell^2} = \delta_{\ell_0} + \frac{1}{2} \frac{d\theta}{d\ell_0}.$$

The relevant term in eqn (22.170) in the saddle-point approximation takes the form

$$f(\theta) \simeq \frac{1}{k} \sqrt{\frac{\ell_0}{2\pi \sin \theta_0}} e^{i\{2\delta_{\ell_0} - (\ell_0 + \frac{1}{2})\theta - \frac{\pi}{4}\}} \int_{-\infty}^{+\infty} \exp \left[i \frac{1}{2} \frac{d\theta}{d\ell_0} \xi^2 \right] d\xi,$$

where $\xi = \ell - \ell_0$. The Gaussian integral can be easily performed by modifying the contour of integration to obtain a convergent integral (this procedure is in fact part of the definition of saddle point technique) and we have

$$f(\theta) = \frac{1}{k} \left(\frac{\ell_0}{\sin \theta} \left| \frac{d\ell_0}{d\theta} \right| \right)^{1/2} e^{i\{2\delta_{\ell_0} - (\ell_0 + \frac{1}{2})\theta - \frac{\pi}{4}\}}. \quad (22.175)$$

The differential cross section is (integrating on the azimuthal angle φ)

$$d\sigma = 2\pi |f(\theta)|^2 \sin \theta d\theta = \frac{2\pi \ell_0}{k^2} \left| \frac{d\ell_0}{d\theta} \right| d\theta = 2\pi b db;$$

i.e. the classical cross section.

22.10.1 Caustics and rainbows

The saddle point approximation breaks down if $d\theta/d\ell_0 = 0$. These angles define a *caustic*; in geometric optics this would correspond to a multiplicity of rays concurring to the same scattering angle. The classical intensity of scattered particles (or light) diverges at these points (see eqn (22.175)).

Near a caustic point θ as a function of ℓ_0 has an expansion

$$\theta \simeq \theta_0 + \alpha(\ell - \ell_0)^2 \equiv \theta_0 + \alpha\xi^2.$$

The corresponding expansion for δ_ℓ is, using eqn (22.171) with the lower sign (attractive case):

$$2\delta_\ell \simeq 2\delta_{\ell_0} + \theta_0\xi + \frac{\alpha}{3}\xi^3.$$

Substitution in eqn (22.170) gives

$$|f(\theta)| \simeq \frac{1}{k} \sqrt{\frac{\ell_0}{2\pi \sin \theta_0}} \left| \int_{\infty}^{+\infty} d\xi \exp \left[i \left(-\xi(\theta - \theta_0) + \frac{\alpha}{3}\xi^3 \right) \right] \right|.$$

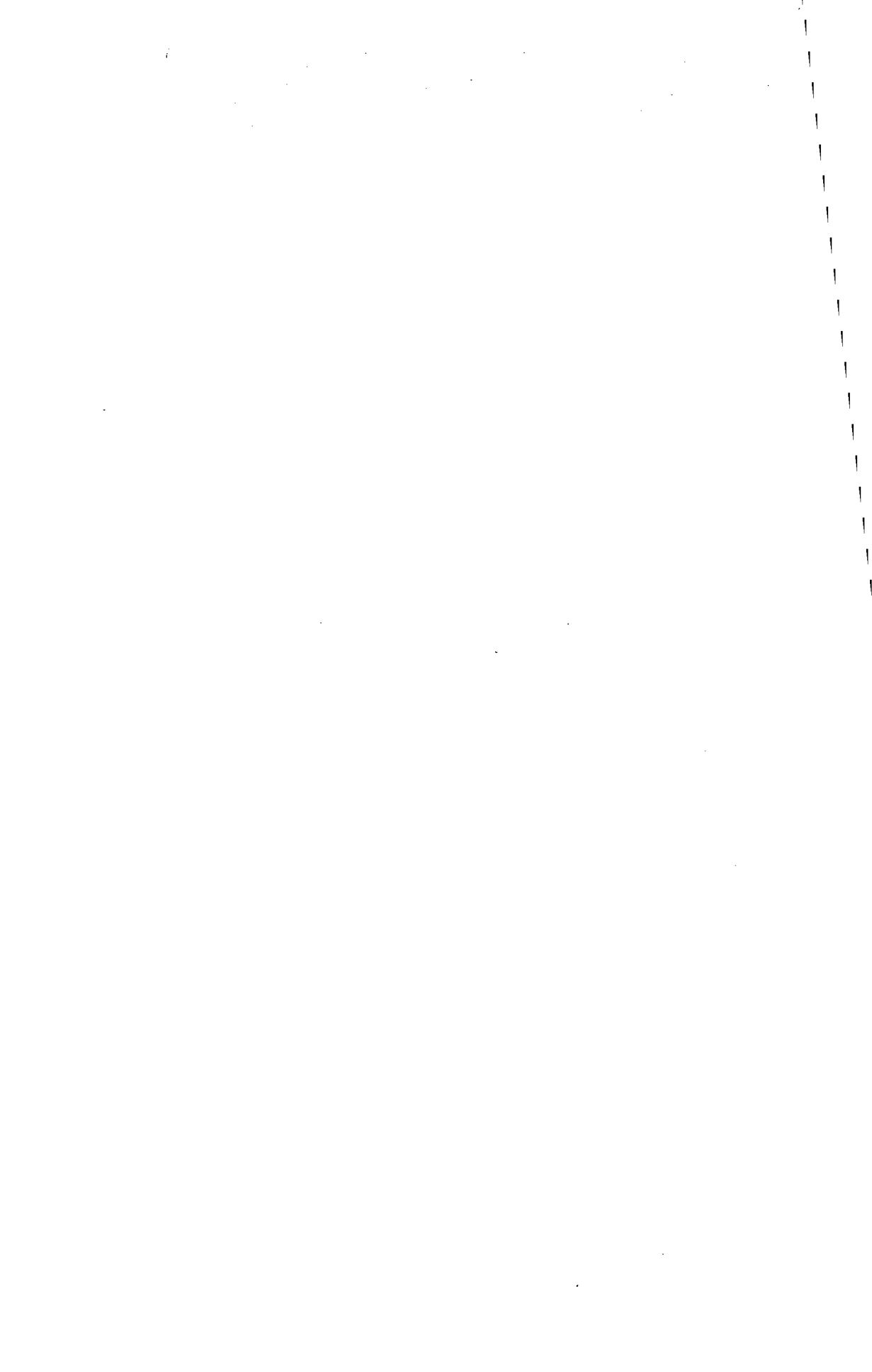
The reader can recognize a typical folding singularity (see Chapter 11). The integral is easily done in terms of Airy functions:

$$\begin{aligned} \int_{\infty}^{+\infty} d\xi e^{i(-\xi(\theta-\theta_0)+\frac{\alpha}{3}\xi^3)} &= \frac{2}{\alpha^{1/3}} \int_0^{\infty} d\xi \cos \left(-\frac{(\theta-\theta_0)}{\alpha^{1/3}} z + \frac{1}{3}z^3 \right) \\ &= \frac{2\pi}{\alpha^{1/3}} \text{Ai} \left(-\frac{(\theta-\theta_0)}{\alpha^{1/3}} \right). \end{aligned}$$

The differential cross section becomes

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 = \frac{2\pi\ell_0}{\alpha^{2/3} k^2} \text{Ai}^2 \left(-\frac{(\theta-\theta_0)}{\alpha^{1/3}} \right). \quad (22.176)$$

This formula can be applied to the study of rainbows, for an instance see the notebooks of this chapter.



Supplements for Part IV

23

23.1 Speakable and unspeakable in quantum mechanics

23.1 Speakable and unspeakable in quantum mechanics

735

The title of this section has been borrowed from the well-known book by J. S. Bell [Bell (2004)]. Here are certain ideas which have been entertained by the physicists, which might not ultimately turn out to be part of our scientific knowledge, but which certainly help in further clarifying various points of the discussion on quantum measurements and entanglement.

23.1.1 Bell's toy model for hidden variables

Bell illustrated the hidden-variable theory with a concrete (if not very realistic) toy model [Bell (1964)]. In the case of a single spin, such a model can simulate quantum mechanics perfectly well. In fact, imagine the state of a single spin- $\frac{1}{2}$ in a pure state, $\sigma \cdot \mathbf{n} |\psi_{\mathbf{n}}\rangle = |\psi_{\mathbf{n}}\rangle$,

$$|\psi_{\mathbf{n}}\rangle = \begin{pmatrix} e^{-i\phi/2} \cos \theta/2 \\ e^{i\phi/2} \sin \theta/2 \end{pmatrix}, \quad (23.1)$$

is replaced by a uniform distribution of a three-dimensional unit vector λ , in a hemisphere with the azimuth in the direction of \mathbf{n} (Figure 23.1). The result of a measurement of the spin component in the direction of \mathbf{a} , $\sigma \cdot \mathbf{a}$, is assumed to be given in this "state" by sign $(\lambda \cdot \mathbf{a}')$ where \mathbf{a}' is to be specified in terms of \mathbf{n} (the state) and \mathbf{a} . An individual experiment would give rather randomly ± 1 , according to which direction λ falls. The average of many measurements of $\sigma \cdot \mathbf{a}$ would, however, give (see Figure 23.1)

$$\overline{\text{sign}(\lambda \cdot \mathbf{a}') } = 1 - \frac{2\theta'}{\pi},$$

where θ' is the angle between the unit vectors \mathbf{a}' and λ . Now we determine \mathbf{a}' such that

$$1 - \frac{2\theta'}{\pi} = \cos \theta = \mathbf{a} \cdot \mathbf{n}.$$

Clearly there is a one-to-one map between θ' and θ in the range $(0, 2\pi)$; \mathbf{a}' can be uniquely determined in terms of \mathbf{a} and λ . Thus the average of the results of measurement of $\sigma \cdot \mathbf{a}$ is predicted to be equal to $\cos \theta = \cos^2 \theta/2 - \sin^2 \theta/2$, in agreement with the quantum mechanical prediction for the state (23.1).

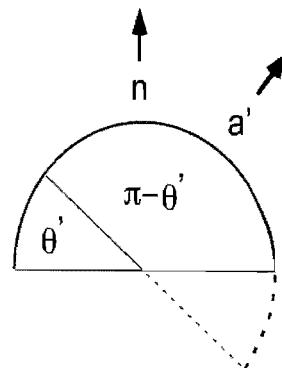


Fig. 23.1

Two entangled spins in the total spin singlet state,

$$|\Psi_0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2) ,$$

may instead be modeled by a uniform distribution of a three-dimensional unit vector λ : no preferred direction is implied. The individual outcome of the measurement of $2\mathbf{s}_1 \cdot \mathbf{a}$, $2\mathbf{s}_2 \cdot \mathbf{b}$ at the two distant sites, denoted as $R(\mathbf{a})$, $R(\mathbf{b})$, can be then assumed to be

$$R(\mathbf{a}) = \text{sign } \mathbf{a} \cdot \lambda; \quad R(\mathbf{b}) = -\text{sign } \mathbf{b} \cdot \lambda . \quad (23.2)$$

This gives for the correlation $F(\mathbf{a}, \mathbf{b}) = \overline{R(\mathbf{a})R(\mathbf{b})}$

$$F(\mathbf{a}, \mathbf{b}) = -1 + \frac{2\theta}{\pi} ,$$

where θ is the angle between \mathbf{a} and \mathbf{b} . Note that for particular configurations of the magnets, $\mathbf{a} \perp \mathbf{b}$, or for $\mathbf{b} = \pm\mathbf{a}$, this theory gives the predictions 0, ∓ 1 , respectively, in agreement with the quantum mechanical prediction, $-\cos\theta$. For a generic orientation, however, the model fails to reproduce quantum mechanics. One could modify one of the rules (23.2), for instance, by replacing \mathbf{a} by \mathbf{a}' as done before, and then rotating \mathbf{a}' towards \mathbf{b} until

$$1 - \frac{2}{\pi}\theta' = \cos\theta ,$$

one could achieve a perfect simulation of quantum mechanics. However, this means that for a given value of the hidden parameter λ , the result of the measurement of $R(\mathbf{a})$ does not only depend on λ and on \mathbf{a} *but also on* the distant magnet \mathbf{b} . This implies an unacceptable non-local and non-causal correlation between the two measurements, as the orientation of the magnet \mathbf{b} could be decided only at the very last moment, as in a delayed-choice experiment.

This toy model well illustrates the fact that a hidden-variable theory, if it is to reproduce exactly quantum mechanical predictions, must possess necessarily non-local and non-causal characters.

23.1.2 Bohm's pilot waves

The same can be seen in one of the most successful (in a sense) hidden-variable theories—the de Broglie–Bohm pilot wave theory. In this theory, the particle position (let us consider the simplest case of a single particle) $\mathbf{r}(t)$ plays a double role of the hidden variable—it complements the wave function $\psi(\mathbf{r}, t)$ and completes it—and that of the actual resulting position of the particle if the position measurement would be made. Bell has emphasized [Bell (2004)] that the measurement of spin components as the one done with a Stern–Gerlach magnet or of the momentum by using a magnetic fields or by using the time-of-flight method, all ultimately reduce to a position measurement.¹

¹This point requires some qualification: a momentum measurement, for instance, requires the position measurement at two different times at least.

By hypothesis, $\mathbf{r}(t)$ satisfies the Bohm equation

$$\frac{d}{dt}\mathbf{r}(t) = \left[\frac{\mathbf{j}(\mathbf{r}, t)}{\rho(\mathbf{r}, t)} \right]_{\mathbf{r}=\mathbf{r}(t)}, \quad (23.3)$$

where $\rho(\mathbf{r}, t)$, $\mathbf{j}(\mathbf{r}, t)$ are the standard probability density and current density functions,

$$\rho(\mathbf{r}, t) = |\psi(\mathbf{r}, t)|^2, \quad \mathbf{j}(\mathbf{r}, t) = \frac{i\hbar}{2m} [\psi \nabla \psi^* - \psi^* \nabla \psi]; \quad (23.4)$$

the wave function obeys the usual Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \psi = H \psi. \quad (23.5)$$

The structure of the set of equations, (23.3)–(23.5), is quite remarkable. The hidden-parameter-particle-position $\mathbf{r}(t)$ is guided by the pilot wave, which is nothing but the usual wave function, evolving according to the Schrödinger equation.

The initial condition at $t = t_0$ is some distribution of $\psi(\mathbf{r}, t_0)$, that is $\rho(\mathbf{r}, t_0) = |\psi(\mathbf{r}, t_0)|^2$. $\mathbf{r}(t_0)$ is assumed to be distributed statistically, according to the distribution $\rho(\mathbf{r}, t_0) d^3\mathbf{r}$. *But this is the only point the statistical feature enters the scheme.* Such an initial distribution can be attributed to the experimental preparation of the particle. As some experimental uncertainty (the width of the beam, etc.) is unavoidable in any experiment, an allowance of some initial uncertainty is perfectly reasonable.

But then both the wave function $\psi(\mathbf{r}, t)$ and the particle position $\mathbf{r}(t)$ evolve uniquely and deterministically in time. With initial position statistically distributed, the final position at time t is distributed according to the distribution

$$|\psi(\mathbf{r}, t)|^2,$$

in perfect agreement with the standard quantum mechanical prediction. In an individual experiment, where a particular initial position is specified, the particle uniquely ends up to a definite point \mathbf{r} .

Remarks

- This scheme has all the characteristics of a hidden-variable theory: even though an initial distribution of $\lambda = \mathbf{r}(t_0)$ is unknown, once a definite value of it is chosen, the experimental outcome at time t is uniquely given by $\mathbf{r}(t)$, determined from the coupled Bohm–Schrödinger equations, (23.3)–(23.5).
- Paradoxically, however, it appears that the roles of the “hidden” and “manifest” parameters are inverted [Bell (2004)]. As $\mathbf{r}(t)$ represents the measured particle position, and it is experimentally observable, what is hidden is the wave function, rather than $\mathbf{r}(t)$!
- An unphysical feature of the scheme is the fact that the position $\mathbf{r}(t)$ is guided by the wave function evolution as in eqn (23.3),

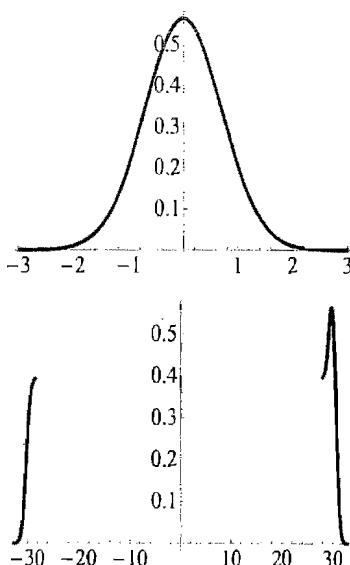


Fig. 23.2 Initial (assumed Gaussian, at $t = 0$) and final distributions (at $t = 30$) in z , in a “Stern–Gerlach” experiment, according to the Bohm equation. The initial spin wave function is $\psi = (1/\sqrt{5})[2|\uparrow\rangle + |\downarrow\rangle]$. We use the Hamiltonian (19.12) with $g = 1$. There are three hundred points in the Figure. $z_{cr} \approx -0.5952$; the two final bumps have relative weights 4 : 1, as expected. Note the different scales in z in the two figures.

but not vice versa. The Schrödinger equation is the standard one, and there is no feedback from Bohm’s equation. The principle of action-reaction is not met, and it is rather difficult to think of the coupled equations as physical, dynamical equations.

- If we accept this feature, and if $r(t)$ were to be interpreted as “the resulting position of the particle, given an initial distribution $|\psi(r, t_0)|^2$ for many repeated experiments, found after a position measurement has been made at time t ”, then the whole scheme might look suspiciously like a (though very suggestive) re-statement of the standard rule of quantum mechanics. A more careful consideration taking into account of observables defined at different times, shows, however, that no classical theories, including Bohm’s theory and stochastic theory of Nelson [Nelson (1966)], can reproduce quantum mechanics in entangled systems [Correggi and Morchio (2002)].
- If instead $r(t)$ is given the status of the real physical position, “physical reality”, existing independent of our intervention, then there are all the problems associated with the hidden-variable theories. The non-local and non-causal nature of the evolution of $r(t)$ is unavoidable. For further discussion of the strange behaviors of Bohm’s evolution equation, see [Bell (2004)].
- Even for a single spin- $\frac{1}{2}$ particle going through a Stern–Gerlach magnetic field, the behavior of $r(t)$ is not really quite acceptable. For instance, one could use the toy model (19.12) to study the evolution of the vertical position of the particle, given an initial (say) Gaussian distribution, e.g., by using Mathematica. It is clear that particles initially at a position above a critical value of z_{cr} will go up, while those at the initial position less than z_{cr} will go down, showing a bifurcation behavior. See Figure 23.2.
- As the probability that the initial position falls precisely at z_{cr} is zero, we do not worry about this. Nevertheless, such a behavior is a signal of a non-linear system, which the de Broglie–Bohm system of course is.
- Such a non-linear behavior (an extreme sensitivity of the large-time results on the short-distance and short-time initial condition) however is quite at odd with what we know about the behavior of quantum mechanical particles. If the evolution, in the above example, from the initial vertical position to the final vertical position, is considered in terms of the path integral, the amplitude for traveling from z_0 to z_1

$$\int_{z(T_0)=z_0}^{z(T_1)=z_1} [\mathcal{D}z] e^{\frac{i}{\hbar} S}, \quad S = \int_{T_0}^{T_1} dt L(z, \dot{z}),$$

is a linear function of z_0 : what happens at time T_1 does not have a very sensitive dependence on the precise value of the initial position z_0 near z_{cr} . The very fact that the physics at short distances and high energies are described by the local quantum field theories

(the standard model of fundamental interactions) with a very high precision, shows this. These theories being of *renormalizable* type, have not such a sensitivity on the short-distance behavior.²

Thus the idea of Bohm's non-linear pilot wave equation, and actually of any hidden-variable theory, that the particles, at the moment they are produced, can "know" in principle all the outcome of all future experiments (measurements), is *very much un-quantum-mechanical*. No wonder their consequences (Bell's inequalities, CHSH inequalities) fail to reproduce quantum mechanics (with which Nature agrees) fully!

²Logically, here, there is a possibility that at extreme short distances of order of 10^{-32} cm, non-linear, quantum gravity effects somehow enter the game.

23.1.3 The many-worlds interpretation

An opposite point of view is that of the "relative-state" formulation [Everett (1957)], which is better known as the "many-worlds" interpretation of quantum mechanics. Here one insists that the evolution of the wave function such as (19.11), (19.13) and (19.16), is a real process. Furthermore, it is supposed that all the terms corresponding to macroscopically distinguishable states are all there, all the time. The uniqueness of our experience is explained by saying that we actually "live" in one of the evolution branches, quite unaware of what happens in the parallel universes. There is no destruction of other branches, no wave function collapse, everything is smooth and described by the Schrödinger equation. The only important issue is to explain (argue) that the weight (relative frequency?) for a particular outcome, or a branch, is indeed given by Born's rule: by the square of the coefficient of each term [Everett (1957)]. There are many questions to be answered, however.

Remarks

- It is supposed that these actual branching process of the world occurs whenever a quantum measurement is performed. But exactly what processes qualify as "quantum measurement"? Has the world been waiting to branch for intelligent beings, perhaps with a Ph. D., to appear and perform a sophisticated atomic experiment [Bell (2004)]? Or does the world split whenever a measurement-like situation present itself accidentally?
- If the measurement is done on a variable, which takes continuous eigenvalues, does the world split in continuous set of worlds?
- The branching process itself is not described by any dynamical equation or Hamiltonian, in spite of the fact that the branching process is regarded as real. No information about when precisely, e.g., a nucleus decays emitting α particle, is given by the scheme. In other words, no new dynamical information is provided by the theory, as compared to the standard quantum mechanical laws. Again, one might ask how much is there in the theory which is genuinely beyond the standard quantum mechanics, apart from possible philosophical implications.

23.1.4 Spontaneous wave function collapse

Both in Bohm's scheme and Everett's viewpoint the standard Schrödinger dynamics is itself maintained intact, although the interpretation may differ from the conventional quantum mechanical (statistical) one. In contrast, the generalization proposed by Ghirardi, Rimini and Weber [Ghirardi, Rimini and Weber (1986)] and others, is a genuine modification of the dynamical quantum-mechanical equations. Namely, the wave function $\psi(t; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ obeys basically the standard Schrödinger equation, but on the right-hand side there is a small non-Hermitian term, which induces a non-unitary quick evolution (jump) to a spatially localized state, from time to time. In terms of the density matrix and for a single particle ($N = 1$) their modified evolution equation reads

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] - \lambda \sum_{i=1}^N (\rho - T_i[\rho]) ,$$

where the first term on the right-hand side is the standard quantum mechanics; the second term (for simplicity we write the expression in one-dimension) with

$$T_i[\rho] = \sqrt{\frac{1}{\pi a^2}} \int dx e^{-(\hat{q}_i - x)^2/2a^2} \rho e^{-(\hat{q}_i - x)^2/2a^2}$$

is the one which forces localization. \hat{q}_i 's are the position operators, and finally, a and λ are new constants of Nature. In terms of wave function, this can be re-phrased [Bell (2004)] as requiring that each wave function collapses spontaneously, with the probability N/τ per unit interval of time, $\tau \equiv 1/\lambda$ (N being the number of the arguments), to a localized wave function

$$\psi(t; \mathbf{r}_1, \dots, \mathbf{r}_N) \rightarrow \psi' = L_i(\mathbf{r}) \psi(t; \mathbf{r}_1, \dots, \mathbf{r}_N) / P_i(\mathbf{r}) ,$$

where

$$L_i(\mathbf{r}) = \left(\frac{1}{\pi a^2} \right)^{1/4} e^{-(\mathbf{r} - \mathbf{r}_i)^2/2a^2}$$

forces the localization of the i -th argument to around \mathbf{r} ;

$$P_i(\mathbf{r}) = \int d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N |L_i(\mathbf{r}) \psi(t; \mathbf{r}_1, \dots, \mathbf{r}_N)|^2$$

gives the probability (density) for the localization center.

The idea is that the effects of the spontaneous localization are practically negligible for microscopic systems, so that the standard quantum mechanical rule is valid for them, whereas any macroscopic wave function is rapidly converted to a space-localized state, effectively eliminating all terms in the expansion such as (19.11), (19.13) and (19.16), except one. Macroscopic systems behave according to classical mechanics. In order to achieve these goals with a good approximation, the parameters are proposed to be in the range

$$\lambda \simeq 10^{-16} \text{ sec}^{-1}; \quad a \simeq 10^{-5} \text{ cm}.$$

Remarks

- With these parameters, the probability for an atom (say) to suffer from the spontaneous collapse is 10^{-15} event per second: it will take 10^8 years before such an event localizes an atom.
- On the other hand, a macroscopic system, say, with $N = 10^{23}$, with an extended wave function, will survive only briefly, for

$$\tau/N \simeq 10^{-5} \text{ s}$$

before localizing [Ghirardi, Rimini and Weber (1986)]. Thus after the first step of the measurement, i.e., after the apparatus gets entangled to the microscopic system as (eqn (19.11))

$$\begin{aligned} |\psi\rangle \otimes |\Phi_0\rangle &= \sum_n c_n |n\rangle \otimes |\Phi_0\rangle \\ \implies U(t) |\psi\rangle \otimes |\Phi_0\rangle &= \sum_n c_n |n\rangle \otimes |\Phi_n\rangle \end{aligned}$$

the whole system quickly collapses to a localized wave function

$$\sum_n c_n |n\rangle \otimes |\Phi_n\rangle \implies |k\rangle \otimes |\Phi'_k\rangle$$

with probability $|c_k|^2$, reproducing the standard quantum mechanical rule.

- As discussed in Subsection 19.3.3 one of the deepest issues in quantum measurement problem is the fact that the time dependence of real quantum jumps (emission of a photon from an excited atom; α or β decay of a metastable nucleus) is not literally encoded in the Schrödinger equation. The latter only gives the time dependence of the probability amplitude of *what would happen if the measurement were done* at any instance. It is somewhat disturbing that the quantum jump (localization) introduced by Ghirardi et al. appears to be unrelated to these quantum transitions in the atomic (molecular, nuclear, etc) systems we usually deal with time-dependent perturbation theory.
- In the limit the study of quantum entanglement is pushed towards macroscopic superposition of states (e.g., in Bose-condensed systems), it might be possible eventually to verify (or rule out) experimentally this kind of genuine modification of quantum dynamics.

Mathematical appendices and tables

24

24.1 Mathematical appendices

24.1.1 Laplace's method

We present here Laplace's method for solving certain linear differential equations in a simple form. The method allows to write the solution in a form of a contour integral in the complex plane. The equations treated by this method are of the form,

$$\sum_{m=0}^n (a_m + b_m x) \frac{d^m y}{dx^m} = 0. \quad (24.1)$$

We seek for a solution in the form of a generalized Laplace transform, i.e., as an integral along a curve \mathcal{C} between two points α, β , of a function Z :

$$y = \int_{\alpha}^{\beta} Z(t) e^{xt} dt. \quad (24.2)$$

The simplification is due to the fact that the operator d/dx acts as a multiplication on the exponential function, so that substituting eqn (24.2) in eqn (24.1) one finds the constraints:

$$\begin{aligned} & \int_{\alpha}^{\beta} \sum_{m=0}^n (a_m t^m + b_m t^m) e^{xt} Z(t) dt \\ &= \int_{\alpha}^{\beta} (P(t) + xQ(t)) Z(t) e^{xt} dt = 0, \quad (24.3) \end{aligned}$$

where two polynomials of degree n

$$P(t) = \sum_{m=0}^n a_m t^m; \quad Q(t) = \sum_{m=0}^n b_m t^m, \quad (24.4)$$

have been introduced. As

$$x e^{xt} = \frac{d}{dt} e^{xt}$$

eqn (24.3) can be partially integrated to give

$$\int_{\alpha}^{\beta} \left\{ P(t)Z(t) - \frac{d}{dt} [Q(t)Z(t)] \right\} e^{xt} + Q(t)Z(t)e^{xt} \Big|_{\alpha}^{\beta} = 0. \quad (24.5)$$

24.1 Mathematical appendices	743
Table: coefficients c^k	754
Table: Mean energies	755
Tables: Fine structures	756
Table: Electronic configurations	758

Therefore we would find the solution if the two terms above vanish separately, *for any* x . The first term gives a first-order differential equation which can be easily integrated, to yield

$$\frac{d}{dt} [Q(t)Z(t)] = P Z \Rightarrow [QZ]' = \frac{P}{Q} Q Z.$$

$$Z(t) = \frac{1}{Q(t)} \exp \left[\int \frac{P(t)}{Q(t)} dt \right]. \quad (24.6)$$

This is a indefinite integral; the arbitrary integration constant can be absorbed in a multiplicative constant in the solution $y(x)$.

In order to satisfy eqn (24.5) we must choose the contour \mathcal{C} between α, β in such a way that

$$[Q(t)Z(t)e^{xt}]_{t=\alpha} = [Q(t)Z(t)e^{xt}]_{t=\beta}.$$

If the function admits zeros, typically at $t \rightarrow \infty$, it suffices to choose a path which connects these zeros. The Cauchy theorem allows us to deform the integration contour as long as we are in the analyticity domain, so that there will be a certain numbers of independent contours. It is possible to show, and we shall check in the concrete applications below, that the number of the independent contours is n , the degree of the differential equation. The integral along each of these contours provides an independent solution of eqn (24.1).

Another possibility consists in choosing $\alpha = \beta$ in some finite region of the complex plane. If it is to give a non-vanishing function eqn (24.2) the function Z must have a singularity inside the region encircled by the contour.

24.1.2 The saddle-point method

The saddle-point method allows us to evaluate the asymptotic expansion of an integral of the type,

$$\int_{\mathcal{C}} dt e^{\lambda f(t)} \quad (24.7)$$

for $\lambda \rightarrow \infty$. \mathcal{C} is a curve in the complex plane \mathbb{C} .

Real case

To illustrate the method, we start with the case of a real variable, often encountered. In this case the contour \mathcal{C} is just an interval (α, β) on the real axis, not necessarily finite. For $\lambda \rightarrow +\infty$ (to be concrete, we assume $\lambda > 0$), the integral eqn (24.7) has the dominant contribution in the region where f has a maximum: the contribution to the integral is exponentially damped away from it. Let us assume that the integrand has a maximum inside the integration region, at $t = t_0$. The $f'(t_0) = 0$ and $f''(t_0) < 0$. Expanding up to second order, we have

$$f(t) \simeq f(t_0) + \frac{1}{2} f''(t_0) (t - t_0)^2 + \dots$$

To simplify the formula we shall include the parameter λ in the definition of f , from now on. The integral is approximated by

$$\begin{aligned} \int_{\alpha}^{\beta} e^{f(t)} dt &\simeq e^{f(t_0)} \int_{-\infty}^{+\infty} e^{\frac{1}{2}f''(t_0)(t-t_0)^2} dt \\ &= e^{f(t_0)} \sqrt{\frac{2\pi}{-f''(t_0)}} \equiv I_{t_0} \quad (24.8) \end{aligned}$$

The notation I_{t_0} underlines the fact that the value of the integral depends only on the property of the function near t_0 .

- (a) Often the parameter λ does not appear directly in the factorized form in front of f as in eqn (24.7), but can be reduced to such a form, by an appropriate change of variables.
- (b) The integration range has been extended to $-\infty$ to ∞ : the error introduced by doing so is exponentially small, of the order of $\exp(f(\alpha) - f_{max})$, and vanishes in the limit, $\lambda \rightarrow \infty$.
- (c) If the function f has more than one maximum, it is necessary to keep the contribution from the absolute maximum of f . For the same reason as in b) the contribution from a local maximum at t_1 is suppressed by a factor, $\exp(f(t_1) - f_{max})$.
- (d) If there are more than one maxima with the same value for f , for instance, $f(t_1) = f(t_2)$ and $f'(t_1) = f'(t_2) = 0$, the situation is more complicated. As can be seen from eqn (24.8) the approximation keeping only the quadratic fluctuations has a characteristic scale for the variation of t : $t - t_0 \sim |f''(t_0)|^{-1/2}$. There are two possibilities:

- (1) The distance between the two maxima is large compared to this scale,

$$|t_2 - t_1| \gg |f''(t_1)|^{-1/2} \quad |t_2 - t_1| \gg |f''(t_2)|^{-1/2} : \quad (24.9)$$

in this case the integral can be approximated by the sum of the two saddle point contributions:

$$\int_{\alpha}^{\beta} e^{f(t)} dt \simeq I_{t_1} + I_{t_2}. \quad (24.10)$$

- (2) The inequality eqn (24.9) is not satisfied. In this case, it is necessary to take into account also the cubic terms in the Taylor expansion. We shall comment on such a case below briefly. Such a case occurs when f'' is very small at the maximum.

Reinstating the parameter λ one can estimate the error. Expanding to the next order,

$$I(\lambda; \alpha, \beta) \simeq e^{\lambda f(t_0)} \int_{-\infty}^{+\infty} e^{\lambda \frac{1}{2}f''(t_0)(t-t_0)^2} e^{\lambda \frac{1}{6}f'''(t_0)(t-t_0)^3} dt$$

The spirit of approximation is to treat the cubic (and higher) terms as perturbation. The first exponent (quadratic term) fixes the scale of the fluctuation, $t - t_0 \sim (\lambda |f''|)^{-1/2} \sim \lambda^{-1/2}$ and therefore

$$\lambda f'''(t_0)(t - t_0)^3 \sim \lambda \cdot \lambda^{-3/2} \sim \lambda^{-1/2}$$

which is small compared to the first term at large λ . Similarly for the higher order terms, e.g., the term $\propto (t - t_0)^4$ gives a contribution suppressed by $\lambda^{-2/2} = \lambda^{-1}$, and so on.

In fact, by expanding the exponent, one finds that

$$I(\lambda; \alpha, \beta) \simeq e^{\lambda f(t_0)} \int_{-\infty}^{+\infty} dt e^{\frac{\lambda}{2} f''(t_0)(t - t_0)^2} \left[1 + \frac{\lambda}{6} f_{t_0}^{(3)}(t - t_0)^3 + \frac{\lambda}{24} f_{t_0}^{(4)}(t - t_0)^4 + \dots \right].$$

By changing the variable as $\tau = \lambda^{1/2}(t - t_0)$ actually the cubic term is seen to vanish by symmetry and

$$I(\lambda; \alpha, \beta) \simeq I_{t_0} [1 + \mathcal{O}(\lambda^{-1})]. \quad (24.11)$$

Example: Let us obtain Stirling's formula for $n!$. $n!$ is the integer case of Euler's Γ function:

$$\Gamma(x) = \int_0^\infty e^{-t} t^{x-1} \quad \Gamma(n) = (n-1)! :$$

the following analysis is actually valid for the complex function Γ . From

$$x! \equiv \Gamma(x+1) = \int_0^\infty e^{-t} t^x dt = \int_0^\infty e^{-t+x \log(t)} dt. \quad (24.12)$$

it follows that the saddle point is given by

$$f(t) = -t + x \log(t), \quad f'(t) = -1 + \frac{x}{t} \quad \Rightarrow \quad t_0 = x,$$

so

$$f(t_0) = -x + x \log(x), \quad f''(t_0) = -\frac{x}{t_0^2} = -\frac{1}{x},$$

and one finds, from eqn (24.8), eqn (24.11), that

$$x! \simeq e^{-x+x \log(x)} \sqrt{\frac{2\pi}{x-1}} = x^x e^{-x} \sqrt{2\pi x} [1 + \mathcal{O}(x^{-1})],$$

which is Stirling's formula.

Complex case

Consider again eqn (24.7). Cauchy's theorem allows us to deform the integration contour \mathcal{C} , leaving the extrema fixed, such that the problem reduces to the one considered above. To estimate integral in terms of f around a point, the contour must be chosen so that the real part of f varies as rapidly as possible (the method is, in fact, sometimes called "the steepest descent method") so that the contribution of the saddle

point gives a good approximation. Let us set $t = x + iy$, $f = u + iv$. Choosing the contour means to assign a curve, $(x(\tau), y(\tau))$, in parametric form. The variation of $\operatorname{Re}[f]$ along the curve is

$$\dot{u} = (\partial_x u \dot{x} + \partial_y u \dot{y}) = |\nabla u| |\dot{\mathbf{x}}| \cos \theta .$$

where the variation with respect to the parameter τ is indicated by the dot, and θ is the angle between the gradient of u and the tangent of the curve. The maximum variation of u occurs for $\cos \theta = \pm 1$, the maximum decrease taking place for $\theta = \pi$. The curve must therefore be parallel to ∇u and perpendicular to the lines $u = \text{const.}$ For an analytic function the Cauchy–Riemann relations $\partial_x u = \partial_y v$, $\partial_y u = -\partial_x v$ imply $\nabla u \perp \nabla v$, so the lines $v = \text{const.}$ are a family of curves perpendicular to the family $u = \text{const.}$ From what has been said above the maximum variation along the curve occurs when the path is taken along $v = \text{const.}$ By a rotation in the complex plane one can take as x the direction of the curve on the saddle point under examination. Along the curve, i.e., along the x axis, u must decrease at the both sides of the saddle point, so $\partial_x u = 0$. In the perpendicular direction, one has $\partial_y u = \partial_x v$ by the analyticity condition. But v is constant along the curve, so $\partial_x v = 0$. Thus both derivatives vanish for u , so must those of v . On the saddle point, therefore, one has $f'(t_0) = 0$, i.e., the derivative with respect to the complex variable t . Note that in the sense of a real function this is not a point of maximum of f , which cannot have a local maximum, due to Liouville's theorem. In fact, writing $t - t_0 = x + iy$ and assuming that $f''(t_0)$ is real (which can be made so, by a global rotation in the plane), one has

$$\operatorname{Re}[f] = u \simeq \operatorname{Re}[f(t_0)] + f''(t_0) \operatorname{Re}[(x + iy)^2] = \operatorname{Re}[f(t_0)] + f''(t_0)(x^2 - y^2).$$

The surface $u = u(x, y)$ has thus a saddle at t_0 , explaining the name given to the method.

At this point the procedure is obvious. One looks for a point t_0 where $f'(t_0) = 0$ and deforms the contour in the way indicated above. One gets

$$f(t) \simeq f(t_0) + \frac{1}{2} f''(t_0)(t - t_0)^2 , \quad f''(t_0) = |f''(t_0)| e^{i\alpha} . \quad (24.13)$$

In order to avoid ambiguities we shall consider always α in the interval $0 \leq \alpha \leq 2\pi$. The following change of variables identifies the contour

$$t - t_0 = e^{i(\frac{\pi}{2} - \frac{\alpha}{2})} \tau ; \quad \tau \in \mathbb{R} \quad (24.14)$$

Indeed, the function f maintains the constant phase, π , through the saddle point:

$$\frac{1}{2} f''(t_0)(t - t_0)^2 = |f''(t_0)| e^{i\alpha} e^{i(\pi - \alpha)} \tau^2 = |f''(t_0)| e^{i\pi} \tau^2 .$$

Thus we have, by using eqn (24.14) and extending the integration limits

as before,

$$\begin{aligned} \int_{\mathcal{C}} dt e^{f(t)} &\simeq e^{f(t_0)} e^{i(\pi-\alpha)} \int_{-\infty}^{+\infty} e^{-\frac{1}{2}|f''|t^2} d\tau \\ &= e^{f(t_0)} e^{i(\frac{\pi}{2}-\frac{\alpha}{2})} \sqrt{\frac{2\pi}{|f''|}}. \end{aligned} \quad (24.15)$$

The phase factor could be included in the square root $-f''(t_0)$; it is, however, better to keep it manifest. The observations made in the real case are valid here: in particular, the one about the error estimate. In addition we underscore a point which could be confusing: the choice of the phase taken in eqn (24.14) and used in eqn (24.15) indicates also the direction of the contour, that corresponds to increasing value of τ . If the deformed path \mathcal{C} is in the opposite sense we get naturally an additional $-$ sign with respect to the formula eqn (24.15). This fact has been neglected in the real case as in the latter case it is customary to write the integral over t in the sense of increasing t , i.e., with $\alpha < \beta$ in eqn (24.8).

24.1.3 Airy functions

The Airy functions Ai, Bi are two linearly independent particular solutions of the differential equation

$$u'' - xu = 0. \quad (24.16)$$

A detailed discussion on their properties can be found, e.g., in [Abramowitz and Stegun (1964)]. For a rapid consultation a useful website is

<http://mathworld.wolfram.com/AiryFunctions.html>.

Here are their main properties:

Integral representation

$$Ai(x) = \frac{1}{\pi} \int_0^\infty dt \cos \left(\frac{1}{3}t^3 + xt \right); \quad (24.17a)$$

$$Bi(x) = \frac{1}{\pi} \int_0^\infty dt \left[e^{-\frac{1}{3}t^3+xt} + \sin \left(\frac{1}{3}t^3 + xt \right) \right]. \quad (24.17b)$$

To see that they are linearly independent, it is useful to consider the Wronskian. Let us recall that the Wronskian of two functions is defined as

$$W(f, g) = fg' - f'g.$$

For two independent solutions of a linear equation of second degree, it can be shown immediately that their Wronskian is constant and non-vanishing. For the solutions Ai, Bi one finds in fact,

$$W(Ai, Bi) = \frac{1}{\pi}. \quad (24.18)$$

This can be proven, e.g., by studying the behavior at $x \rightarrow 0$. We find

$$\text{Ai}(x) \simeq c_1 - c_2 x ; \quad \text{Bi}(x) = \sqrt{3}(c_1 + c_2 x) , \quad (24.19a)$$

$$c_1 = \frac{1}{3^{2/3}\Gamma(\frac{2}{3})} ; \quad c_2 = \frac{1}{3^{1/3}\Gamma(\frac{1}{3})} . \quad (24.19b)$$

By using the property of the Γ functions eqn (24.18) can be easily shown. We shall see how to calculate the coefficients c_i later.

We have written eqn (24.19) in order to show explicitly the regularity of the functions at the origin. Let us recall that the point $x = 0$ represented the classical turning point, a singular point of the WKB approximation. The exact solution which is a linear combination of Ai and Bi naturally has no such singularity.

Asymptotic expansion

The following asymptotic expansion can be obtained by applying the saddle point method to the integral representation eqn (24.17).

$$\text{Ai}(|x|) \sim \frac{1}{2\sqrt{\pi}} |x|^{-1/4} e^{-2/3|x|^{3/2}} ; \quad (24.20a)$$

$$\text{Ai}(-|x|) \sim \frac{|x|^{-1/4}}{\sqrt{\pi}} \sin\left(\frac{2}{3}|x|^{3/2} + \frac{\pi}{4}\right) = \frac{|x|^{-1/4}}{\sqrt{\pi}} \cos\left(\frac{2}{3}|x|^{3/2} - \frac{\pi}{4}\right) ;$$

$$\text{Bi}(|x|) \sim \frac{1}{\sqrt{\pi}} |x|^{-1/4} e^{2/3|x|^{3/2}} ; \quad (24.20b)$$

$$\text{Bi}(-|x|) \sim \frac{|x|^{-1/4}}{\sqrt{\pi}} \cos\left(\frac{2}{3}|x|^{3/2} + \frac{\pi}{4}\right) = -\frac{|x|^{-1/4}}{\sqrt{\pi}} \sin\left(\frac{2}{3}|x|^{3/2} - \frac{\pi}{4}\right) .$$

In the formulas a multiplicative factor

$$(1 + \mathcal{O}(|x|^{-3/2})) ,$$

i.e. an error of order of $\mathcal{O}(|x|^{-3/2})$ at large x , is to be understood.

Laplace's method for the Airy function

Equation (24.16) is of the form eqn (24.1) so one can apply the method by Laplace. In the present case

$$P(t) = t^2 \quad Q(t) = -1; \quad \frac{1}{Q} e^{\int \frac{P}{Q} dt} = -e^{-\frac{t^3}{3}} \Rightarrow Z(t) = \exp\left(-\frac{t^3}{3}\right) .$$

We have chosen the multiplicative constant arbitrarily, with positive sign in the preceding formula. The limits of integration α, β in eqn (24.2) can be chosen to be the two zeros of the function $Z(t)$. The function $Z(t)$ vanishes only at $|t| \rightarrow \infty$ with $\text{Re}[t^3] > 0$. Writing $t = |t| \exp(i\theta)$ we must have $\cos(3\theta) \geq 0$. This inequality divides the complex plane t in six sectors of angular aperture $60^\circ = \pi/3$. The angular intervals selected are

$$-\frac{\pi}{6} \leq \theta \leq \frac{\pi}{6} ; \quad \frac{\pi}{2} \leq \theta \leq \frac{\pi}{2} + \frac{\pi}{6} = \frac{2}{3}\pi ; \quad \pi + \frac{\pi}{6} = \frac{7}{6}\pi \leq \theta \leq \frac{3\pi}{2} ,$$

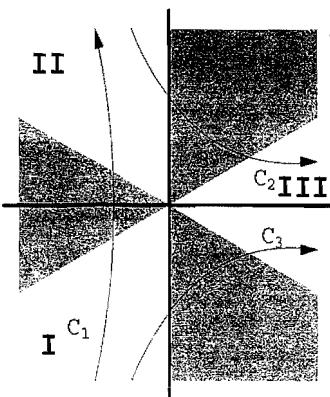


Fig. 24.1 Three possible contours defining the Airy function.

indicated respectively as III, II, I in Figure 24.1. By setting

$$I(\mathcal{C}_i) = \int_{\mathcal{C}_i} \exp\left(xt - \frac{t^3}{3}\right), \quad (24.21)$$

three possible solutions are $I(\mathcal{C}_1)$, $I(\mathcal{C}_2)$, $I(\mathcal{C}_3)$. Of these only two are linearly independent, the Cauchy theorem implies in fact, after deformation of the contours:

$$I(\mathcal{C}_3) = I(\mathcal{C}_1) + I(\mathcal{C}_2)$$

It is a simple matter to verify that

$$\text{Ai}(x) = \frac{1}{2\pi i} I(\mathcal{C}_1); \quad \text{Bi}(x) = \frac{1}{2\pi} (I(\mathcal{C}_2) + I(\mathcal{C}_3)). \quad (24.22)$$

The integration converges for any complex value of x , and is differentiable in x , therefore the functions $\text{Ai}(x)$, $\text{Bi}(x)$ are analytic functions in the whole complex plane x .

For $I(\mathcal{C}_1)$ we deform the contour until it coincides with the imaginary axis. Set $t = i\tau$ and divide the integral in two parts:

$$\begin{aligned} I(\mathcal{C}_1) &= i \left[\int_0^\infty e^{i(x\tau + \frac{\tau^3}{3})} d\tau + \int_{-\infty}^0 e^{i(x\tau + \frac{\tau^3}{3})} d\tau \right] \\ &= i \int_0^\infty \left[e^{i(x\tau + \frac{\tau^3}{3})} + e^{-i(x\tau + \frac{\tau^3}{3})} \right] d\tau = 2i \int_0^\infty \cos\left(x\tau + \frac{\tau^3}{3}\right) d\tau = 2\pi i \text{Ai}(x). \end{aligned}$$

Analogously the contour for $\mathcal{C}_2, \mathcal{C}_3$ can be deformed so that they coincide with the imaginary half-axis, or with real positive half line, yielding:

$$\begin{aligned} I(\mathcal{C}_2) + I(\mathcal{C}_3) &= i \int_{-\infty}^0 e^{i(x\tau + \frac{\tau^3}{3})} d\tau + i \int_{-\infty}^0 e^{i(x\tau + \frac{\tau^3}{3})} d\tau + 2 \int_0^\infty e^{xt - \frac{t^3}{3}} dt = \\ &= 2 \int_0^\infty e^{xt - \frac{t^3}{3}} dt - i \int_0^\infty \left[e^{i(x\tau + \frac{\tau^3}{3})} - e^{-i(x\tau + \frac{\tau^3}{3})} \right] d\tau = \\ &= 2 \int_0^\infty \left[e^{xt - \frac{t^3}{3}} + \sin\left((xt + \frac{t^3}{3})\right) \right] dt = 2\pi \text{Bi}(x). \end{aligned}$$

From their integral representation it is simple to extract the series, and in particular, to obtain the small x behavior of the functions Ai, Bi . Consider for example Ai . The term t^3 is real along the bisector of the sections I, II, so one can divide $I(\mathcal{C}_1)$ in two parts, extending the integration along the bisector and setting in the two sectors

$$II : t = e^{i(\frac{\pi}{2} + \frac{\pi}{6})}\tau = e^{i\frac{2}{3}\pi}\tau; \quad I : t = e^{i(\pi + \frac{\pi}{3})}\tau = e^{i\frac{4}{3}\pi}\tau.$$

We note that in the sector I) for $|\tau|$ increasing one has a path away from the origin, while \mathcal{C}_1 approaches it, this means another $-$ sign in the definition of the integral. By expanding the exponential factor

$$\begin{aligned} I(\mathcal{C}_1) &= \int_0^\infty d\tau \sum_{n=0}^{\infty} \frac{1}{n!} \left[e^{i\frac{2}{3}\pi} e^{-\frac{\tau^3}{3}} (x\tau e^{i\frac{2}{3}\pi})^n - e^{i\frac{4}{3}\pi} e^{-\frac{\tau^3}{3}} (x\tau e^{i\frac{4}{3}\pi})^n \right] \\ &= 2i \sum_{n=0}^{\infty} \frac{1}{n!} \sin\left(\frac{2}{3}\pi(n+1)\right) \int_0^\infty e^{-\frac{\tau^3}{3}} x^n \tau^n d\tau. \end{aligned}$$

Setting $z = t^3/3$ the integrals can be written as

$$\int_0^\infty e^{-\frac{\tau^3}{3}} \tau^n d\tau = 3^{\frac{n-2}{3}} \int_0^\infty e^{-z} z^{\frac{n-2}{3}} = 3^{\frac{n-2}{3}} \Gamma\left(\frac{n+1}{3}\right).$$

The sum over n can be decomposed into groups according to the residue with respect to division by 3: $n = 3k$; $n = 3k + 1$; $n = 3k + 2$, and we find respectively

$$\begin{aligned} \sin\left(\frac{2}{3}\pi(3k+1)\right) &= \sin\frac{2\pi}{3} = \frac{\sqrt{3}}{2}; & \sin\left(\frac{2}{3}\pi(3k+2)\right) &= \sin\frac{4\pi}{3} = -\frac{\sqrt{3}}{2}; \\ \sin\left(\frac{2}{3}\pi(3k+3)\right) &= 0. \end{aligned}$$

By substituting

$$I(C_1) = 2i\frac{\sqrt{3}}{2} \sum_{k=0}^{\infty} \left\{ \frac{3^{k-\frac{2}{3}} \Gamma(k+\frac{1}{3})}{(3k)!} x^{3k} - \frac{3^{k+\frac{1}{3}} \Gamma(k+\frac{2}{3})}{(3k+1)!} x^{3k+1} \right\},$$

and finally

$$\text{Ai}(x) = \frac{\sqrt{3}}{2\pi} \sum_{k=0}^{\infty} \left\{ \frac{3^{k-\frac{2}{3}} \Gamma(k+\frac{1}{3})}{(3k)!} x^{3k} - \frac{3^{k-\frac{1}{3}} \Gamma(k+\frac{2}{3})}{(3k+1)!} x^{3k+1} \right\}.$$

In particular, making use of the functional relation $\Gamma(z)\Gamma(1-z) = \pi/\sin(\pi z)$:

$$\text{Ai}(0) = \frac{\sqrt{3}}{2\pi} 3^{-2/3} \Gamma\left(\frac{1}{3}\right) = \frac{3^{-2/3}}{\Gamma\left(\frac{2}{3}\right)}; \quad \text{Ai}'(0) = -\frac{\sqrt{3}}{2\pi} 3^{-\frac{1}{3}} \Gamma\left(\frac{2}{3}\right) = -\frac{3^{-\frac{1}{3}}}{\Gamma\left(\frac{1}{3}\right)}.$$

An analogous exercise for $\text{Bi}(x)$ is left to the reader. From the infinite radius of convergence of the power series one can deduce that the functions Ai, Bi are entire functions.

The saddle point and asymptotic series

For simplicity we shall limit to illustrate the asymptotic expansion of the Airy function for real x , leaving the comments on the complex case to the end.

Let us apply the saddle-point method to the integrals $I(C_i)$. In the notation used in Section 24.1.2

$$f(t) = xt - \frac{t^3}{3}. \tag{24.23}$$

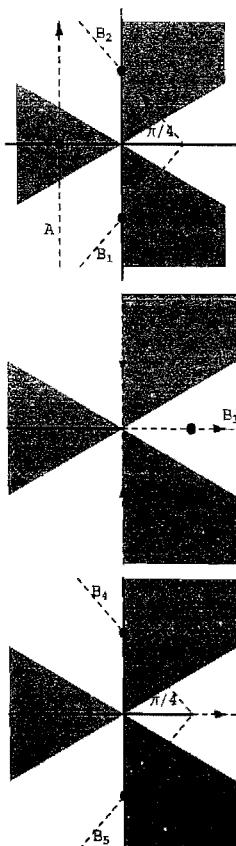
We note that by a change of the variable $t \rightarrow xt$, it takes the form $x^{3/2}(t - t^3/3)$, so the the limit $|x| \rightarrow \infty$ is exactly the one appropriate to the saddle point method. We look for the stationary points for $f(t)$:

$$0 = f'(t) = x - t^2 \Rightarrow t_0 = \begin{cases} \pm\sqrt{x} & x > 0 \\ \pm i\sqrt{|x|} & x < 0 \end{cases} \tag{24.24}$$

As explained in Subsection 24.1.2 the contribution comes from the neighbourhood of the saddle point, so we shall collect various contributions to write the full asymptotic formula for $I(C_i)$.

By indicating by $J(t_0)$ the expression obtained from eqn (24.15) one arrives at the following table:

Saddle point	$f(t_0)$	$f''(t_0)$	fase	$e^{i(\frac{\pi}{2} - \frac{\alpha}{2})}$	$J(t_0)$
$t_0 = \sqrt{x}$	$\frac{2}{3} x ^{3/2}$	$-2 x ^{1/2}$	$\alpha = \pi$	1	$\frac{\sqrt{\pi}}{ x ^{1/4}} e^{\frac{2}{3} x ^{3/2}}$
$t_0 = -\sqrt{x}$	$-\frac{2}{3} x ^{3/2}$	$2 x ^{1/2}$	$\alpha = 0$	$e^{i\frac{\pi}{2}}$	$i \frac{\sqrt{\pi}}{ x ^{1/4}} e^{-\frac{2}{3} x ^{3/2}}$
$t_0 = i\sqrt{ x }$	$-i\frac{2}{3} x ^{3/2}$	$-i2 x ^{1/2}$	$\alpha = \frac{3\pi}{2}$	$e^{-i\frac{\pi}{4}}$	$e^{-i\frac{\pi}{4}} \frac{\sqrt{\pi}}{ x ^{1/4}} e^{-i\frac{2}{3} x ^{3/2}}$
$t_0 = -i\sqrt{ x }$	$+i\frac{2}{3} x ^{3/2}$	$i2 x ^{1/2}$	$\alpha = \frac{\pi}{2}$	$e^{i\frac{\pi}{4}}$	$e^{i\frac{\pi}{4}} \frac{\sqrt{\pi}}{ x ^{1/4}} e^{+i\frac{2}{3} x ^{3/2}}$



To check the table the reader should keep in mind the fact that for $x < 0$ one has for instance:

$$f(i\sqrt{|x|}) = xt - \frac{t^3}{3} \Big|_{i\sqrt{|x|}} = -|x|t - \frac{t^3}{3} \Big|_{i\sqrt{|x|}} = -i\frac{2}{3}|x|^{3/2}.$$

Let us consider the various asymptotic expressions.

For $x > 0$ the contour C_1 can be deformed to A indicated in Figure 24.2(a), so it has contribution only from the saddle point $t_0 = -\sqrt{|x|}$; vice versa, the contours C_2, C_3 can be deformed into the paths of the type B_3 shown in Figure 24.2(b). We find therefore

$$I(C_1) \simeq i \frac{\sqrt{\pi}}{|x|^{1/4}} e^{-\frac{2}{3}|x|^{3/2}}; \quad \text{Ai}(x) \rightarrow \frac{1}{\sqrt{\pi}} \frac{1}{2} x^{-1/4} e^{-\frac{2}{3}|x|^{3/2}}; \quad (24.25a)$$

$$I(C_2) = I(C_3) = \frac{\sqrt{\pi}}{|x|^{1/4}} e^{\frac{2}{3}|x|^{3/2}}; \quad \text{Bi}(x) \rightarrow \frac{1}{\sqrt{\pi}} x^{-1/4} e^{+\frac{2}{3}|x|^{3/2}}. \quad (24.25b)$$

In the limit $|x| \rightarrow \infty$ the path B_3 extends to infinity at the left of the saddle point also: it is an analogue of the limit $\alpha, \beta \rightarrow \infty$ in the real case. The part of the paths C_2, C_3 along the imaginary axis does not contain the real exponential factor e^{xt} and in any case, exponentially suppressed.

Fig. 24.2 .

For $x < 0$ the paths through $\pm i\sqrt{|x|}$ must have the slope of $\mp\pi/4$. The contours C_2, C_3 can be deformed into the paths B_4, B_5 of Figure 24.2(c), respectively. The contour C_1 goes into $B_1 + B_2$ of Figure 24.2(a): note that the contour B_2 is traced in a wrong direction, i.e., opposite to the standard slope $-\pi/4$ so the integration over has a sign – with respect to $J(+i\sqrt{|x|})$.

Summarizing:

$$\begin{aligned} I(C_1) &= I(B_1) + I(B_2) \simeq J(-i\sqrt{|x|}) - J(i\sqrt{|x|}) \\ &= \frac{\sqrt{\pi}}{|x|^{\frac{1}{4}}} \left[e^{i(\frac{2}{3}|x|^{3/2} + \frac{\pi}{4})} - e^{-i(\frac{2}{3}|x|^{3/2} + \frac{\pi}{4})} \right] \\ &= 2i \frac{\sqrt{\pi}}{|x|^{\frac{1}{4}}} \sin \left(\frac{2}{3}|x|^{3/2} + \frac{\pi}{4} \right); \\ \text{Ai}(x) &\rightarrow \frac{1}{\sqrt{\pi}} x^{-\frac{1}{4}} \sin \left(\frac{2}{3}|x|^{3/2} + \frac{\pi}{4} \right) \\ &= \frac{1}{\sqrt{\pi}} x^{-\frac{1}{4}} \cos \left(\frac{2}{3}|x|^{3/2} - \frac{\pi}{4} \right); \end{aligned} \quad (24.26a)$$

$$\begin{aligned} \text{Bi}(x) &= \frac{1}{2\pi} (I(C_2) + I(C_3)) = \frac{1}{2\pi} (I(B_4) + I(B_5)) \\ &\simeq \frac{1}{2\pi} \left[J(-i\sqrt{|x|}) + J(i\sqrt{|x|}) \right] \\ &= \frac{1}{2} \frac{|x|^{-\frac{1}{4}}}{\sqrt{\pi}} \left[e^{i(\frac{2}{3}|x|^{3/2} + \frac{\pi}{4})} + e^{-i(\frac{2}{3}|x|^{3/2} + \frac{\pi}{4})} \right] \\ &= \frac{|x|^{-\frac{1}{4}}}{\sqrt{\pi}} \cos \left(\frac{2}{3}|x|^{3/2} + \frac{\pi}{4} \right) = -\frac{|x|^{-\frac{1}{4}}}{\sqrt{\pi}} \sin \left(\frac{2}{3}|x|^{3/2} - \frac{\pi}{4} \right). \end{aligned} \quad (24.26b)$$

Also in this case the integration along B_4, B_5 can be extended to $|x| \rightarrow \infty$ on the both sides, whereas along the real axis the same contour is suppressed exponentially as $e^{\pm t} = e^{-|x|t}$. The expressions eqn (24.25) and eqn (24.26) coincide with eqn (24.20). In Figure 24.3 the function $\text{Ai}(x)$ is reproduced: it is indeed indistinguishable with its asymptotic expression for $|x| > 1$.

Note The above derivation of the asymptotic expression requires a further comment. In the general discussion on the saddle point method in Subsection 24.1.2 we established that the sum must be taken from various saddle points and eventually dropping the exponentially suppressed terms. If we consider for instance the case $x > 0$, there are two saddle points: the one at $+\sqrt{|x|}$ is dominant, as can be seen in Table, but in the evaluation of $I(C_1)$ we made use of the other saddle point, $t_0 = -\sqrt{|x|}$. The reason is that when tracing the contour from the region I to II the saddle point $+\sqrt{|x|}$ is taken twice, in opposite directions, and the two contributions cancel to each other, and leaving the contribution from the other saddle point, $t_0 = -\sqrt{|x|}$. The situation is illustrated in Figure 24.4. Analogously, we have considered for $x < 0$ both saddle points for C_1 while for C_2 only the saddle point at $+i\sqrt{|x|}$ is taken into account.

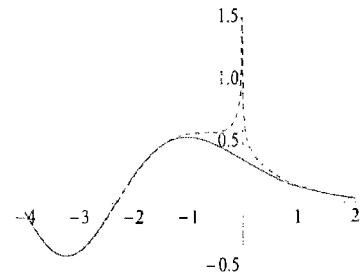


Fig. 24.3 $\text{Ai}(x)$ and its asymptotic expression (dashed curve)

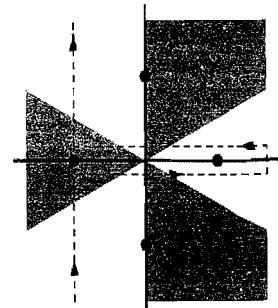


Fig. 24.4 Cancellation of the contributions of the saddle point in $\sqrt{|x|}$ for C_1 . The contour parallel to the real axis is infinitely near the real axis itself.

Table: Coefficients c^k

ℓ_1	ℓ_2	m_1	m_2	$k = 0$	$k = 1$	$k = 2$	$k = 3$	$k = 4$
s	s	0	0	1	0	0	0	0
s	p	0	1	0	$-1/\sqrt{3}$	0	0	0
s	p	0	0	0	$1/\sqrt{3}$	0	0	0
s	p	0	-1	0	$-1/\sqrt{3}$	0	0	0
p	p	1	1	1	0	$-1/5$	0	0
p	p	0	1	0	0	$-\sqrt{3}/5$	0	0
p	p	1	0	0	0	$\sqrt{3}/5$	0	0
p	p	0	0	1	0	$2/5$	0	0
p	p	1	-1	0	0	$-\sqrt{6}/5$	0	0
p	p	0	-1	0	0	$-\sqrt{3}/5$	0	0
s	d	0	2	0	0	$1/\sqrt{5}$	0	0
s	d	0	1	0	0	$-1/\sqrt{5}$	0	0
s	d	0	0	0	0	$1/\sqrt{5}$	0	0
s	d	0	-1	0	0	$-1/\sqrt{5}$	0	0
s	d	0	-2	0	0	$1/\sqrt{5}$	0	0
p	d	1	2	0	$-\sqrt{\frac{2}{5}}$	0	$\sqrt{\frac{3}{5}}/7$	0
p	d	0	2	0	0	0	$\sqrt{3}/7$	0
p	d	1	1	0	$1/\sqrt{5}$	0	$\frac{-3}{7\sqrt{5}}$	0
p	d	0	1	0	$-1/\sqrt{5}$	0	$-2\sqrt{\frac{6}{5}}/7$	0
p	d	1	0	0	$-1/\sqrt{15}$	0	$3\sqrt{\frac{2}{5}}/7$	0
p	d	0	0	0	$2/\sqrt{15}$	0	$3\sqrt{\frac{3}{5}}/7$	0
p	d	1	-1	0	0	0	$-\sqrt{6}/7$	0
p	d	0	-1	0	$-1/\sqrt{5}$	0	$-2\sqrt{\frac{6}{5}}/7$	0
p	d	1	-2	0	0	0	$3/7$	0
p	d	0	-2	0	0	0	$\sqrt{3}/7$	0
d	d	2	2	1	0	$-2/7$	0	$1/21$
d	d	1	2	0	0	$-\sqrt{6}/7$	0	$\sqrt{5}/21$
d	d	0	2	0	0	$-2/7$	0	$\sqrt{\frac{5}{3}}/7$
d	d	2	1	0	0	$\sqrt{6}/7$	0	$-\sqrt{5}/21$
d	d	1	1	1	0	$1/7$	0	$-4/21$
d	d	0	1	0	0	$-1/7$	0	$-\sqrt{\frac{10}{3}}/7$
d	d	2	0	0	0	$-\frac{2}{7}$	0	$\sqrt{\frac{5}{3}}/7$
d	d	1	0	0	0	$1/7$	0	$\sqrt{\frac{10}{3}}/7$
d	d	0	0	1	0	$2/7$	0	$2/7$
d	d	2	-1	0	0	0	0	$-\sqrt{\frac{5}{7}}/3$
d	d	1	-1	0	0	$-\sqrt{6}/7$	0	$-2\sqrt{10}/21$
d	d	0	-1	0	0	$-1/7$	0	$-\sqrt{\frac{10}{3}}/7$
d	d	2	-2	0	0	0	0	$\sqrt{\frac{10}{7}}/3$
d	d	1	-2	0	0	0	0	$\sqrt{\frac{5}{7}}/3$
d	d	0	-2	0	0	$-2/7$	0	$\sqrt{\frac{5}{3}}/7$

Table 24.1 Coefficients $c^k(\ell_1, m_1, \ell_2, m_2)$.

Table: Mean energies

s	s	$F^0[s, s]$
p	p	$F^0[p, p] - \frac{2F^2[p, p]}{25}$
d	d	$F^0[d, d] - \frac{2F^2[d, d]}{63} - \frac{2F^4[d, d]}{63}$
f	f	$F^0[f, f] - \frac{4F^2[f, f]}{195} - \frac{2F^4[f, f]}{143} - \frac{100F^6[f, f]}{5577}$

s	s'	$F^0[s, s'] - \frac{G^0[s, s']}{2}$
s	p	$F^0[s, p] - \frac{G^1[s, p]}{6}$
s	d	$F^0[s, d] - \frac{G^2[s, d]}{10}$
s	f	$F^0[s, f] - \frac{G^3[s, f]}{4}$
p	p'	$F^0[p, p'] - \frac{G^0[p, p']}{6} - \frac{G^2[p, p']}{15}$
p	d	$F^0[p, d] - \frac{G^1[p, d]}{15} - \frac{3G^3[p, d]}{70}$
p	f	$F^0[p, f] - \frac{3G^2[p, f]}{70} - \frac{2G^4[p, f]}{63}$
d	d'	$F^0[d, d'] - \frac{G^0[d, d']}{10} - \frac{G^2[d, d']}{35} - \frac{G^4[d, d']}{35}$
d	f	$F^0[d, f] - \frac{3G^1[d, f]}{70} - \frac{2G^3[d, f]}{105} - \frac{5G^5[d, f]}{231}$
f	f'	$F^0[f, f'] - \frac{G^0[f, f']}{14} - \frac{2G^2[f, f']}{105} - \frac{G^4[f, f']}{77} - \frac{50G^6[f, f']}{3003}$

Table 24.2 Mean energy for equivalent and non-equivalent electrons

Tables: Fine structures

		E_{fund}	ΔE	Fine Structure
<i>H</i>	$1s$	-109678.7717	2S	0
<i>He</i>	$1s^2$	-198310.6691	1S	0
<i>Li</i>	$1s^2 2s$	-43487.15	2S	0
<i>Be</i>	$1s^2 2s^2$	-75192.64	1S	0
<i>B</i>	$1s^2 2s^2 2p$	-66928.04	$\overline{^2P}$	10.19
				$\begin{cases} ^2P_{1/2} = 0 \\ ^2P_{3/2} = 15.287 \end{cases}$
<i>C</i>	$1s^2 2s^2 2p^2$	-90820.45	$\overline{^3P}$	29.59
				$\begin{cases} ^3P_0 = 0 \\ ^3P_1 = 16.417 \\ ^3P_2 = 43.413 \end{cases}$
			1D	10192.66
			1S	21648.02
<i>N</i>	$1s^2 2s^2 2p^3$	-117225.70	4S	0
			$\overline{^2D}$	19227.95
			$\overline{^2P}$	28839.18
				$\begin{cases} ^2D_{5/2} = 19224.46 \\ ^2D_{3/2} = 19233.18 \\ ^2P_{1/2} = 28838.92 \\ ^2P_{3/2} = 28839.31 \end{cases}$
<i>O</i>	$1s^2 2s^2 2p^4$	-109837.02	$\overline{^3P}$	77.9747
			1D	15867.86
			1S	33792.58
<i>F</i>	$1s^2 2s^2 2p^5$	-140524.5	$\overline{^2P}$	134.71
				$\begin{cases} ^2P_{3/2} = 0 \\ ^2P_{1/2} = 404.141 \end{cases}$
<i>Ne</i>	$1s^2 2s^2 2p^6$	-173929.75	1S	0
<i>Na</i>	$1s^2 2s^2 2p^6 3s$	-41449.45	2S	0
<i>Mg</i>	$1s^2 2s^2 2p^6 3s^2$	-61671.05	1S	0
<i>Al</i>	$1s^2 2s^2 2p^6 3s^2 3p$	-48278.48	$\overline{^2P}$	74.71
				$\begin{cases} ^2P_{1/2} = 0 \\ ^2P_{3/2} = 112.061 \end{cases}$

Table 24.3 Electronic configuration and fine structures. The energy is given in the unit of cm⁻¹.

	E_{fund}		ΔE	Fine Structure
Si	$1s^2 2s^2 2p^6 3s^2 3p^2$	-65747.76	$\overline{3P}$	149.68 $\begin{cases} {}^3P_0 = 0 \\ {}^3P_1 = 77.112 \\ {}^3P_2 = 223.157 \end{cases}$
			1D	6298.85
			1S	15394.36
P	$1s^2 2s^2 2p^6 3s^2 3p^3$	-84580.83	4S	0
			$\overline{2D}$	11370.39 $\begin{cases} {}^2D_{3/2} = 11361.02 \\ {}^2D_{5/2} = 11376.63 \end{cases}$
			$\overline{2P}$	18739.58 $\begin{cases} {}^2P_{1/2} = 18722.71 \\ {}^2P_{3/2} = 18748.01 \end{cases}$
S	$1s^2 2s^2 2p^6 3s^2 3p^4$	-83559.10	$\overline{3P}$	195.76 $\begin{cases} {}^3P_2 = 0 \\ {}^3P_1 = 396.055 \\ {}^3P_0 = 573.640 \end{cases}$
			1D	9238.61
			1S	22179.95
F	$1s^2 2s^2 2p^6 3s^2 3p^5$	-104591.00	$\overline{2P}$	294.12 $\begin{cases} {}^2P_{3/2} = 0 \\ {}^2P_{1/2} = 882.35 \end{cases}$
Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$	-127109.84	1S	0
K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s$	-35009.81	2S	0
Ca	$1s^2 2s^2 2p^6 3s^2 3p4s^2$	-49305.95	1S	0
Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 3d4s^2$	-52922.00	$\overline{2D}$	101.00 $\begin{cases} {}^2D_{3/2} = 0 \\ {}^2D_{5/2} = 168.34 \end{cases}$
Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$	-55072.50	$\overline{3F}$	222.51 $\begin{cases} {}^3F_2 = 0 \\ {}^3F_3 = 170.134 \\ {}^3F_4 = 386.875 \end{cases}$
			1D	7255.35
			$\overline{3P}$	8547.29 $\begin{cases} {}^3P_0 = 8436.617 \\ {}^3P_1 = 8492.421 \\ {}^3P_2 = 8602.342 \end{cases}$

Table 24.4 Fine structure and energy levels (in cm^{-1})

Table: Electronic configurations

1	H	Hydrogen	$1s$			$^2S_{1/2}$	13.5984	
2	He	Helium	$1s^2$			1S_0	24.5874	
3	Li	Lithium	$1s^2$	$2s$		$^2S_{1/2}$	5.3917	
4	Be	Beryllium	$1s^2$	$2s^2$		1S_0	9.3227	
5	B	Boron	$1s^2$	$2s^2$	$2p$	$^2P_{1/2}$	8.298	
6	C	Carbon	$1s^2$	$2s^2$	$2p^2$	3P_0	11.2603	
7	N	Nitrogen	$1s^2$	$2s^2$	$2p^3$	$^4S_{3/2}$	14.5341	
8	O	Oxygen	$1s^2$	$2s^2$	$2p^4$	3P_2	13.6181	
9	F	Fluorine	$1s^2$	$2s^2$	$2p^5$	$^2P_{3/2}$	17.4228	
10	Ne	Neon	$1s^2$	$2s^2$	$2p^6$	1S_0	21.5645	
11	Na	Sodium	[Ne]	$3s$		$^2S_{1/2}$	5.1391	
12	Mg	Magnesium	[Ne]	$3s^2$		1S_0	7.6462	
13	Al	Aluminum	[Ne]	$3s^2$	$3p$	$^2P_{1/2}$	5.9858	
14	Si	Silicon	[Ne]	$3s^2$	$3p^2$	3P_0	8.1517	
15	P	Phosphorus	[Ne]	$3s^2$	$3p^3$	$^4S_{3/2}$	10.4867	
16	S	Sulfur	[Ne]	$3s^2$	$3p^4$	3P_2	10.36	
17	Cl	Chlorine	[Ne]	$3s^2$	$3p^5$	$^2P_{3/2}$	12.9676	
18	Ar	Argon	[Ne]	$3s^2$	$3p^6$	1S_0	15.7596	
19	K	Potassium	[Ar]		$4s$	$^2S_{1/2}$	4.3407	
20	Ca	Calcium	[Ar]		$4s^2$	1S_0	6.1132	
21	Sc	Scandium	[Ar]	$3d$	$4s^2$	$^2D_{3/2}$	6.5615	
22	Ti	Titanium	[Ar]	$3d^2$	$4s^2$	3F_2	6.8281	
23	V	Vanadium	[Ar]	$3d^3$	$4s^2$	$^4F_{3/2}$	6.7462	
24	Cr	Chromium	[Ar]	$3d^5$	$4s$	7S_3	6.7665	
25	Mn	Manganese	[Ar]	$3d^5$	$4s^2$	$^6S_{5/2}$	7.434	
26	Fe	Iron	[Ar]	$3d^6$	$4s^2$	5D_4	7.9024	
27	Co	Cobalt	[Ar]	$3d^7$	$4s^2$	$^4F_{9/2}$	7.881	
28	Ni	Nickel	[Ar]	$3d^8$	$4s^2$	3F_4	7.6398	
29	Cu	Copper	[Ar]	$3d^{10}$	$4s$	$^2S_{1/2}$	7.7264	
30	Zn	Zinc	[Ar]	$3d^{10}$	$4s^2$	1S_0	9.3942	
31	Ga	Gallium	[Ar]	$3d^{10}$	$4s^2$	$^2P_{1/2}$	5.9993	
32	Ge	Germanium	[Ar]	$3d^{10}$	$4s^2$	3P_0	7.8994	
33	As	Arsenic	[Ar]	$3d^{10}$	$4s^2$	$^4S_{3/2}$	9.7886	
34	Se	Selenium	[Ar]	$3d^{10}$	$4s^2$	4P_4	9.7524	
35	Br	Bromine	[Ar]	$3d^{10}$	$4s^2$	4P_5	11.8138	
36	Kr	Krypton	[Ar]	$3d^{10}$	$4s^2$	4P_6	1S_0	13.9996

Table 24.5 Electronic configurations

37	Rb	Rubidium	[Kr]	5s	$^2S_{1/2}$	4.1771		
38	Sr	Strontium	[Kr]	$5s^2$	1S_0	5.6949		
39	Y	Yttrium	[Kr]	4d	$5s^2$	$^2D_{3/2}$	6.2173	
40	Zr	Zirconium	[Kr]	$4d^2$	$5s^2$	3F_2	6.6339	
41	Nb	Niobium	[Kr]	$4d^4$	5s	$^6D_{1/2}$	6.7589	
42	Mo	Molybdenum	[Kr]	$4d^5$	5s	7S_3	7.0924	
43	Tc	Technetium	[Kr]	$4d^5$	$5s^2$	$^6S_{5/2}$	7.28	
44	Ru	Ruthenium	[Kr]	$4d^7$	5s	5F_5	7.3605	
45	Rh	Rhodium	[Kr]	$4d^8$	5s	$^4F_{9/2}$	7.4589	
46	Pd	Palladium	[Kr]	$4d^{10}$		1S_0	8.3369	
47	Ag	Silver	[Kr]	$4d^{10}$	5s	$^2S_{1/2}$	7.5762	
48	Cd	Cadmium	[Kr]	$4d^{10}$	$5s^2$	1S_0	8.9938	
49	In	Indium	[Kr]	$4d^{10}$	$5s^2$	$^2P_{1/2}$	5.7864	
50	Sn	Tin	[Kr]	$4d^{10}$	$5s^2$	3P_0	7.3439	
51	Sb	Antimony	[Kr]	$4d^{10}$	$5s^2$	$^4S_{3/2}$	8.6084	
52	Te	Tellurium	[Kr]	$4d^{10}$	$5s^2$	3P_2	9.0096	
53	I	Iodine	[Kr]	$4d^{10}$	$5s^2$	$^2P_{3/2}$	10.4513	
54	Xe	Xenon	[Kr]	$4d^{10}$	$5s^2$	1S_0	12.1298	
55	Cs	Cesium	[Xe]		6s	$^2S_{1/2}$	3.8939	
56	Ba	Barium	[Xe]		$6s^2$	1S_0	5.2117	
57	La	Lanthanum	[Xe]		5d	$6s^2$	$^2D_{3/2}$	5.5769
58	Ce	Cerium	[Xe]	4f	5d	$6s^2$	1G_4	5.5387
59	Pr	Praseodymi	[Xe]	$4f^3$		$6s^2$	$^4I_{9/2}$	5.473
60	Nd	Neodymium	[Xe]	$4f^4$		$6s^2$	5I_4	5.525
61	Pm	Promethium	[Xe]	$4f^5$		$6s^2$	$^6H_{5/2}$	5.582
62	Sm	Samarium	[Xe]	$4f^6$		$6s^2$	7F_0	5.6437
63	Eu	Europium	[Xe]	$4f^7$		$6s^2$	$^8S_{7/2}$	5.6704
64	Gd	Gadolinium	[Xe]	$4f^7$	5d	$6s^2$	9D_2	6.1498
65	Tb	Terbium	[Xe]	$4f^9$		$6s^2$	$^6H_{15/2}$	5.8638
66	Dy	Dysprosium	[Xe]	$4f^{10}$		$6s^2$	5I_8	5.9389
67	Ho	Holmium	[Xe]	$4f^{11}$		$6s^2$	$^4I_{15/2}$	6.0215
68	Er	Erbium	[Xe]	$4f^{12}$		$6s^2$	3H_6	6.1077
69	Tm	Thulium	[Xe]	$4f^{13}$		$6s^2$	$^2F_{7/2}$	6.1843
70	Yb	Ytterbium	[Xe]	$4f^{14}$		$6s^2$	1S_0	6.2542
71	Lu	Lutetium	[Xe]	$4f^{14}$	5d	$6s^2$	$^2D_{3/2}$	5.4259
72	Hf	Hafnium	[Xe]	$4f^{14}$	$5d^2$	$6s^2$	3F_2	6.8251
73	Ta	Tantalum	[Xe]	$4f^{14}$	$5d^3$	$6s^2$	$^4F_{3/2}$	7.5496
74	W	Tungsten	[Xe]	$4f^{14}$	$5d^4$	$6s^2$	5D_0	7.864
75	Re	Rhenium	[Xe]	$4f^{14}$	$5d^5$	$6s^2$	$^6S_{5/2}$	7.8335
76	Os	Osmium	[Xe]	$4f^{14}$	$5d^6$	$6s^2$	5D_4	8.4382
77	Ir	Iridium	[Xe]	$4f^{14}$	$5d^7$	$6s^2$	$^4F_{9/2}$	8.967
78	Pt	Platinum	[Xe]	$4f^{14}$	$5d^9$	6s	3D_3	8.9588
79	Au	Gold	[Xe]	$4f^{14}$	$5d^{10}$	6s	$^2S_{1/2}$	9.2255
80	Hg	Mercury	[Xe]	$4f^{14}$	$5d^{10}$	$6s^2$	1S_0	10.4375
81	Tl	Thallium	[Xe]	$4f^{14}$	$5d^{10}$	$6s^2$	$^2P_{1/2}$	6.1082
82	Pb	Lead	[Xe]	$4f^{14}$	$5d^{10}$	$6s^2$	3P_0	7.4167
83	Bi	Bismuth	[Xe]	$4f^{14}$	$5d^{10}$	$6s^2$	$^4S_{3/2}$	7.2855
84	Po	Polonium	[Xe]	$4f^{14}$	$5d^{10}$	$6s^2$	3P_2	8.414
85	At	Astatine	[Xe]	$4f^{14}$	$5d^{10}$	$6s^2$	$^2P_{3/2}$	
86	Rn	Radon	[Xe]	$4f^{14}$	$5d^{10}$	$6s^2$	1S_0	10.7485
87	Fr	Francium	[Rn]		7s	$^2S_{1/2}$	4.0727	
88	Ra	Radium	[Rn]		$7s^2$	1S_0	5.2784	
89	Ac	Actinium	[Rn]		6d	$7s^2$	$^2D_{3/2}$	5.17
90	Th	Thorium	[Rn]		$6d^2$	$7s^2$	3F_2	6.3067
91	Pa	Protactini	[Rn]	$5f^2$	6d	$7s^2$	$(4,3/2)_{11/2}$	5.89
92	U	Uranium	[Rn]	$5f^3$	6d	$7s^2$	$(9/2,3/2)_6$	6.1941

Table: Quarks and their charges

Quarks		$SU_L(2)$	$U_Y(1)$	$U_{EM}(1)$
$\begin{pmatrix} u_L \\ d'_L \end{pmatrix}$	$\begin{pmatrix} c_L \\ s'_L \end{pmatrix}$	$\begin{pmatrix} t_L \\ b'_L \end{pmatrix}$	$\frac{1}{2}$	$\frac{1}{3}$
$u_R,$	$c_R,$	t_R	$\frac{1}{2}$	$\frac{4}{3}$
$d_R,$	$s_R,$	b_R	$\frac{1}{2}$	$-\frac{2}{3}$

Table 24.6 The primes indicate that the mass eigenstates are different from the states transforming as multiplets of $SU_L(2) \times U_Y(1)$. They are linearly related by the Cabibbo-Kobayashi-Maskawa mixing matrix.

Table: Leptons and their charges

Leptons		$SU_L(2)$	$U_Y(1)$	$U_{EM}(1)$
$\begin{pmatrix} \nu'_{eL} \\ e_L \end{pmatrix}$	$\begin{pmatrix} \nu'_{\mu L} \\ \mu_L \end{pmatrix}$	$\begin{pmatrix} \nu'_{\tau L} \\ \tau_L \end{pmatrix}$	$\frac{1}{2}$	-1
$e_R,$	$\mu_R,$	τ_R	$\frac{1}{2}$	-2

Table 24.7 The primes indicate again that the mass eigenstates are different from the states transforming as multiplets of $SU_L(2) \times U_Y(1)$, as required by the observed neutrino oscillations.

Table: Quark masses

u (MeV)	c (GeV)	t (GeV)	d (MeV)	s (MeV)	b (GeV)
1.5 – 4	1.15 – 1.35	174.3 ± 5.1	4 – 8	80 – 130	4.1 – 4.4

Table 24.8

Table: Lepton masses

ν_e (eV)	ν_μ (MeV)	ν_τ (MeV)
< 3	< 0.19	< 18.2
e (MeV)	μ (MeV)	τ (MeV)
$0.51099892 \pm 4 \cdot 10^{-8}$	$105.658369 \pm 9 \cdot 10^{-6}$	1776.99 ± 0.26

Table 24.9**Table: Gauge boson masses**

photon	gluons	W^\pm (GeV)	Z (GeV)
0	0	80.425 ± 0.038	91.1876 ± 0.0021

Table 24.10**Table: Neutrino masses**

ν_e	ν_μ	ν_τ
$\Delta_{12} m^2 = (6 - 9) \cdot 10^{-5}$ eV 2		
$\Delta_{23} m^2 = (1 - 3) \cdot 10^{-3}$ eV 2		

Table 24.11 Solar neutrinos and reactor (SNO, SuperKamiokande, KamLAND) experiments give the first results. Atmospheric neutrino data and the long baseline experiment (SuperKamiokande, K2K) provide the second. The mixing angle relevant to the solar and reactor neutrino oscillation is large, $\tan^2 \theta_{12} \sim 0.40^{+0.10}_{-0.07}$, while the one related to the atmospheric neutrino data is maximal, $\sin^2 2\theta_{23} \sim 1$. Cosmological considerations give $\sum m_{\nu_i} < O(1 \text{ eV})$.

Table: Physical constants and conversion factors

Quantity	Symbol	Value
Speed of light in vacuum	c	$2.997\ 924\ 58 \times 10^{10} \text{ cm s}^{-1}$ (exact)*
Planck constant	h	$6.626\ 068\ 96(33) \times 10^{-34} \text{ erg s}$
Planck constant ("h-bar")	$\hbar \equiv h/2\pi$	$1.054\ 571\ 628(53) \times 10^{-34} \text{ erg s}$
Energy-length conversion factor	$\hbar c$	$197.326\ 963\ 1(49) \text{ MeV fm}$
(-) Electron charge	e	$1.602\ 176\ 487(40) \times 10^{-19} \text{ C} = 4.803\ 204\ 27(12) \times 10^{-10} \text{ esu}$
Electron mass	m_e	$0.510\ 998\ 910(13) \text{ MeV/c}^2 = 9.109\ 382\ 15(45) \times 10^{-28} \text{ g}$
Proton mass	m_p	$938.272\ 013(23) \text{ MeV/c}^2 = 1.672\ 621\ 637(83) \times 10^{-24} \text{ g}$
Neutron mass	m_n	$939.565\ 346(23) \text{ MeV/c}^2 = 1.674\ 927\ 211(84) \times 10^{-24} \text{ g}$
Denteron mass	m_d	$1875.612\ 793(47) \text{ MeV/c}^2 = 3.343\ 583\ 20(17) \times 10^{-24} \text{ g}$
α particle mass	m_α	$3\ 727.379(93) \text{ MeV/c}^2 = 6.644\ 656\ 20(33) \times 10^{-24} \text{ g}$
Fine-structure constant	$\alpha = e^2/\hbar c$	$7.297\ 352\ 537\ 6(50) \times 10^{-3} = 1/137.035\ 999\ 679(94)$
Bohr radius	$r_B = \hbar^2/m_e e^2$	$0.529\ 177\ 208\ 59(36) \times 10^{-8} \text{ cm}$
Compton wavelength (electron)	$\lambda_C = h/m_e c$	$2.817\ 940\ 289\ 4 \times 10^{-13} \text{ cm}$
Classical electron radius	$r_e = \alpha^2 r_B$	$2.426\ 310\ 217\ 5 \times 10^{-10} \text{ cm}$
Rydberg constant	R_∞	$1.097\ 373\ 156.852\ 7 \text{ cm}^{-1}$
Rydberg energy	$hcR_\infty = m_e e^4/2\hbar^2 = e^2/2r_B$	$13.605\ 691\ 93(34) \text{ eV}$
Bohr magneton	$\mu_B = e\hbar/2m_e$	$5.788\ 381\ 7555(79) \times 10^{-11} \text{ MeV T}^{-1}$
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$3.152\ 451\ 2326(45) \times 10^{-14} \text{ MeV T}^{-1}$
Gravitational constant	G_N	$6.674\ 28(67) \times 10^{-11} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-2}$
Avogadro constant	N_A	$6.022\ 141\ 79(30) \times 10^{23} \text{ mol}^{-1}$
Boltzmann constant	k	$1.380\ 6504(24) \times 10^{-23} \text{ JK}^{-1}$
Fermi constant	$G_F/(\hbar c)^3$	$1.166\ 37(1) \times 10^{-5} \text{ GeV}^{-2}$
Conversion of energy unit	1 eV	$= 1.602\ 176\ 487(40) \times 10^{-16} \text{ erg}$
Conversion of length unit	1 \AA	$= 1.0 \times 10^{-8} \text{ cm}$

Table 24.12 Some physical constants and conversion factors. These and other data by the Committee on Data for Science and Technology (CODATA) can be found at <http://physics.nist.gov/constants>. The number in a parenthesis is the standard uncertainty. * The meter is defined to be the length of the path traveled by light in vacuum in a time interval of $1/299792458$ of a second. See also [Yao, et. al. (2006)].

References

- Abers, E. S., and Lee, B. W. (1973). *Phys. Rep.*, **9**, 1.
- Abragam, A. (1961). *The Principles of Nuclear Magnetism* (Oxford: Clarendon).
- Abramowitz, M., and Stegun, I. A. (1964). *Handbook of Mathematical Functions* (New York: Dover).
- Agarwal, G. S., and Arun Kumar, S. (1991). *Phys. Rev. Lett.*, **67**, 3665.
- Aguilar, J., and Combes, J. M. (1971). *Comm. Math. Phys.*, **22**, 269.
- Aharonov, Y., and Bohm, D. (1959). *Phys. Rev.*, **115**, 485.
- Akhiezer, N. I., and Glazman, I. M. (1966). *Theory of Linear Operators in Hilbert Space* (New York: Dover).
- Amati, D., Ciafaloni, M., and Veneziano, G. (1989). *Phys. Lett.*, **B216**, 41.
- Arnold, V. I. (1997). *Mathematical Methods of Classical Mechanics* tr. Weinstein, A., and Vogtmann, K. (Berlin/Heidelberg: Springer). [Russian original: Matematicheskie Metody Klassiceskoj Mechaniki (Moscow: Nauka, 1974).]
- Aspect, A., Grangier, P., and Roger, G. (1981). *Phys. Rev. Lett.*, **49**, 91.
- Aspect, A., Dalibard, J., and Roger, G. (1981). *Phys. Rev. Lett.*, **49**, 1804.
- Ballantine, L. E. (1998). *Quantum Mechanics: A Modern Development* (Singapore: World Scientific).
- Balsa, R., Plo, M., Esteve, J. G., and Pacheco, A. F. (1983). *Phys. Rev.*, **D28**, 1945.
- Bardou, F., Bouchaud, J-P., Aspect, A., and Cohen-Tannoudji, C. (2002). *Lévy Statistics and Laser Cooling: How Rare Events Bring Atoms to Rest* (Cambridge: Cambridge University Press).
- Bell, J. S. (1964). *Physics*, **1**, 195.
- Bell, J. S. (2004). *Speakable and Unspeakable in Quantum Mechanics* (Oxford: Clarendon).
- Bell, J. S. (1990). Against Measurement *Phys. World* **3:33-40** CERN-TH-5611-89.
- Bender, C. M., and Wu, T. T. (1973). *Phys. Rev.*, **D7**, 1620.
- Berestetskii, V. B., Lifshitz, E. M., and Pitaevskii, L. (1980). *Quantum Electrodynamics*, Landau and Lifshitz Course of Theoretical

- Physics, Vol. 4 tr. by J.B. Sykes and J.S. Bell (Oxford: Pergamon).
- Berry, M. V., and Mount, K. E. (1972). *Reps. Prog. Phys.*, **35**, 815.
- Berry, M. V. (1984). *Proc. R. Soc. Lond.*, **A 392**, 45.
- Berry, M. V. (1980). *Eur. J. Phys.*, **1**, 240.
- Berry, M. V. (1983). Semiclassical Mechanics of regular and irregular motion, in *Les Houches Lecture Series Session XXXVI*, ed. G. Looss, H. G. Hellemans and R. Stora (Amsterdam: North Holland), 171.
- Bethe, H. A., and Jackiw, R. (1986). *Intermediate Quantum Mechanics* (Reading MA: Addison Wesley).
- Bethe, H. A., and Salpeter, E. E. (1977). *Quantum Mechanics of One And Two-Electron Atoms* (New York: Plenum).
- Bjorken, J. D., and Drell, S. (1964). *Relativistic Quantum Mechanics* (New York: MacGraw-Hill).
- Bjorken, J. D., and Drell, S. (1965). *Relativistic Quantum Fields* (New York: MacGraw-Hill).
- Bogoliubov, N. N., and Shirkov, D. V. (1959). *Introduction to the Theory of Quantized Fields* (New York: Wiley-Interscience).
- Bohm, D. (1952). *Phys. Rev.*, **85**, 166.
- Bohr, A., and Mottelson, B. R. (1969). *Nuclear Structure*, Vol. I (New York: Benjamin).
- Bohr, A., and Mottelson, B. R. (1975). *Nuclear Structure*, Vol. II (New York: Benjamin).
- Bonneau, G., Faraut, J., and Valent, G. (2001). *Am. J. of Phys.*, **69**, 322.
- Born, M., Heisenberg, W., and Jordan, P. (1926). *Z. f. Phys.*, **35**, 557.
- Born, M. (1989) (8th edn). *Atomic Physics*, 8th edn (New York: Dover).
- Born, M. (1927). *Mechanics of the Atom* (London: Bell). [German original: Vorlesungen über Atommechanik (Berlin: Springer, 1925).]
- Boyd, J. P. (2001). *Chebyshev and Fourier Spectral Methods* (New York: Dover).
- Brenner, M. P., Hilgenfeldt, S., and Lohse, D. (2002). *Rev. Mod. Phys.*, **74**, 425.
- Brillouin, L. (1938). *Les Tenseur en Mécanique et en Élasticité*, Libraires de l'académie de médecine. (Paris: Masson), Chap. IX.
- Bürgers, A., Vintgen, D., and Rost, J. M. (1995). *J. Phys.*, **B 28**, 3163.
- Cardy, J., and Calabrese, P. (2004). *J. Stat. Mech.*, **0406**, P002.
- Chiao, Y., Kwiat, P. G., and Steinberg, A. M. (1995). *Quantum Non-locality in Two Photon experiments at Berkeley*. ArXiv:quant-ph/9501016;
- Chiao, Y. (1993). Faster than Light? *Sci. Am.* Aug 1993, 38.

- Christensen, J. H., Cronin, J. W., Fitch, V. L., and Turley, R. (1964). *Phys. Rev. Lett.*, **13**, 138.
- Clauser, J. F., Holt, R. H., Horne, M. A., and Shimony, A. (1969). *Phys. Rev. Lett.*, **23**, 880.
- Cohen-Tannoudji, C., Dupont-Roc, J., and Grynberg, G. (1988). *Précédé d'Interaction entre Photons et Atoms*, Editions du CNRS.
- Cohen-Tannoudji, C. (1968). *Optical Pumping and Interaction of Atoms with the Electromagnetic Field*, Cargèse Lectures in Physics, Vol. 2 ed. M. Levy (New York: Gordon and Breach).
- Colella, R., Overhauser, A. W., and Werner, S. A. (1975). *Phys. Rev. Lett.*, **34**, 1472.
- Coleman, S. (1979). The uses of instantons, Erice Lectures 1977, in *the Whys of Subnuclear Physics* (New York: Plenum).
- Condon, E. U., and Shortley, G. H. (1935). *The Theory of Atomic Structure* (Cambridge: Cambridge University Press).
- Cooper, F., Khare, A., and Sukhatme, U. (2002). *Supersymmetry in Quantum Mechanics* (Singapore: World Scientific).
- Correggi, M., and Morchio, G. (2002). *Ann. of Phys.*, **296**, 371.
- Courant, R., and Hilbert, D. (1989). *Methods of Mathematical Physics*, Vol.1,2 (New York: Wiley-Interscience).
- Dalfovo, F., Giorgini, S., Pitaevskii, L., and Stringari, S. (1999). *Rev. Mod. Phys.*, **71**, 463.
- Dalgarno, A., and Lewis, J. T. (1955). *Proc. Roy. Soc.*, **A233**, 70.
- Davydov, A. S. (1965). *Quantum Mechanics* (Oxford: Pergamon).
- Delves, J. M. (1972). *J. Phys. A*, **5**, 1123.
- DeWitt, B. S. (1957). *Rev. Mod. Phys.*, **29**, 377.
- Di Giacomo, A. (1992). *Lezioni di Fisica Teorica* (Pisa: Edizioni ETS).
- Dingle, R. B. (1973). *Asymptotic Expansions: Their Derivation and Interpretation* (New York: Academic).
- Dirac, P. A. M. (1931). *Proc. Roy. Soc.*, **A 133**, 60. Dirac, P. A. M. (1948). *Phys. Rev.*, **74**, 817.
- Dirac, P. A. M. (1958). *Principles of Quantum Mechanics*, 4th edn. (Oxford: Clarendon).
- Dodonov, V. V., and Man'ko, V. I. (1978). *Phys. Rev.*, **A20**, 550.
- Dyson, F. J. (1952). *Phys. Rev.*, **85**, 631.
- Einstein, A., Podolsky, B., and Rosen, N. (1935). *Phys. Rev.*, **47**, 777.
- Erdélyi, A. (1956). *Asymptotic Expansions* (New York: Dover).
- Everett, H., III. (1957). *Phys. Mod. Phys.*, **29**, 454.
- Ezawa, J.F. (2008). *Quantum Hall Effects: Field Theoretical Approach and Related Topics* 2nd edn. (Singapore: World scientific).
- Fermi, E. (1927). *Atti Accad. Naz. Lincei*, **6**, 602. Fermi, E. (1928). *Atti Accad. Naz. Lincei*, **7**, 342.

- Fermi, E., and Amaldi, E. (1934). *Memorie Accad. d'Italia*, **6**, 119.
- Feynman, R. P. (1948). *Rev. Mod. Phys.*, **20**, 367.
- Feynman, R. P., and Hibbs, A. R. (1965). *Quantum Mechanics and Path Integrals* (New York: McGraw-Hill).
- Feynman, R. P., Leighton, R. B., and Sands, M. (2005). *The Feynman Lectures on Physics*, 2nd edn., Vol.3 (Reading MA: Addison-Wesley).
- Fischer, C., Brage, T., and Jönsson, P. (1997). *Computational Atomic Structure* (Bristol: IOP).
- Fradkin, E. (1986). *Phys. Rev.*, **B 33**, 3263.
- Fritzsch, H., Gell-Mann, M., and Leutwyler, H. (1973). *Phys. Lett.*, **B47**, 365.
- Furry, W. H. (1947). *Phys. Rev.*, **71**, 360.
- Gaitan, D. F. (1990). Ph D Thesis, University of Mississippi.
- Geim, A. K., and Novoselov, K. S. (2007). *Nature Materials*, **6**, 183;
- Geim, A. K., and MacDonald, A. H. (2007). *Physics Today*, **60**, 35.
- Ghirardi, G. C., Rimini, A., and Weber, T. (1986). *Phys. Rev.*, **D 34**, 470.
- Glashow, S. L., Iliopoulos, J., and Maiani, L. (1970). *Phys. Rev.*, **D2**, 1285.
- Gleason, A. M. (1957). *Journ. Math. Mech.*, **6**, 885.
- Goldberger, M. L., and Watson, K. M. (1964). *Collision Theory* (New York: Dover).
- Goldstone, J., Salam, A., and Weinberg, S. (1962). *Phys. Rev.*, **127**, 965.
- Gradshteyn, I. S., and Ryzhik, I. M. (1965). *Table of Integrals, Series and Products* (New York: Academic).
- Green, M., Schwartz, J., and Witten, E. (1987). *Superstring Theory*, Vol. I, II. (Cambridge: Cambridge University Press).
- Guida, R., Konishi, K., and Suzuki, H. (1995) *Ann. of Phys.*, **241**, 152. Guida, R., Konishi, K., and Suzuki, H. (1996). *Ann. of Phys.*, **249**, 109.
- Gutzwiller, M. C. (1990). *Chaos in Classical and Quantum Mechanics* (New York: Springer-Verlag).
- Hamermesh, M. (1962). *Group Theory and its Application to Physical Problems* (New York: Dover).
- Hardy, G. H. (1991). *Divergent Series*, 2 edn. (New York: Chelsea).
- Heisenberg, W. (1925). *Z. f. Phys.*, **33**, 879.
- Heisenberg, W. (1926). *Z. f. Phys.*, **38**, 411.
- Heisenberg, W. (1930). *The Physical Principles of the Quantum Theory*, tr. by C. Eckart and C. Hoyt (New York: Dover)
- Herzberg, G. (1944). *Atomic Spectra and Atomic Structure* (New York: Dover).

- Herbst, I. W., and Simon, B. (1978). *Phys. Rev. Lett.*, **41**, 67.
- Hylleraas, E. A. (1929). *Z. f. Phys.*, **54**, 347.
- Itzykson, C., and Zuber, J-B. (1980). *Quantum Field Theory* (New York: McGraw-Hill).
- Jackiw, R., and Redlich, A. N. (1983). *Phys. Rev. Lett.*, **50**, 555.
- Jackiw, R. (1991). *Delta-Function Potentials in Two- and Three-Dimensional Quantum Mechanics*, Bég Memorial Volume, eds. A. Ali and P. Hoodbhoy (Singapore: World Scientific).
- Joachain, C. J. (1975). *Quantum Collision Theory* (Amsterdam: North-Holland).
- Joos, E., Zeh, H. D., Kiefer, C., Giulini, D., Kupsch, J., and Stamatescu, I.-O. (2002). *Decoherence and the Appearance of a Classical World in Quantum Theory*, 2nd edn. (New York: Springer).
- Keller, J. R. (1958). *Ann. of Phys.*, **4**, 180.
- Kemble, E. C. (1937). *The Fundamental Principles of Quantum Mechanics*, Sec. 35 (New York: MacGraw-Hill).
- Ketterle, W. (2002). Nobel Lecture: *When Atoms Behave as Waves: Bose-Einstein Condensation and Atom Laser*, *Rev. of Mod. Phys.*, **74**, 1131.
- Kinoshita, T. (1957). *Phys. Rev.*, **105**, 1490. Kinoshita, T. (1959). *Phys. Rev.*, **115**, 366.
- Kleinert, H. (2006). *Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets* (Singapore: World Scientific).
- Kochen, S. and Specker, E. (1967). *J. Math. Mech.*, **17**, 59.
- Kogan, V.I., and Galitsky, V.M. (1963). *Problems in Quantum Physics* (Englewood Cliffs: Prentice-Hall).
- Konishi, K., and Paffuti, G. (2006). *Int. Jour. of Mod. Phys.*, **A21**, 3199.
- Konishi, K., Paffuti, G., and Provero, P. (1990). *Phys. Lett.*, **B234**, 276.
- Kravtsov, Yu. A. (1968). *Sov. Phys. Acoust.*, **14**, 1.
- Laudau, L. D., and Lifshitz, E. M. (1976 a). *Course of Theoretical Physics, Vol. 1: Mechanics*. 3rd edn. (Oxford: Pergamon).
- Laudau, L. D., and Lifshitz, E. M. (1976 b). *Course of Theoretical Physics, Vol. 2: Classical Fields*. 3rd edn. (Oxford: Pergamon).
- Laudau, L. D., and Lifshitz, E. M. (1976 c). *Course of Theoretical Physics, Vol. 3: Quantum Mechanics (Non-Relativistic Theory)* 3rd edn. (Oxford: Pergamon).
- Langer, R. E. (1937). *Phys. Rev.*, **51**, 669.
- Lee, T. D., and Yang, C. N. (1956). *Phys. Rev.*, **104**, 254.
- Lee, T. D., and Wu, C. S. (1966). *Annual Review of Nuclear Science*, **16**, 471.

- Le Guillou, J. C., and Zinn-Justin, J. (1990). *Large-Order Behaviour of Perturbation Theory* (Amsterdam: North-Holland).
- Lewis, H. R. Jr., and Riesenfeld, W. B. (1969). *Journ. Math. Phys.*, **10**, 1458.
- Lifshitz, E. M. and Pitaevskii, L. (1981). *Landau and Lifshitz Course of Theoretical Physics, Vol. 9: Statistical Physics*. tr. by J.B. Sykes and M.J. Kearsley (Oxford: Pergamon).
- Loeffel, J. J. and Martin, A. (1972). *Cargèse Lectures on Physics*, Vol. 5, 415. ed. D. Bessis (New York: Gordon and Breach).
- Ludwig, G. (1968). *Wave Mechanics* (Oxford: Pergamon).
- MacDonald, J. K. L. (1934). *Phys. Rev.*, **46**, 828.
- Maggiore, M. (1993). *Phys. Lett.*, **B304**, 65.
- Maslov, V. P. and Fedoriuk, M. V. (1981). *Semiclassical Approximation in Quantum Mechanics* (Dordrecht: Reidel).
- Mermin, D. (1990) *Am. J. Phys.*, **58**, 731; *Phys. Rev. Lett.*, **65**, 1838.
- Messiah, A. (2000) *Quantum Mechanics* (New York: Dover).
- Messiah, A., and Greenberg, O. W. (1964). *Phys. Rev.*, **136**, 249.
- Maggiore, M. (2005). *A Modern Introduction to Quantum Field Theory* (Oxford: Clarendon).
- Millikan, R. A. (1916). *Phys. Rev.*, **D7**, 355.
- Mukhanov, V. F., Feldman, H. A., and Brandenberger, R. H. (1992). *Phys. Rep.*, **215**, 203.
- Nagata, L. (1998). *Vast* (New York: Bantam).
- Nambu, Y. (1960). *Phys. Rev. Lett.*, **4**, 380.
- Nambu, Y., and Jona-Lasinio, G. (1961). *Phys. Rev.*, **122**, 345.
- Nelson, E. (1966). *Phys. Rev.*, **150**, 1079.
- Newton, R. G. (1966). *Scattering Theory of Waves and Particles* (New York: Dover).
- Nielsen, M. A., and Chuang, I. L. (2000). *Quantum Computation and Quantum Information* (Cambridge: Cambridge University Press).
- Pauli, W. (1925). *Z. f. Physik*, **31**, 765.
- Pauli, W. (1940). *Phys. Rev.*, **58**, 716.
- Pauling, L., and Bright Wilson, E. Jr. (1935). *Introduction to Quantum Mechanics with Application to Chemistry* (New York: Dover).
- Pekeris, C. L. (1962). *Phys. Rev.*, **126**, 1470.
- Penrose, R. (1989). *The Emperor's New Mind* Oxford: Oxford University Press.
- Percival, J. C. (1977). *Adv. Chem. Phys.*, **36**, 1.
- Peres, A. (1995). *Quantum Theory: Concepts and Methods* (Dordrecht/Boston/London: Kluwer).
- Peskin, M. E., and Schröder, D. V. (1995). *An Introduction to Quantum Field Theory* (New York: Addison-Wesley).

- Polchinski, J. (1998). *String Theory*, Vols. I, II (Cambridge: Cambridge University Press).
- Preskill, J. D. (2006). <http://www.theory.caltech.edu/~preskill>.
- Prange, E., and Girvin, M. (1990). *The Quantum Hall Effect*, 2nd edn. (New York/Heidelberg/Berlin: Springer).
- Reed, M., and Simon, B. (1980). *Method of Modern Mathematical Physics, Vol. 1: Functional Analysis* (New York: Academic).
- Reed, M., and Simon, B. (1980). *Method of Modern Mathematical Physics, Vol. 4: Analysis of Operators* (New York: Academic).
- Reinhardt, W. (1982). *Ann. Rev. Phys. Chem.*, **33**, 223.
- Rodberg, L. S., and Thaler, R. M. (1967). *Introduction to the Quantum Theory of Scattering* (New York: Academic).
- Salam, A. (1968). in *Elementary Particle Theory*, ed. N. Svartholm (Stockholm: Almqvist Forlag AB) 367.
- Schechter, M. (1981). *Operator Method in Quantum Mechanics* (Amsterdam: North-Holland).
- Schiff, L. I. (1968). *Quantum Mechanics* (New York: McGraw-Hill).
- Schrödinger, E. (1926a). *Ann. Phys.*, **79**, 361, 489, 734. Schrödinger, E. (1926b). *Ann. Phys.*, **80**, 437. Schrödinger, E. (1926c). *Ann. Phys.*, **81**, 109.
- Schrödinger, E. (1935) *Naturwissenschaften*, **23**, 807, 823, 844. English translation in Wheeler and Zurek (1983).
- Schulman, L. S. (1981). *Techniques and Applications of Path Integration* (New York: Wiley-Interscience).
- Sebawe Abdulla, M., and Colgrave, R. K. (1985). *Phys. Rev.*, **A32**, 1958.
- Semenoff, G. W. (1984). *Phys. Rev. Lett.*, **53**, 2449.
- Shaw, R. (1954). Ph D Thesis, University of Cambridge.
- Simon, B. (1972). *Comm. Math. Phys.*, **27**, 1. Simon, B. (1972). *Ann. Math.*, **97**, 247.
- Slater, J. C. (1960). *Quantum Theory of Atomic Structure* (New York: McGraw-Hill).
- Sokal, A.D. (1980). *J. Math. Phys.*, **21**, 261.
- Steinberger, J. (1970). K^0 Decay and CP Violation, CERN Report, 70-1.
- Strocchi, F. (1985). *Elements of Quantum Mechanics of Infinite Systems* (Singapore: World Scientific).
- Taylor, J. R. (1908). *Cambridge Phil. Soc.*, **15** 114.
- Taylor, J. C. (1976). *Gauge Theories of Weak Interactions* (Cambridge: Cambridge University Press).
- Temple, G. (1934). *Proc. Nat. Acad. Sci.*, **20**, 529.
- Ter Haar, D. (1967). *The Old Quantum Theory* (Oxford: Pergamon).

- 't Hooft, G., and Veltman, M. (1977). Diagrammer, *CERN Yellow report CERN 73-9*.
- 't Hooft, G. (1980). Lectures given at Cargese Summer Inst., Cargese, France, Aug 26 - Sep 8, 1979. NATO Adv. Study Inst. Ser.B Phys.**59**, 117.
- Thomas, L. H. (1927). Proc. Camb. Phil. Soc., **23**, 542.
- Tomonaga, S. (1968). *Quantum Mechanics*, Vol. 1 (Amsterdam: North-Holland).
- Tonomura, A. et. al. (1989). *Am. J. Phys.*, **57**, 117.
- Tonomura, A., Yano, S., Osakabe, N., Matsuda, T., Yamada, H., Kawasaki, T., and Endo, J. (1986). *Phys. Rev. Lett.*, **56**, 792.
- Tonomura, A. (2000). *Int. J. Mod. Phys.*, **A 15**, 3427.
- Trott, M. (2006). *The Mathematica Guidebook for Symbolics* (New York/Heidelberg/Berlin: Springer).
- van der Waerden, B. L. (1968). *Sources of Quantum Mechanics* (New York: Dover).
- van Vleck, J. H. (1928). *Proc. Natl. Acad. Sci. USA*, **14**, 178.
- Vidal, G., Latorre, J. I., Rico, E., and Kitaev, A. (2003). *Phys. Rev. Lett.*, **90**, 227902.
- von Neumann, J. (1932). *Mathematical Foundations of Quantum Mechanics* tr. R.T. Beyer (Princeton NJ: Princeton University Press). [German original: Mathematische Grundlagen der Quantenmechanik, Berlin: Springer 1932].
- Wallace, D. (2007). *The Quantum Measurement Problem: the State of Play*, arXiv:0712.0149.
- Weinberg, S. (1967). *Phys. Rev. Lett.*, **19**, 1264.
- Weinberg, S. (1989). *Phys. Rev. Lett.*, **62**, 485.
- Weinstein, D. H. (1928). *Proc. Roy. Soc. (London)*, **119**, 276.
- Wheeler, J. A., and Zurek, W. H. (1983). *Quantum Theory and Measurement* (Princeton NJ: Princeton University Press).
- Williams, E. J. (1930). *Proc. Roy. Soc.*, **A 128**, 459.
- Wilson, K. (1974). *Phys. Rept.*, **12 C**, 75.
- Witten, E. (1981). *Nucl. Phys.*, **B 188**, 513.
- Wittig, C. (2005). *J. Phys. Chem.*, **B 109**, 8428.
- Wolf, F., and Korsch, H. J. (1988). *Phys. Rev.*, **A37**, 1934.
- Wolfram, S. (2003). *The Mathematica Book* 5th edn. (Champaign IL: Wolfram Media Inc.).
- Wu, T. T. and Yang, C. N. (1975). *Phys. Rev.*, **D12**, 3845.
- Whittaker, E. T., and Watson, G. N. (1927). *A Course of Modern Analysis* (Cambridge: Cambridge University Press).
- Yang, C. N., and Mills, R. L. (1954). *Phys. Rev.*, **96**, 191.
- Yao, D. M., et. al. (Particle Data Group) (2006). *J. Phys.*, **G 33**, 1.

- Zinn-Justin, J. (1989). *Quantum Field Theory and Critical Phenomena* (Oxford: Clarendon).

Index

- δ function, 41
 α decay, 290
Absorption of light, 237
Adiabatic invariant, 552
Adiabatic theorem, 312
Airy functions, 269
Alpha decay, 482
Angular momenta
 composition of, 103
Angular momentum
 operators L_z, L_+, L_- , 96
 eigenstates, 98
 formulas, 575
 matrix elements, 99
Anharmonic oscillator
 perturbation, 633
Anti-particle, 490
Anti-unitary operator, 122
Anyons, 129
Arrow of time, 122
Atom
 closed shell, 425
 multiplets, 419
 orbitals, 409
Bell's inequalities, 533
Berry phase, 317
Beta decay, 231
Black-body radiation, 11
Bohr
 atomic model, 15
 correspondence principle, 16
 radius, 16
Bohr radius, *see* Bohr
Bohr-Sommerfeld quantization, 272
Bohr-Sommerfeld quantization
 condition, 17
Borel transformation, 640
Born approximation, 461
Born-Oppenheimer approximation, 727
Bose-Einstein condensation, 131
Boson, 128
Boundary condition, 58
Bra, 155
Canonical anti-commutation relation,
 491, 588
Canonical commutation relation, 36
Canonical equations, 548
Canonical transformations, 550
Casimir effect, 66
Cauchy's sequence, 157
Central field approximation, 406
Chronological product, 188
CHSH inequality, 509, 535
Clebsch-Gordan coefficients, 104
Collective coordinates, 200
Combination rule, *see* Ritz's
Commutation relation
 canonical, 36
Completeness, 46, 158
 one-dimensional delta potential, 559
Compton effect, 19
Connection formula, 268, 270
Conservation law
 due to symmetry, 111
Contextuality, 538
Continuity equation, 51
Coulomb scattering, 468
Counting quantum states, 274
Covering space
 universal, 573
CP violation
 B-meson systems, 661
 K-meson systems, 657
CPT theorem, 660
Creation and annihilation operators, 67
Cross section
 partial, 458
 total, 455
Cryptodeterminism, 532
Current density, 51
 in electromagnetic field, 383
Cyclic oscillator, 331
Darwin term, 682
de Broglie's wave, 18
Decay, 228
Decay width, 228
Decoherence, 527
Delayed-choice experiment, 509
Delta function, 41
Delta potential
 completeness relation, 559
 discontinuity condition, 74
 two and three dimensional, 595
Density matrix
 Stokes parameters, 177
DeWitt's ambiguity, 181
Dipole approximation, 235
Dipole moment, 386
Dirac equation, 488
Dirac's sea, 489
Directional quantization, 95
Dispersion relation, 642
Dispersion-free state, 532
Domain, *see* operator
Duality
 wave-particle, 6
Dynamical variables
 operators, 29
Dyson, 636
Effect
 Aharonov-Bohm, 392
 Lo Surdo-Stark, 438
 Mössbauer, 87
 Meissner, 396
 Paschen-Back, 445
 quantum Hall, 399
 Stark-Lo Surdo, 438
 Zeeman, 445
Effective range, 468
Ehrenfest's theorem, 50
Eigenstate, 30
Eigenvalue, 30, 152
 improper, 163
 proper, 163
Eigenvector, 30
Eikonal approximation, 464
Einstein
 the photoelectric effect, 14
Einstein's coefficients, 240
Einstein's relation, 14
Electromagnetic transitions, 233
Electronic configuration, 406
 filling pattern, 407
 incomplete shells, 420
Energy
 of electromagnetic radiation fields, 555
Energy quantum, 14
Entanglement, 24
Entanglement entropy, 515
EPR paradox, 503, 522
Equipartition law, 9
Equivalent electrons, 407
Exchange integral, 705
Expansion in \hbar , 266

- Factorization, 24
 Fermi momentum, 693
 Fermi's constant, 231
 Fermi's golden rule, 227
 Fermion, 128
 left-handed, 489
 right-handed, 489
 Feynman graphs, 194, 613
 Feynman rules, 194
 Feynman's theorem, 189
 Feynman–Hellman theorem, 52
 Fine structure, 422, 435
 Fine structure constant, 389
 Finite mass corrections
 to helium atom, 259
 Flux quantization, 397
 Fock representation, 586
 Franck–Hertz, 16
 Fundamental group, 129, 572

 Galilean transformation, 123
 Gamma matrices, 488
 Gamow–Siegert, 293
 Gauge invariance, 384
 Gauge principle, 112
 Gauge transformation, 382
 of wave function, 385
 Gaussian integrals, 612
 Gleason's theorem, 530
 Graphene, 496
 Green function, 183, 343
 analytic property of, 346
 free particle, 184
 Gross–Pitaevski equation, 731
 Group, 566
 $SU(2)$, 571
 $SU(3)$, 575
 Abelian, 566
 Lie, 570
 non-Abelian, 566
 Group representation, 568
 Gyromagnetic ratio, 388
 electron's, 490

 Hamilton principal function, 552
 Hamilton's equation, 548
 Hamilton–Jacobi equation, 552
 Hamiltonian, 37
 Harmonic oscillator
 coherent states, 68
 Heisenberg picture, 171
 one-dimensional, 63
 theorem on cyclic, 331
 Harmonic oscillator eigenstates
 in p representation, 154
 Hartree approximation, 700
 Hartree–Fock approximation, 427
 Heisenberg equation, 170
 Heisenberg picture, 170
 Heisenberg's uncertainty principle, 27

 Helicity, 236
 Helium atom
 elementary variational approach to, 252
 variational calculation, 255
 Hermitian operator, 33
 Hidden variables, 532
 Higgs mechanism, 396
 Hilbert space, 23, 155
 complete, 157
 separable, 157
 Holographic principle, 532
 Homotopy group
 first, 572, 654
 n-th, 572
 Hund's rule, 423
 Hydrogen atom, 143
 degeneracy, 146
 levels, 145
 radial eigenfunction, 147
 Hyperfine structure, 423

 Identical particles, 128
 Impulse approximation, 315, 316
 Incoherent light, 234
 Induced (stimulated) emission, 238
 Infinitesimal generator, 162
 Information paradox, 532
 Instanton, 199
 Interferometer
 Fabry–Pérot, 77
 Ionization potential, 408

 Jacobi's identity, 549

 KAM theorem, 655
 Keller quantization, 650
 Ket, 155
 Klein–Gordon equation, 487

 Laguerre polynomial
 associated, 146
 Laguerre polynomials
 generating function, 146
 Landau levels, 397
 Landau–Zener transition, 314
 Laplace–Beltrami operator, 181
 Larmor's theorem, 444
 Legendre polynomials, 564
 associated, 97, 565
 generating function, 565
 Legendre transformation, 548
 Level density, 661
 Lie algebra, 571

 Magnetic moment
 intrinsic, 388
 Magnetic monopole
 Dirac's quantization, 402
 Malus' law, 26

 Mass polarization, 685
 Matrix mechanics, 275
 Maximum observables, 35
 Mean free path, 455
 Mean-field approximation, 700
 Meson theory
 Yukawa's, 481
 Millikan, photoelectric effect, 14
 Minimum action principle, 545
 Mixed state, 174
 Monte Carlo method, 201
 Mott cross section, 474

 n-point correlation functions, 189
 Nambu–Goldstone theorem, 117
 Neutrino mass, 232
 Neutrino oscillation, 232
 Norm of a state, 156
 Norm of a state, 23
 Normalization condition, 22

 Observable
 compatible, 33
 Operator
 adjoint of, 160
 annihilation, 67
 anti-unitary, 121
 bounded, 158
 creation, 67
 domain of, 159
 Hermitian, see op. symmetric
 of rotation, 91
 self-adjoint, 161, 163
 spectra of, 163
 symmetric, 160
 unitary, 167
 Operator p
 eigenstates, 43
 Optical theorem, 458
 Orbitals, 703
 Oscillator
 three-dimensional, 141

 Parabolic interpolation, 270
 Parity, 117
 explicit operator of, 119
 intrinsic, 118
 Parity violation, 658
 Particle encircling a solenoid, 327
 Particle in moving walls, 320
 Particle on a ring
 with defect, 328
 Path integral, 186
 Path integral, functional integral, 183
 Pauli matrices, 100
 Pauli's exclusion principle, 133
 Permutation group, 129, 566, 581
 Perturbation
 change of boundary condition, 615
 periodic, 223

- Perturbation theory, 207
 degenerate, 213
 first order, 209
 iterative solution, 209
 time-dependent, 219
 time-independent, 207
- Phase
 geometrical, 318
- Phase shift, 457, 563
 WKB, 299
- Photoelectric effect, 14
- Photon polarization, 26
- Planck distribution, 12
- Poisson's parenthesis, 549
- Polarizability, 217, 218
- Polarization
 photon, 24, 176
- Positive operator-valued measure, 520
- Potential
 periodic, 80
- Potential barrier, 71
- Potential well
 spherical, 140
- POVM, 520
- Projection-valued measurement, 520
- Pure state, 174
- PVM, 520
- Quadrupole moment, 387
- Quantization
 of angular momentum, 94
 semi-classical, 650
- Quantized field
 Dirac, 491
 electromagnetic, 689
 Klein-Gordon, 490
 non-relativistic, 589
- Quantum anomaly, 600
- Quantum entanglement, 503
- Quantum eraser, 526
- Quantum mechanics
 of infinite systems, 116
- Quantum non-locality, 538
- Quantum number, 35
 principal, 136
- Quantum transition, 219
- Quantum Zeno effect, 366
- quartic oscillator
 WKB, 283
- Rabi frequency, 226
- Radiation
 monochromatic, 236
 wide-band, 236
- Radioactivity, 482
- Ray of normalized functions, 22
- Rayleigh-Jeans' formula, 12
- Reduced mass, 135
- Reduced matrix element, 126
- Reflection coefficient, 72
- Renormalizable quantum field theory, 487
- Representation, 151
 irreducible, 569
- p representation, 152
- q representation, 152
- Resolvent set, 163
- Resonances, 371
- Resonant oscillation, 225
 walls, 324
- Rotation matrix, 106
 spin- $\frac{1}{2}$, 107
- Rutherford's formula, 472
- Rydberg
 constant, 15
 formula, 410
- S matrix, 560
- Scale transformation
 complex, 370
- Scattering
 delta function potential, 75
 of identical particles, 473
- Scattering amplitude, 454
- Scattering cross section, 454
- Scattering length, 466
- Scattering process
 wave packet description of, 560
- Schrödinger equation, 37
 from variational principle, 246
 general properties, 49
 one-dimensional, 53
 radial, 137
 time-independent, 38
- Schrödinger picture, 170
- Schrödinger's cat, 527
- Schur's lemma, 569
- Schwarz inequality, 157
- Second quantization, 589
- Selection rule, 127
- Selection rules
 dipole transition, 236
- Semi-classical approximation, 265, 648
- Slater determinants, 424
- Sono-luminescence, 337
- Space
 simply-connected, 129, 573
- Spectral decomposition, 162, 347
- Spectral density, 661
- Spectral flow, 329
- Spectral term, 422
- Spectral terms, 434
- Spectral theorem, 165
- Spectrum
 of a self-adjoint operator, 163
- Spherical Hankel function, 139
- Spherical Bessel functions, 138
- Spherical harmonics, 98
- Spherical tensor, 126
- Spherical wave, 137
- Spin, 92
 in variable magnetic field, 310
- Spin-statistic connection, 492
- Spinor (projective) representation, 573
- Spontaneous emission, 239
- Spontaneous symmetry breaking, 117
- Standard model, 113
- Stark effect, 215
- State
 mixed, 174
 pure, 174
- State density, 228
- Statistics
 Bose-Einstein, 127
 Fermi-Dirac, 127
- Stern-Gerlach, 95
- Superconductivity, 395
 London equation, 395
- Superselection rules, 22, 601
- Supersymmetry, 590
- Symanzik, 637
- Symmetries, 111
 conservation law, 114
- Symmetry
 continuous, 112
 degeneracy due to, 115
 parity, 117
- T-ordered product, 308
- Theorem
 Hellinger and Töplitz, 160
 Kato-Rellich, 636
 Kochen-Specker, 536
 von Neumann, 605
 von Neumann on commuting operators, 166
 Wigner's, 122
 Wigner-Eckart, 126
- Thomas precession, 389, 674
- Thomas-Fermi approximation, 693
- Time evolution
 Heisenberg picture, 169, 309
 time-dependent H , 307
- Time reversal, 121
- Tonomura
 Aharonov-Bohm effect, 392
 electron interference, 6
- Topological quantization, 397, 403, 572
- Transition into continuum, 226
- Transition matrix, 76, 79
- Transmission coefficient, 72
- Triangular inequality, 156
- Trotter's formula, 187
- Truncated Hilbert space, 249
- Tunnel effect, 74
 path integral, 198
 tunnel effect, 284
- Two-state system, 616
- Uncertainty principle, 27, 37, 173

- Uncertainty relation, 26, 36
 - energy-time, 231
- Unitary groups, 573
- Unitary transformation, 167
 - time dependent, 309
- Variational principle, 245
- Virial theorem
 - classical, 554
 - quantum mechanical, 52
- Wave function
 - localized, 81
- Weisskopf-Wigner approximation, 230
- Weyl's algebra, 606
- Weyl's commutation relation, 605
- Weyl's criterion, 163
- Weyl's prescription, 677
- Width
 - of metastable state, 370
- Width of spectral lines, 231
- Wien
 - displacement law, 12
 - formula of, 12
- Wigner's $3j$ -symbols, 706
- WKB
 - Langer correction, 281
 - quantization condition, 272
- WKB approximation, 267
- Yang-Mills theory, 112, 487
- Young tableaux, 581
- Zero modes, 200
- Zero-point energy, 66