

# Fundamental Quantum Mechanics for Engineers

Leon van Dommelen

5/5/07 Version 3.1 beta 3.



# Dedication

To my parents



# Preface

## Why Another Book on Quantum Mechanics?

This document was written because of the recognition that with current emphasis on nanotechnology, quantum mechanics is becoming increasingly essential to mechanical engineering students. Yet, the typical quantum mechanics texts for physics students are not written in a style that mechanical engineering students would likely feel comfortable with. Also, the coverage often does not seem to be intended to emphasize understanding of the larger-scale quantum system that a density functional computation, say, would be used for. Hence this document, written by a mechanical engineering professor for mechanical engineers.

My initial goal was to write something that would “read like a mystery novel.” Something a reader would not be able to put down until she had finished it. Obviously, this goal was unrealistic. I am far from a professional writer, and this is quantum mechanics, after all, not a murder mystery. But I have been told that this book is very well written, so maybe there is something to be said for aiming high.

To prevent the reader from getting bogged down in mathematical details, I mostly avoid nontrivial derivations in the text. Instead I have put the outlines of these derivations in notes at the end of this document: personally, I enjoy checking the correctness of the mathematical exposition, and I would not want to rob my students of the opportunity to do so too.

While typical physics texts jump back and forward from issue to issue, I thought that would just be distracting for my audience. Instead, I try to follow a consistent approach, with as central theme the method of separation-of-variables, a method that most mechanical graduate students have seen before. To cut down on the issues to be mentally absorbed at any given time, I purposely avoid bringing up new issues until I really need them. Such a just-in-time learning approach also immediately answers the question why the new issue is relevant, and how it fits into the grand scheme of things.

The desire to keep it straightforward is the main reason that topics such as Clebsch-Gordan coefficients (except for the unavoidable introduction of singlet and triplet states) and Pauli spin matrices have been shoved out of the way to a final chapter. My feeling is, if I can give

my students a solid understanding of the basics of quantum mechanics, they should be in a good position to learn more about individual issues by themselves when they need them. On the other hand, if they feel completely lost in all the different details of quantum mechanics, they are not likely to learn the basics either.

I also try to go slow on the more abstract vector notation permeating quantum mechanics, usually phrasing such issues in terms of a specific basis. Abstract notation may seem to be completely general and beautiful to a mathematician, but I do not think it is going to be intuitive to a typical engineer.

When I derive the first quantum eigenfunctions, for a pipe and for the harmonic oscillator, I make sure to emphasize that they are not *supposed* to look like anything that we told them before. It is only natural for students to want to relate what we told them before about the motion to the completely different story we are telling them now. So it should be clarified that (1) no, they are not going crazy, and (2) yes, we will eventually explain how what they learned before fits into the grand scheme of things.

Another difference of approach in this book is the way it treats classical physics concepts that the students are likely unaware about, such as canonical momentum, magnetic dipole moments, Larmor precession, and Maxwell's equations. They are largely "derived" in quantum terms, with no appeal to classical physics. I see no need to rub in the student's lack of knowledge of specialized areas of classical physics if a satisfactory quantum derivation is readily given.

This book is not intended to be an exercise in mathematical skills. Review questions are targeted towards understanding the ideas, with the mathematics as simple as possible. I also try to keep the mathematics in successive questions uniform, to reduce the algebraic effort required.

Finally, this document faces the very real conceptual problems of quantum mechanics head-on, including the collapse of the wave function, the indeterminacy, the nonlocality, and the symmetrization requirements. The usual approach, and the way I was taught quantum mechanics, is to shove all these problems under the table in favor of a good sounding, but upon examination self-contradictory and superficial story. Such superficiality put me off solidly when they taught me quantum mechanics, culminating in the unforgettable moment when the professor told us, seriously, that the wave function *had* to be symmetric with respect to exchange of bosons *because* they are all truly the same, and then, when I was popping my eyes back in, continued to tell us that the wave function is *not* symmetric when fermions are exchanged, which are all truly the same. I would not do the same to my own students. And I really do not see this professor as an exception. Other introductions to the ideas of quantum mechanics that I have seen left me similarly unhappy on this point. One thing that really bugs me, none had a solid discussion of the many worlds interpretation. This is obviously not because the results would be incorrect, (they have not been contradicted for half a century,) but simply because the teachers just do not like these results. I do not like the results myself, but basing teaching on what the teacher would *like* to be true rather on what the evidence

indicates *is* true remains absolutely unacceptable in my book.

## Acknowledgments

This document is mostly based on my reading of the excellent book by Griffiths, [3]. It includes a concise summary of the material of Griffith's chapters 1-5 (about 250 pages), written by someone who is learning the material himself at the same time.

Somewhat to my surprise, I find that my coverage actually tends to be closer to Yariv's book, [6]. I still think Griffiths is more readable for an engineer, though Yariv has some items Griffiths does not.

The many-worlds discussion is based on Everett's exposition, [1]. It is brilliant but quite impenetrable.

Some other parts of this document are taken from Feynman's notes, [2], a hard to read source. Since it is hard to determine the precise statements being made, much of that has been augmented by data from web sources, mainly those referenced.

The nanomaterials lectures of colleague Anter El-Azab that I audited inspired me to add a bit on simple quantum confinement to the first system studied, the particle in the box. That does add a bit to a section that I wanted to keep as simple as possible, but then I figure it also adds a sense that this is really relevant stuff for future engineers. I also added a discussion of the effects of confinement on the density of states to the section on the free electron gas.

## Comments and Feedback

If you find an error, please let me know. The same if you find points that are unclear to the intended readership, ME graduate students with a typical exposure to mathematics and physics, or equivalent. General editorial comments are also welcome. I'll skip the philosophical discussions. I am an engineer.

Feedback can be e-mailed to me at quantum@dommelen.net.

This is a living document. I am still adding some things here and there, and fixing various mistakes and doubtful phrasing. Even before every comma is perfect, I think the document can be of value to people looking for an easy to read introduction to quantum mechanics at a calculus level. So I am treating it as software, with version numbers indicating the level of confidence I have in it all.

# History

- The first version of this manuscript was posted Oct 24, 2004.
- A revised version was posted Nov 27, 2004, fixing a major blunder related to a nasty problem in using classical spring potentials for more than a single particle. The fix required extensive changes. This version also added descriptions of how the wave function of larger systems is formed.
- A revised version was posted on May 4, 2005. I finally read the paper by Everett, III on the many worlds interpretation, and realized that I had to take the crap out of pretty much all my discussions. I also rewrote everything to try to make it easier to follow. I added the motion of wave packets to the discussion and expanded the one on Newtonian motion.
- May 11 2005. I got cold feet on immediately jumping into separation of variables, so I added a section on a particle in a pipe.
- Mid Feb, 2006. A new version was posted. Main differences are correction of a number of errors and improved descriptions of the free electron and band spectra. There is also a rewrite of the many worlds interpretation to be clearer and less preachy.
- Mid April, 2006. Various minor fixes. Also I changed the format from the “article” to the “book” style.
- Mid Jan, 2007. Added sections on confinement and density of states, a commutator reference, a section on unsteady perturbed two state systems, and an advanced chapter on angular momentum, the Dirac equation, the electromagnetic field, and NMR. Fixed a dubious phrasing about the Dirac equation and other minor changes.
- Mid Feb 2007. There are now lists of key points and review questions for chapter 1. Answers are in the new solution manual.
- 4/2 2007. There are now lists of key points and review questions for chapter 2. That makes it the 3 beta 2 version. So I guess the final beta version will be 3 beta 6. Various other fixes. I also added, probably unwisely, a note about zero point energy.
- 5/5 2007. There are now lists of key points and review questions for chapter 3. That makes it the 3 beta 3 version. Various other fixes, like spectral line broadening, Helium’s refusal to take on electrons, and countless other less than ideal phrasings. And full solutions of the harmonic oscillator, spherical harmonics, and hydrogen wave function ODEs, Mandelshtam-Tamm energy-time uncertainty, (all in the notes.) A dice is now a die, though it sounds horrible to me. Zero point energy went out again as too speculative.

## **Wish List**

I would like to add key points and review questions to all basic sections.

It would be nice to put frames around key formulae.

There is supposed to be a second volume or additional chapter on computational methods, in particular density-functional theory.



# Contents

<b>Dedication</b>	<b>iii</b>
<b>Preface</b>	<b>v</b>
Why another book on quantum mechanics? . . . . .	v
Acknowledgments . . . . .	vii
Comments and Feedback . . . . .	vii
History . . . . .	viii
Wish list . . . . .	ix
<b>List of Figures</b>	<b>xvii</b>
<b>List of Tables</b>	<b>xxi</b>
<b>1 Mathematical Prerequisites</b>	<b>1</b>
1.1 Complex Numbers . . . . .	1
1.2 Functions as Vectors . . . . .	4
1.3 The Dot, oops, INNER Product . . . . .	6
1.4 Operators . . . . .	9
1.5 Eigenvalue Problems . . . . .	10
1.6 Hermitian Operators . . . . .	11
1.7 Additional Points . . . . .	13
1.7.1 Dirac notation . . . . .	14
1.7.2 Additional independent variables . . . . .	14
<b>2 Basic Ideas of Quantum Mechanics</b>	<b>15</b>
2.1 The Revised Picture of Nature . . . . .	15
2.2 The Heisenberg Uncertainty Principle . . . . .	17
2.3 The Operators of Quantum Mechanics . . . . .	19
2.4 The Orthodox Statistical Interpretation . . . . .	21
2.4.1 Only eigenvalues . . . . .	21
2.4.2 Statistical selection . . . . .	22
2.5 Schrödinger's Cat [Background] . . . . .	24
2.6 A Particle Confined Inside a Pipe . . . . .	25
2.6.1 The physical system . . . . .	25
2.6.2 Mathematical notations . . . . .	26

2.6.3	The Hamiltonian . . . . .	26
2.6.4	The Hamiltonian eigenvalue problem . . . . .	27
2.6.5	All solutions of the eigenvalue problem . . . . .	28
2.6.6	Discussion of the energy values . . . . .	32
2.6.7	Discussion of the eigenfunctions . . . . .	33
2.6.8	Three-dimensional solution . . . . .	35
2.6.9	Quantum confinement . . . . .	38
2.7	The Harmonic Oscillator . . . . .	40
2.7.1	The Hamiltonian . . . . .	41
2.7.2	Solution using separation of variables . . . . .	41
2.7.3	Discussion of the eigenvalues . . . . .	44
2.7.4	Discussion of the eigenfunctions . . . . .	47
2.7.5	Degeneracy . . . . .	50
2.7.6	Non-eigenstates . . . . .	52
<b>3</b>	<b>Single-Particle Systems</b>	<b>55</b>
3.1	Angular Momentum . . . . .	55
3.1.1	Definition of angular momentum . . . . .	55
3.1.2	Angular momentum in an arbitrary direction . . . . .	56
3.1.3	Square angular momentum . . . . .	58
3.1.4	Angular momentum uncertainty . . . . .	61
3.2	The Hydrogen Atom . . . . .	62
3.2.1	The Hamiltonian . . . . .	62
3.2.2	Solution using separation of variables . . . . .	63
3.2.3	Discussion of the eigenvalues . . . . .	67
3.2.4	Discussion of the eigenfunctions . . . . .	70
3.3	Expectation Value and Standard Deviation . . . . .	74
3.3.1	Statistics of a die . . . . .	75
3.3.2	Statistics of quantum operators . . . . .	77
3.3.3	Simplified expressions . . . . .	78
3.3.4	Some examples . . . . .	79
3.4	The Commutator . . . . .	82
3.4.1	Commuting operators . . . . .	82
3.4.2	Noncommuting operators and their commutator . . . . .	84
3.4.3	The Heisenberg uncertainty relationship . . . . .	84
3.4.4	Commutator reference [Reference] . . . . .	86
3.5	The Hydrogen Molecular Ion . . . . .	88
3.5.1	The Hamiltonian . . . . .	88
3.5.2	Energy when fully dissociated . . . . .	89
3.5.3	Energy when closer together . . . . .	90
3.5.4	States that share the electron . . . . .	91
3.5.5	Comparative energies of the states . . . . .	92
3.5.6	Variational approximation of the ground state . . . . .	93
3.5.7	Comparison with the exact ground state . . . . .	95

<b>4</b>	<b>Multiple-Particle Systems</b>	<b>97</b>
4.1	Generalization to Multiple Particles . . . . .	97
4.2	The Hydrogen Molecule . . . . .	98
4.2.1	The Hamiltonian . . . . .	98
4.2.2	Initial approximation to the lowest energy state . . . . .	99
4.2.3	The probability density . . . . .	99
4.2.4	States that share the electron . . . . .	100
4.2.5	Variational approximation of the ground state . . . . .	102
4.2.6	Comparison with the exact ground state . . . . .	102
4.3	Two-State Systems . . . . .	103
4.4	Spin . . . . .	105
4.5	Instantaneous Interactions [Background] . . . . .	106
4.6	Multiple-Particle Systems Including Spin . . . . .	111
4.6.1	Wave function for a single particle with spin . . . . .	111
4.6.2	Inner products including spin . . . . .	112
4.6.3	Wave function for multiple particles with spin . . . . .	113
4.6.4	Example: the hydrogen molecule . . . . .	114
4.6.5	Triplet and singlet states . . . . .	114
4.7	Identical Particles . . . . .	115
4.8	Ways to Symmetrize the Wave Function . . . . .	116
4.9	Matrix Formulation . . . . .	120
4.10	Global Symmetrization [Background] . . . . .	121
<b>5</b>	<b>Examples of Multiple-Particle Systems</b>	<b>123</b>
5.1	Heavier Atoms . . . . .	123
5.1.1	The Hamiltonian eigenvalue problem . . . . .	123
5.1.2	Approximate solution using separation of variables . . . . .	124
5.1.3	Hydrogen and helium . . . . .	125
5.1.4	Lithium to neon . . . . .	126
5.1.5	Sodium to argon . . . . .	130
5.1.6	Kalium to krypton . . . . .	130
5.2	Chemical Bonds . . . . .	131
5.2.1	Covalent sigma bonds . . . . .	131
5.2.2	Covalent pi bonds . . . . .	132
5.2.3	Polar covalent bonds and hydrogen bonds . . . . .	133
5.2.4	Promotion and hybridization . . . . .	134
5.2.5	Ionic bonds . . . . .	136
5.2.6	Limitations of valence bond theory . . . . .	137
5.3	Confined Electrons . . . . .	137
5.3.1	The Hamiltonian eigenvalue problem . . . . .	138
5.3.2	Solution by separation of variables . . . . .	138
5.3.3	Discussion of the solution . . . . .	140
5.3.4	A numerical example . . . . .	142
5.3.5	The density of states and confinement [Advanced] . . . . .	142
5.4	Band Structure . . . . .	148

5.4.1	Derivation [Advanced] . . . . .	149
5.5	Quantum Statistical Mechanics . . . . .	159
<b>6</b>	<b>Time Evolution</b>	<b>163</b>
6.1	The Schrödinger Equation . . . . .	163
6.1.1	Energy conservation . . . . .	164
6.1.2	Stationary states . . . . .	165
6.1.3	Time variations of symmetric two-state systems . . . . .	166
6.1.4	Time variation of expectation values . . . . .	167
6.1.5	Newtonian motion . . . . .	167
6.2	Unsteady perturbations of two-state systems . . . . .	169
6.2.1	Schrödinger equation for a two-state system . . . . .	169
6.2.2	Stimulated and spontaneous emission . . . . .	171
6.2.3	Absorption of radiation . . . . .	172
6.3	Conservation Laws and Symmetries [Background] . . . . .	175
6.4	The Position and Linear Momentum Eigenfunctions . . . . .	179
6.4.1	The position eigenfunction . . . . .	179
6.4.2	The linear momentum eigenfunction . . . . .	181
6.5	Wave Packets in Free Space . . . . .	182
6.5.1	Solution of the Schrödinger equation. . . . .	183
6.5.2	Component wave solutions . . . . .	184
6.5.3	Wave packets . . . . .	185
6.5.4	The group velocity . . . . .	186
6.6	Motion near the Classical Limit . . . . .	188
6.6.1	General procedures . . . . .	188
6.6.2	Motion through free space . . . . .	190
6.6.3	Accelerated motion . . . . .	190
6.6.4	Decelerated motion . . . . .	190
6.6.5	The harmonic oscillator . . . . .	191
6.7	Scattering . . . . .	193
6.7.1	Partial reflection . . . . .	193
6.7.2	Tunneling . . . . .	194
<b>7</b>	<b>Some Additional Topics</b>	<b>197</b>
7.1	All About Angular Momentum [Advanced] . . . . .	197
7.1.1	The fundamental commutation relations . . . . .	198
7.1.2	Ladders . . . . .	199
7.1.3	Possible values of angular momentum . . . . .	202
7.1.4	A warning about angular momentum . . . . .	203
7.1.5	Triplet and singlet states . . . . .	204
7.1.6	Clebsch-Gordan coefficients . . . . .	207
7.1.7	Pauli spin matrices . . . . .	211
7.2	The Relativistic Dirac Equation [Advanced] . . . . .	213
7.2.1	The Dirac idea . . . . .	213
7.2.2	Emergence of spin from relativity . . . . .	215

7.3	The Electromagnetic Field [Advanced] . . . . .	218
7.3.1	The Hamiltonian . . . . .	218
7.3.2	Maxwell's equations . . . . .	220
7.3.3	Electrons in magnetic fields . . . . .	227
7.4	Nuclear Magnetic Resonance [Advanced] . . . . .	229
7.4.1	Description of the method . . . . .	229
7.4.2	The Hamiltonian . . . . .	230
7.4.3	The unperturbed system . . . . .	232
7.4.4	Effect of the perturbation . . . . .	234
7.5	Some Topics Not Covered [Advanced] . . . . .	236
7.6	The Meaning of Quantum Mechanics [Background] . . . . .	239
7.6.1	Failure of the Schrödinger Equation? . . . . .	240
7.6.2	The Many-Worlds Interpretation . . . . .	242
<b>Notes</b>		<b>249</b>
<b>Bibliography</b>		<b>273</b>
<b>Web Pages</b>		<b>275</b>
<b>Notations</b>		<b>277</b>
<b>Index</b>		<b>295</b>



# List of Figures

1.1	The classical picture of a vector. . . . .	4
1.2	Spike diagram of a vector. . . . .	4
1.3	More dimensions. . . . .	4
1.4	Infinite dimensions. . . . .	5
1.5	The classical picture of a function. . . . .	5
1.6	Forming the dot product of two vectors. . . . .	6
1.7	Forming the inner product of two functions. . . . .	7
2.1	A visualization of an arbitrary wave function. . . . .	16
2.2	Combined plot of position and momentum components. . . . .	18
2.3	The uncertainty principle illustrated. . . . .	18
2.4	Classical picture of a particle in a closed pipe. . . . .	25
2.5	Quantum mechanics picture of a particle in a closed pipe. . . . .	25
2.6	Definitions. . . . .	26
2.7	One-dimensional energy spectrum for a particle in a pipe. . . . .	32
2.8	One-dimensional ground state of a particle in a pipe. . . . .	34
2.9	Second and third lowest one-dimensional energy states. . . . .	34
2.10	Definition of all variables. . . . .	36
2.11	True ground state of a particle in a pipe. . . . .	37
2.12	True second and third lowest energy states. . . . .	38
2.13	The harmonic oscillator. . . . .	40
2.14	The energy spectrum of the harmonic oscillator. . . . .	45
2.15	Ground state $\psi_{000}$ of the harmonic oscillator . . . . .	47
2.16	Wave functions $\psi_{100}$ and $\psi_{010}$ . . . . .	48
2.17	Energy eigenfunction $\psi_{213}$ . . . . .	49
2.18	Arbitrary wave function (not an energy eigenfunction). . . . .	52
3.1	Spherical coordinates of an arbitrary point P. . . . .	56
3.2	Spectrum of the hydrogen atom. . . . .	68
3.3	Ground state wave function $\psi_{100}$ of the hydrogen atom. . . . .	70
3.4	Eigenfunction $\psi_{200}$ . . . . .	71
3.5	Eigenfunction $\psi_{210}$ , or $2p_z$ . . . . .	72
3.6	Eigenfunction $\psi_{211}$ (and $\psi_{21-1}$ ). . . . .	72
3.7	Eigenfunctions $2p_x$ , left, and $2p_y$ , right. . . . .	73
3.8	Hydrogen atom plus free proton far apart. . . . .	89
3.9	Hydrogen atom plus free proton closer together. . . . .	90

3.10	The electron being anti-symmetrically shared. . . . .	91
3.11	The electron being symmetrically shared. . . . .	92
4.1	State with two neutral atoms. . . . .	100
4.2	Symmetric state . . . . .	101
4.3	Antisymmetric state . . . . .	101
4.4	Separating the hydrogen ion. . . . .	107
4.5	The Bohm experiment . . . . .	107
4.6	The Bohm experiment, after the Venus measurement. . . . .	108
4.7	Spin measurement directions. . . . .	108
4.8	Earth's view of events. . . . .	110
4.9	A moving observer's view of events. . . . .	110
5.1	Approximate solutions for hydrogen (left) and helium (right). . . . .	126
5.2	Approximate solutions for lithium (left) and beryllium (right). . . . .	128
5.3	Example approximate solution for boron. . . . .	129
5.4	Covalent sigma bond consisting of two $2p_z$ states. . . . .	132
5.5	Covalent pi bond consisting of two $2p_x$ states. . . . .	132
5.6	Covalent sigma bond consisting of a $2p_z$ and a $1s$ state. . . . .	133
5.7	Shape of an $sp^3$ hybrid state. . . . .	135
5.8	Shapes of the $sp^2$ (left) and $sp$ (right) hybrids. . . . .	136
5.9	Allowed wave number vectors. . . . .	140
5.10	Schematic energy spectrum of the free electron gas. . . . .	141
5.11	Occupied wave number states and Fermi surface in the ground state . . . . .	141
5.12	Density of states for the free electron gas. . . . .	144
5.13	Energy states, top, and density of states, bottom, when there is confinement in the $y$ -direction, as in a quantum well. . . . .	144
5.14	Energy states, top, and density of states, bottom, when there is confinement in both the $y$ - and $z$ -directions, as in a quantum wire. . . . .	146
5.15	Energy states, top, and density of states, bottom, when there is confinement in all three directions, as in a quantum dot or artificial atom. . . . .	147
5.16	Sketch of free electron and banded energy spectra. . . . .	148
5.17	Cross section of the full wave number space. . . . .	150
5.18	The $\vec{k}$ -grid and $k$ -sphere in wave number space. . . . .	155
5.19	Tearing apart of the wave number space energies. . . . .	158
5.20	Energy, as radial distance from the origin, for varying wave number vector directions. . . . .	158
5.21	Occupied levels in the ground state for two valence electrons per lattice cell. . . . .	159
6.1	Emission and absorption of radiation by an atom. . . . .	171
6.2	Approximate Dirac delta function $\delta_\varepsilon(x-\xi)$ is shown left. The true delta function $\delta(x - \xi)$ is the limit when $\varepsilon$ becomes zero, and is an infinitely high, infinitely thin spike, shown right. It is the eigenfunction corresponding to a position $\xi$ . . . . .	180
6.3	The real part (red) and envelope (black) of an example wave. . . . .	184
6.4	The wave moves with the phase speed. . . . .	185

6.5	The real part (red) and magnitude or envelope (black) of a typical wave packet	185
6.6	The velocities of wave and envelope are not equal. . . . .	186
6.7	A particle in free space. . . . .	190
6.8	An accelerating particle. . . . .	191
6.9	An decelerating particle. . . . .	191
6.10	Unsteady solution for the harmonic oscillator. The third picture shows the maximum distance from the nominal position that the wave packet reaches. . . . .	192
6.11	A partial reflection. . . . .	193
6.12	An tunneling particle. . . . .	194
6.13	Penetration of an infinitely high potential energy barrier. . . . .	194
7.1	Example bosonic ladders. . . . .	201
7.2	Example fermionic ladders. . . . .	201
7.3	Triplet and singlet states in terms of ladders . . . . .	207
7.4	Clebsch-Gordan coefficients of two spin 1/2 particles. . . . .	208
7.5	Clebsch-Gordan coefficients for $l_b = 1/2$ . . . . .	209
7.6	Clebsch-Gordan coefficients for $l_b = 1$ . . . . .	210
7.7	Relationship of Maxwell's first equation to Coulomb's law. . . . .	221
7.8	Maxwell's first equation for a more arbitrary region. The figure to the right includes the field lines through the selected points. . . . .	222
7.9	The net number of field lines leaving a region is a measure for the net charge inside that region. . . . .	222
7.10	Since magnetic monopoles do not exist, the net number of magnetic field lines leaving a region is always zero. . . . .	223
7.11	Electric power generation. . . . .	224
7.12	Two ways to generate a magnetic field: using a current (left) or using a varying electric field (right). . . . .	225
7.13	Larmor precession of the expectation spin (or magnetic moment) vector around the magnetic field. . . . .	233
7.14	Probability of being able to find the nuclei at elevated energy versus time for a given perturbation frequency $\omega$ . . . . .	235
7.15	Maximum probability of finding the nuclei at elevated energy. . . . .	235
7.16	A perturbing magnetic field, rotating at precisely the Larmor frequency, causes the expectation spin vector to come cascading down out of the ground state. .	236
7.17	Bohm's version of the Einstein, Podolski, Rosen Paradox . . . . .	242
7.18	Non entangled positron and electron spins; up and down. . . . .	243
7.19	Non entangled positron and electron spins; down and up. . . . .	243
7.20	The wave functions of two universes combined . . . . .	243
7.21	The Bohm experiment repeated. . . . .	245
7.22	Repeated experiments on the same electron. . . . .	246



# List of Tables

2.1	One-dimensional eigenfunctions of the harmonic oscillator, [3, p. 56]. . . . .	43
3.1	The first few spherical harmonics, from [3, p. 139]. . . . .	59
3.2	The first few radial wave functions for hydrogen, from [3, p. 154]. . . . .	66
5.1	Abbreviated periodic table of the elements, showing element symbol, atomic number, ionization energy, and electronegativity. . . . .	127



# Chapter 1

## Mathematical Prerequisites

Quantum mechanics is based on a number of advanced mathematical ideas that are described in this section.

### 1.1 Complex Numbers

Quantum mechanics is full of complex numbers, numbers involving

$$i = \sqrt{-1}.$$

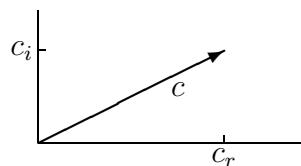
Note that  $\sqrt{-1}$  is not an ordinary, “real”, number, since there is no real number whose square is  $-1$ ; the square of a real number is always positive. This section summarizes the most important properties of complex numbers.

First, any complex number, call it  $c$ , can by definition always be written in the form

$$c = c_r + i c_i \tag{1.1}$$

where both  $c_r$  and  $c_i$  are ordinary real numbers, not involving  $\sqrt{-1}$ . The number  $c_r$  is called the real part of  $c$  and  $c_i$  the imaginary part.

We can think of the real and imaginary parts of a complex number as the components of a two-dimensional vector:



The length of that vector is called the “magnitude,” or “absolute value”  $|c|$  of the complex number. It equals

$$|c| = \sqrt{c_r^2 + c_i^2}.$$

Complex numbers can be manipulated pretty much in the same way as ordinary numbers can. A relation to remember is:

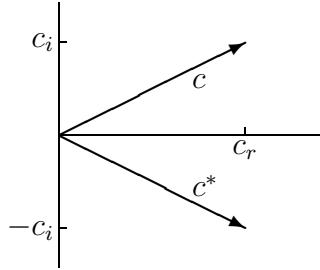
$$\frac{1}{i} = -i \quad (1.2)$$

which can be verified by multiplying top and bottom of the fraction by  $i$  and noting that by definition  $i^2 = -1$  in the bottom.

The complex conjugate of a complex number  $c$ , denoted by  $c^*$ , is found by replacing  $i$  everywhere by  $-i$ . In particular, if  $c = c_r + ic_i$ , where  $c_r$  and  $c_i$  are real numbers, the complex conjugate is

$$c^* = c_r - ic_i \quad (1.3)$$

The following picture shows that graphically, you get the complex conjugate of a complex number by flipping it over around the horizontal axis:



You can get the magnitude of a complex number  $c$  by multiplying  $c$  with its complex conjugate  $c^*$  and taking a square root:

$$|c| = \sqrt{c^*c} \quad (1.4)$$

If  $c = c_r + ic_i$ , where  $c_r$  and  $c_i$  are real numbers, multiplying out  $c^*c$  shows the magnitude of  $c$  to be

$$|c| = \sqrt{c_r^2 + c_i^2}$$

which is indeed the same as before.

From the above graph of the vector representing a complex number  $c$ , the real part is  $c_r = |c| \cos \alpha$  where  $\alpha$  is the angle that the vector makes with the horizontal axis, and the imaginary part is  $c_i = |c| \sin \alpha$ . So we can write any complex number in the form

$$c = |c| (\cos \alpha + i \sin \alpha)$$

The critically important Euler identity says that:

$$\cos \alpha + i \sin \alpha = e^{i\alpha} \quad (1.5)$$

So, any complex number can be written in “polar form” as

$$c = |c|e^{i\alpha}$$

where both the magnitude  $|c|$  and the angle  $\alpha$  are real numbers.

Any complex number of magnitude one can therefore be written as  $e^{i\alpha}$ . Note that the only two real numbers of magnitude one, 1 and  $-1$ , are included for  $\alpha = 0$ , respectively  $\alpha = \pi$ . The number  $i$  is obtained for  $\alpha = \pi/2$  and  $-i$  for  $\alpha = -\pi/2$ .

(See note {1} if you want to know where the Euler identity comes from.)

### Key Points

- ◊ Complex numbers include the square root of minus one,  $i$ , as a valid number.
- ◊ All complex numbers can be written as a real part plus  $i$  times an imaginary part, where both parts are normal real numbers.
- ◊ The complex conjugate of a complex number is obtained by replacing  $i$  everywhere by  $-i$ .
- ◊ The magnitude of a complex number is obtained by multiplying the number by its complex conjugate and then taking a square root.
- ◊ The Euler identity relates exponentials to sines and cosines.

### 1.1 Review Questions

- 1** Multiply out  $(2 + 3i)^2$  and then find its real and imaginary part.
- 2** Show more directly that  $1/i = -i$ .
- 3** Multiply out  $(2 + 3i)(2 - 3i)$  and then find its real and imaginary part.
- 4** Find the magnitude or absolute value of  $2 + 3i$ .
- 5** Verify that  $(2 - 3i)^2$  is still the complex conjugate of  $(2 + 3i)^2$  if both are multiplied out.
- 6** Verify that  $e^{-2i}$  is still the complex conjugate of  $e^{2i}$  after both are rewritten using the Euler identity.
- 7** Verify that  $(e^{i\alpha} + e^{-i\alpha})/2 = \cos \alpha$ .
- 8** Verify that  $(e^{i\alpha} - e^{-i\alpha})/2i = \sin \alpha$ .

## 1.2 Functions as Vectors

The second mathematical idea that is critical for quantum mechanics is that functions can be treated in a way that is fundamentally not that much different from vectors.

A vector  $\vec{f}$  (which might be velocity  $\vec{v}$ , linear momentum  $\vec{p} = m\vec{v}$ , force  $\vec{F}$ , or whatever) is usually shown in physics in the form of an arrow:

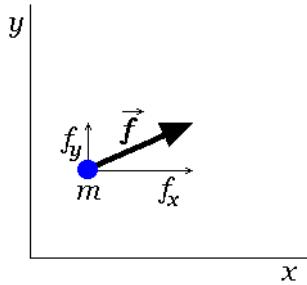


Figure 1.1: The classical picture of a vector.

However, the same vector may instead be represented as a spike diagram, by plotting the value of the components versus the component index:

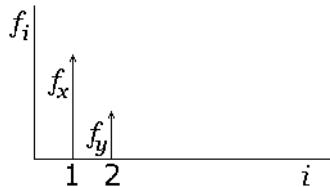


Figure 1.2: Spike diagram of a vector.

(The symbol  $i$  for the component index is not to be confused with  $i = \sqrt{-1}$ .)

In the same way as in two dimensions, a vector in three dimensions, or, for that matter, in thirty dimensions, can be represented by a spike diagram:

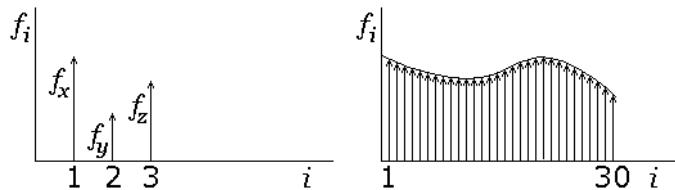


Figure 1.3: More dimensions.

For a large number of dimensions, and in particular in the limit of infinitely many dimensions, the large values of  $i$  can be rescaled into a continuous coordinate, call it  $x$ . For example,  $x$  might be defined as  $i$  divided by the number of dimensions. In any case, the spike diagram becomes a function  $f(x)$ :

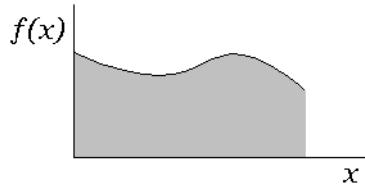


Figure 1.4: Infinite dimensions.

The spikes are usually not shown:

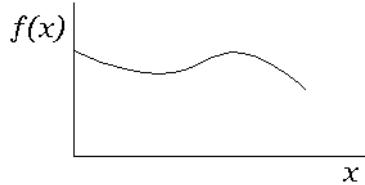


Figure 1.5: The classical picture of a function.

In this way, a function is just a vector in infinitely many dimensions.

### Key Points

- ◊ Functions can be thought of as vectors with infinitely many components.
- ◊ This allows quantum mechanics do the same things with functions as we can do with vectors.

### 1.2 Review Questions

- 1 Graphically compare the spike diagram of the 10-dimensional vector  $\vec{v}$  with components  $(0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5)$  with the plot of the function  $f(x) = 0.5x$ .
- 2 Graphically compare the spike diagram of the 10-dimensional unit vector  $\hat{i}_3$ , with components  $(0, 0, 1, 0, 0, 0, 0, 0, 0, 0)$ , with the plot of the function  $f(x) = 1$ . (No, they do not look alike.)

## 1.3 The Dot, oops, INNER Product

The dot product of vectors is an important tool. It makes it possible to find the length of a vector, by multiplying the vector by itself and taking the square root. It is also used to check if two vectors are orthogonal: if their dot product is zero, they are. In this subsection, the dot product is defined for complex vectors and functions.

The usual dot product of two vectors  $\vec{f}$  and  $\vec{g}$  can be found by multiplying components with the same index  $i$  together and summing that:

$$\vec{f} \cdot \vec{g} \equiv f_1 g_1 + f_2 g_2 + f_3 g_3$$

(The emphatic equal,  $\equiv$ , is commonly used to indicate “is by definition equal” or “is always equal.”) Figure 1.6 shows multiplied components using equal colors.

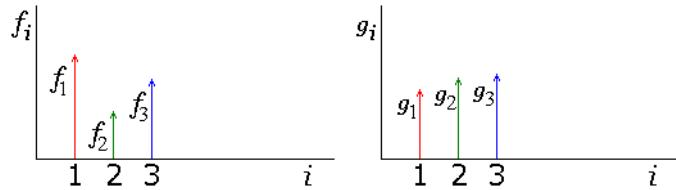


Figure 1.6: Forming the dot product of two vectors.

Note the use of numeric subscripts,  $f_1$ ,  $f_2$ , and  $f_3$  rather than  $f_x$ ,  $f_y$ , and  $f_z$ ; it means the same thing. Numeric subscripts allow the three term sum above to be written more compactly as:

$$\vec{f} \cdot \vec{g} \equiv \sum_{\text{all } i} f_i g_i$$

The  $\Sigma$  is called the “summation symbol.”

The length of a vector  $\vec{f}$ , indicated by  $|\vec{f}|$  or simply by  $f$ , is normally computed as

$$|\vec{f}| = \sqrt{\vec{f} \cdot \vec{f}} = \sqrt{\sum_{\text{all } i} f_i^2}$$

However, this does not work correctly for complex vectors. The difficulty is that terms of the form  $f_i^2$  are no longer necessarily positive numbers. For example,  $i^2 = -1$ .

Therefore, it is necessary to use a generalized “inner product” for complex vectors, which puts a complex conjugate on the first vector:

$$\langle \vec{f} | \vec{g} \rangle \equiv \sum_{\text{all } i} f_i^* g_i$$

(1.6)

If vector  $\vec{f}$  is real, the complex conjugate does nothing, and the inner product  $\langle \vec{f} | \vec{g} \rangle$  is the same as the dot product  $\vec{f} \cdot \vec{g}$ . Otherwise, in the inner product  $\vec{f}$  and  $\vec{g}$  are no longer interchangeable; the conjugates are only on the *first* factor,  $\vec{f}$ . Interchanging  $\vec{f}$  and  $\vec{g}$  changes the inner product value into its complex conjugate.

The length of a nonzero vector is now always a positive number:

$$|\vec{f}| = \sqrt{\langle \vec{f} | \vec{f} \rangle} = \sqrt{\sum_{\text{all } i} |f_i|^2} \quad (1.7)$$

Physicists take the inner product “bracket” verbally apart as

$$\begin{array}{c} \langle \vec{f} | \quad | \vec{g} \rangle \\ \text{bra} \quad \not\in \quad \text{ket} \end{array}$$

and refer to vectors as bras and kets.

The inner product of functions is defined in exactly the same way as for vectors, by multiplying values at the same  $x$  position together and summing. But since there are infinitely many  $x$ -values, the sum becomes an integral:

$$\langle f | g \rangle = \int_{\text{all } x} f^*(x) g(x) dx \quad (1.8)$$

as illustrated in figure 1.7.

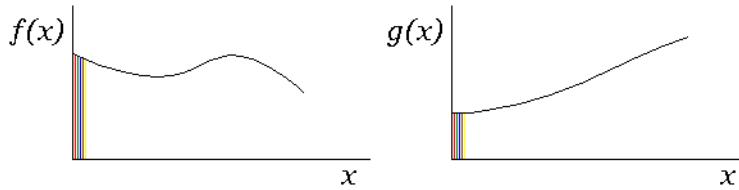


Figure 1.7: Forming the inner product of two functions.

The equivalent of the length of a vector is in case of a function called its “norm:”

$$\|f\| \equiv \sqrt{\langle f | f \rangle} = \sqrt{\int_{\text{all } x} |f(x)|^2 dx} \quad (1.9)$$

The double bars are used to avoid confusion with the absolute value of the function.

A vector or function is called “normalized” if its length or norm is one:

$$\langle f | f \rangle = 1 \text{ iff } f \text{ is normalized.} \quad (1.10)$$

(“iff” should really be read as “if and only if.”)

Two vectors, or two functions,  $f$  and  $g$  are by definition orthogonal if their inner product is zero:

$$\langle f | g \rangle = 0 \text{ iff } f \text{ and } g \text{ are orthogonal.} \quad (1.11)$$

Sets of vectors or functions that are all

- mutually orthogonal, and
- normalized

occur a lot in quantum mechanics. Such sets should be called “orthonormal”, though the less precise term “orthogonal” is often used instead. This document will refer to them correctly as being orthonormal.

So, a set of functions or vectors  $f_1, f_2, f_3, \dots$  is orthonormal if

$$0 = \langle f_1 | f_2 \rangle = \langle f_2 | f_1 \rangle = \langle f_1 | f_3 \rangle = \langle f_3 | f_1 \rangle = \langle f_2 | f_3 \rangle = \langle f_3 | f_2 \rangle = \dots$$

and

$$1 = \langle f_1 | f_1 \rangle = \langle f_2 | f_2 \rangle = \langle f_3 | f_3 \rangle = \dots$$

### Key Points

- ◊ For complex vectors and functions, the normal dot product becomes the inner product.
- ◊ To take an inner product of vectors, (1) take complex conjugates of the components of the first vector; (2) multiply corresponding components of the two vectors together; and (3) sum these products.
- ◊ To take an inner product of functions, (1) take the complex conjugate of the first function; (2) multiply the two functions; and (3) integrate the product function. The real difference from vectors is integration instead of summation.
- ◊ To find the length of a vector, take the inner product of the vector with itself, and then a square root.
- ◊ To find the norm of a function, take the inner product of the function with itself, and then a square root.
- ◊ A pair of functions, or a pair of vectors, are orthogonal if their inner product is zero.
- ◊ A set of functions, or a set of vectors, form an orthonormal set if every one is orthogonal to all the rest, and every one is of unit norm or length.

### 1.3 Review Questions

- 1** Find the following inner product of the two vectors:

$$\left\langle \begin{pmatrix} 1+i \\ 2-i \end{pmatrix} \middle| \begin{pmatrix} 2i \\ 3 \end{pmatrix} \right\rangle$$

**2** Find the length of the vector

$$\begin{pmatrix} 1+i \\ 3 \end{pmatrix}$$

**3** Find the inner product of the functions  $\sin(x)$  and  $\cos(x)$  on the interval  $0 \leq x \leq 1$ .

**4** Show that the functions  $\sin(x)$  and  $\cos(x)$  are orthogonal on the interval  $0 \leq x \leq 2\pi$ .

**5** Verify that  $\sin(x)$  is not a normalized function on the interval  $0 \leq x \leq 2\pi$ , and normalize it by dividing by its norm.

**6** Verify that the most general multiple of  $\sin(x)$  that is normalized on the interval  $0 \leq x \leq 2\pi$  is  $e^{i\alpha} \sin(x)/\sqrt{\pi}$  where  $\alpha$  is any arbitrary real number. So, using the Euler identity, the following multiples of  $\sin(x)$  are all normalized:  $\sin(x)/\sqrt{\pi}$ , (for  $\alpha = 0$ ),  $-\sin(x)/\sqrt{\pi}$ , (for  $\alpha = \pi$ ), and  $i\sin(x)/\sqrt{\pi}$ , (for  $\alpha = \pi/2$ ).

**7** Show that the functions  $e^{4i\pi x}$  and  $e^{6i\pi x}$  are an orthonormal set on the interval  $0 \leq x \leq 1$ .

---

## 1.4 Operators

This section defines operators, which are a generalization of matrices. Operators are the principal components of quantum mechanics.

In a finite number of dimensions, a matrix  $A$  can transform any arbitrary vector  $v$  into a different vector  $A\vec{v}$ :

$$\vec{v} \xrightarrow{\text{matrix } A} \vec{w} = A\vec{v}$$

Similarly, an operator transforms a function into another function:

$$f(x) \xrightarrow{\text{operator } A} g(x) = Af(x)$$

Some simple examples of operators:

$$f(x) \xrightarrow{\hat{x}} g(x) = xf(x)$$

$$f(x) \xrightarrow{\frac{d}{dx}} g(x) = f'(x)$$

Note that a hat is often used to indicate operators; for example,  $\hat{x}$  is the symbol for the operator that corresponds to multiplying by  $x$ . If it is clear that something is an operator, such as  $d/dx$ , no hat will be used.

It should really be noted that the operators that we are interested in in quantum mechanics are “linear” operators: if we increase  $f$  by a number,  $Af$  increases by that same number; also, if we sum  $f$  and  $g$ ,  $A(f + g)$  will be  $Af$  plus  $Ag$ .

### Key Points

- ◊ Matrices turn vectors into other vectors.
- ◊ Operators turn functions into other functions.

### 1.4 Review Questions

- 1 So what is the result if the operator  $d/dx$  is applied to the function  $\sin(x)$ ?
- 2 If, say,  $\widehat{x^2} \sin(x)$  is simply the function  $x^2 \sin(x)$ , then what *is* the difference between  $\widehat{x^2}$  and  $x^2$ ?
- 3 A less self-evident operator than the above examples is a shift operator like  $\Delta_{\pi/2}$  that shifts the graph of a function towards the left by an amount  $\pi/2$ :  $\Delta_{\pi/2}f(x) = f\left(x + \frac{1}{2}\pi\right)$ . (Curiously enough, shift operators turn out to be responsible for the law of conservation of momentum.) Show that  $\Delta_{\pi/2}$  turns  $\sin(x)$  into  $\cos(x)$ .
- 4 The inversion operator Inv turns  $f(x)$  into  $f(-x)$ . It plays a part in the question to what extent physics looks the same when seen in the mirror. Show that Inv leaves  $\cos(x)$  unchanged, but turns  $\sin(x)$  into  $-\sin(x)$ .

## 1.5 Eigenvalue Problems

To analyze quantum mechanical systems, it is normally necessary to find so-called eigenvalues and eigenvectors or eigenfunctions. This section defines what they are.

A nonzero vector  $\vec{v}$  is called an eigenvector of a matrix  $A$  if  $A\vec{v}$  is a multiple of the same vector:

$$A\vec{v} = a\vec{v} \text{ iff } \vec{v} \text{ is an eigenvector of } A \quad (1.12)$$

The multiple  $a$  is called the eigenvalue. It is just a number.

A nonzero function  $f$  is called an eigenfunction of an operator  $A$  if  $Af$  is a multiple of the same function:

$$Af = af \text{ iff } f \text{ is an eigenfunction of } A. \quad (1.13)$$

For example,  $e^x$  is an eigenfunction of the operator  $d/dx$  with eigenvalue 1, since  $de^x/dx = 1e^x$ .

However, eigenfunctions like  $e^x$  are not very common in quantum mechanics since they become very large at large  $x$ , and that typically does not describe physical situations. The eigenfunctions of  $d/dx$  that do appear a lot are of the form  $e^{ikx}$ , where  $i = \sqrt{-1}$  and  $k$  is an

arbitrary real number. The eigenvalue is  $ik$ :

$$\frac{d}{dx} e^{ikx} = ike^{ikx}$$

Function  $e^{ikx}$  does not blow up at large  $x$ ; in particular, the Euler identity (1.5) says:

$$e^{ikx} = \cos(kx) + i \sin(kx)$$

The constant  $k$  is called the wave number.

### Key Points

- ◊ If a matrix turns a nonzero vector into a multiple of that vector, that vector is an eigenvector of the matrix, and the multiple is the eigenvalue.
- ◊ If an operator turns a nonzero function into a multiple of that function, that function is an eigenfunction of the operator, and the multiple is the eigenvalue.

### 1.5 Review Questions

- 1 Show that  $e^{ikx}$ , above, is also an eigenfunction of  $d^2/dx^2$ , but with eigenvalue  $-k^2$ . In fact, it is easy to see that the square of any operator has the same eigenfunctions, but with the square eigenvalues. (Since the operators of quantum mechanics are linear.)
- 2 Show that any function of the form  $\sin(kx)$  and any function of the form  $\cos(kx)$ , where  $k$  is a constant called the wave number, is an eigenfunction of the operator  $d^2/dx^2$ , though they are not eigenfunctions of  $d/dx$
- 3 Show that  $\sin(kx)$  and  $\cos(kx)$ , with  $k$  a constant, are eigenfunctions of the inversion operator  $\text{Inv}$ , which turns any function  $f(x)$  into  $f(-x)$ , and find the eigenvalues.

## 1.6 Hermitian Operators

Most operators in quantum mechanics are of a special kind called “Hermitian”. This section lists their most important properties.

We call an operator Hermitian when it can always be flipped over to the other side if it appears in a inner product:

$$\langle f | Ag \rangle = \langle Af | g \rangle \text{ always iff } A \text{ is Hermitian.} \quad (1.14)$$

That is the definition, but Hermitian operators have the following additional special properties:

- They always have real eigenvalues, not involving  $i = \sqrt{-1}$ . (But the eigenfunctions, or eigenvectors if the operator is a matrix, might be complex.) Physical values such as position, momentum, and energy are ordinary real numbers since they are eigenvalues of Hermitian operators {2}.
- Their eigenfunctions can always be chosen so that they are normalized and mutually orthogonal, in other words, an orthonormal set. This tends to simplify the various mathematics a lot.
- Their eigenfunctions form a “complete” set. This means that *any* function can be written as some linear combination of the eigenfunctions. In practical terms, that means that you only need to look at the eigenfunctions to completely understand what the operator does. {3}.

In the linear algebra of real matrices, Hermitian operators are simply symmetric matrices. A basic example is the inertia matrix of a solid body in Newtonian dynamics. The orthonormal eigenvectors of the inertia matrix give the directions of the principal axes of inertia of the body.

The following properties of inner products involving Hermitian operators are often needed, so we list them here:

$$\text{If } A \text{ is Hermitian: } \langle g | Af \rangle = \langle f | Ag \rangle^*, \quad \langle f | Af \rangle \text{ is real.} \quad (1.15)$$

The first says that you can swap  $f$  and  $g$  if you take complex conjugate. (It is simply a reflection of the fact that if you change the sides in an inner product, you turn it into its complex conjugate. Normally, that puts the operator at the other side, but for a Hermitian operator, it does not make a difference.) The second is important because ordinary real numbers typically occupy a special place in the grand scheme of things. (The fact that the inner product is real merely reflects the fact that if a number is equal to its complex conjugate, it must be real; if there was an  $i$  in it, the number would change by a complex conjugate.)

### Key Points

- ◊ Hermitian operators can be flipped over to the other side in inner products.
- ◊ Hermitian operators have only real eigenvalues.
- ◊ Hermitian operators have a complete set of orthonormal eigenfunctions (or eigenvectors).

### 1.6 Review Questions

- 1 Show that the operator  $\hat{2}$  is a Hermitian operator, but  $\hat{i}$  is not.

- 2** Let's generalize the previous question, by showing that any complex constant  $c$  comes out of the right hand side of an inner product unchanged, but out of the left hand side as its complex conjugate;

$$\langle f|cg \rangle = c\langle f|g \rangle \quad \langle cf|g \rangle = c^*\langle f|g \rangle.$$

As a result, a number  $c$  is only a Hermitian operator if it is real: if  $c$  is complex, the two expressions above are not the same.

- 3** Show that an operator such as  $\hat{x}^2$ , corresponding to multiplying by a real function, is an Hermitian operator.
- 4** Show that the operator  $d/dx$  is *not* a Hermitian operator, but  $id/dx$  is, assuming that the functions on which they act vanish at the ends of the interval  $a \leq x \leq b$  on which they are defined. (Less restrictively, it is only required that the functions are “periodic”; they must return to the same value at  $x = b$  that they had at  $x = a$ .)
- 5** Show that if  $A$  is a Hermitian operator, then so is  $A^2$ . As a result, under the conditions of the previous question,  $-d^2/dx^2$  is a Hermitian operator too. (And so is just  $d^2/dx^2$ , of course, but  $-d^2/dx^2$  is the one with the positive eigenvalues, the squares of the eigenvalues of  $id/dx$ .)
- 6** A complete set of orthonormal eigenfunctions of the operator  $-d^2/dx^2$  of the previous question on the interval  $0 \leq x \leq \pi$  that are zero at the end points are the infinite set of functions

$$\frac{\sin(x)}{\sqrt{\pi/2}}, \frac{\sin(2x)}{\sqrt{\pi/2}}, \frac{\sin(3x)}{\sqrt{\pi/2}}, \frac{\sin(4x)}{\sqrt{\pi/2}}, \dots$$

Check that these functions are indeed zero at  $x = 0$  and  $x = \pi$ , that they are indeed orthonormal, and that they are eigenfunctions of  $-d^2/dx^2$  with the positive real eigenvalues

$$1, 4, 9, 16, \dots$$

Completeness is a much more difficult thing to prove, but they are. It is a special case of the completeness question of the next question.

- 7** A complete set of orthonormal eigenfunctions of the operator  $id/dx$  that are periodic on the interval  $0 \leq x \leq 2\pi$  are the infinite set of functions

$$\dots, \frac{e^{-3ix}}{\sqrt{2\pi}}, \frac{e^{-2ix}}{\sqrt{2\pi}}, \frac{e^{-ix}}{\sqrt{2\pi}}, \frac{1}{\sqrt{2\pi}}, \frac{e^{ix}}{\sqrt{2\pi}}, \frac{e^{2ix}}{\sqrt{2\pi}}, \frac{e^{3ix}}{\sqrt{2\pi}}, \dots$$

Check that these functions are indeed periodic, orthonormal, and that they are eigenfunctions of  $id/dx$  with the real eigenvalues

$$\dots, 3, 2, 1, 0, -1, -2, -3, \dots$$

Completeness is a much more difficult thing to prove, but they are. The answer has an outline of an elementary proof.

## 1.7 Additional Points

This subsection describes a few further issues of importance for this document.

### 1.7.1 Dirac notation

Physicists like to write inner products such as  $\langle f|Ag\rangle$  in “Dirac notation”:

$$\langle f|A|g\rangle$$

since this conforms more closely to how you would think of it in linear algebra:

$$\begin{array}{ccc} \langle \vec{f} | & A & | \vec{g} \rangle \\ \text{bra} & \text{operator} & \text{ket} \end{array}$$

The various advanced ideas of linear algebra can be extended to operators in this way, but we will not need them.

In any case,  $\langle f|Ag\rangle$  and  $\langle f|A|g\rangle$  mean the same thing:

$$\int_{\text{all } x} f^*(x) (Ag(x)) dx$$

### 1.7.2 Additional independent variables

In many cases, the functions involved in an inner product may depend on more than a single variable  $x$ . For example, they might depend on the position  $(x, y, z)$  in three dimensional space.

The rule to deal with that is to ensure that the inner product integrations are over *all* independent variables. For example, in three spatial dimensions:

$$\langle f|g\rangle = \int_{\text{all } x} \int_{\text{all } y} \int_{\text{all } z} f^*(x, y, z) g(x, y, z) dx dy dz$$

Note that the time  $t$  is a somewhat different variable from the rest, and time is *not* included in the inner product integrations.

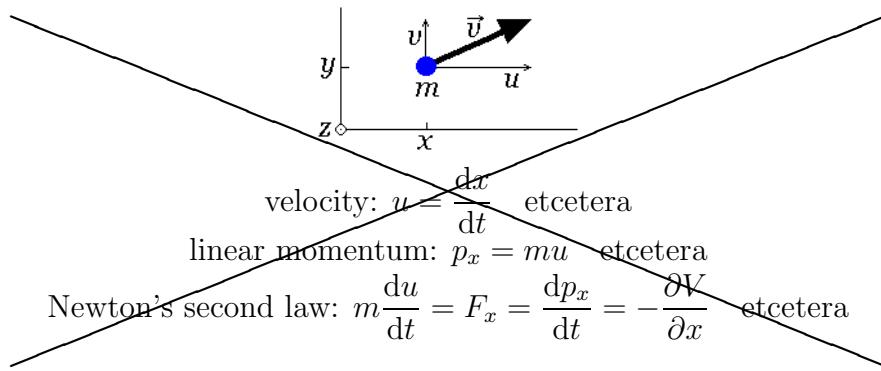
# Chapter 2

## Basic Ideas of Quantum Mechanics

### 2.1 The Revised Picture of Nature

This section describes the view quantum mechanics has of nature, which is in terms of a mysterious function called the “wave function”.

According to quantum mechanics, the way that the old Newtonian physics describes nature is wrong if examined closely enough. Not just a bit wrong. Totally wrong. For example, the Newtonian picture for a particle of mass  $m$  looks like:



The problems? A numerical position for the particle simply *does not exist*. A numerical velocity or linear momentum for the particle *does not exist*.

What does exist according to quantum mechanics is the so-called wave function  $\Psi(x, y, z; t)$ . Its square magnitude,  $|\Psi|^2$ , can be shown as grey tones (darker where the magnitude is larger):

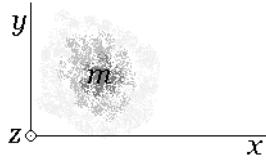


Figure 2.1: A visualization of an arbitrary wave function.

The physical meaning of the wave function is known as “Born’s statistical interpretation”: darker regions are regions where the particle is more likely to be found if the location is narrowed down. More precisely, if  $\vec{r} = (x, y, z)$  is a given location, then

$$|\Psi(\vec{r}; t)|^2 d^3\vec{r} \quad (2.1)$$

is the probability of finding the particle within a small volume, of size  $d^3\vec{r} = dx dy dz$ , around that given location, *if* such a measurement is attempted.

(And if such a position measurement is actually done, it affects the wave function: after the measurement, the new wave function will be restricted to the volume to which the position was narrowed down. But it will spread out again in time if allowed to do so afterwards.)

The particle must be somewhere. In quantum mechanics, that is expressed by the fact that the total probability to find the particle, integrated over all possible locations, must be 100% (certainty):

$$\int_{\text{all } \vec{r}} |\Psi(\vec{r}; t)|^2 d^3\vec{r} = 1 \quad (2.2)$$

In other words, proper wave functions are normalized,  $\langle \Psi | \Psi \rangle = 1$ .

The position of macroscopic particles is typically very much narrowed down by incident light, surrounding objects, earlier history, etcetera. For such particles, the “blob size” of the wave function is extremely small. As a result, claiming that a macroscopic particle, is, say, at the center point of the wave function blob may be just fine in practical applications. But when we are interested in what happens on very small scales, the nonzero blob size can make a big difference.

In addition, even on macroscopic scales, position can be ill defined. Consider what happens if we take the wave function blob apart and send half to Mars and half to Venus. Quantum mechanics allows it; this is what happens in a “scattering” experiment. We would presumably need to be extremely careful to do it on such a large scale, but there is no *fundamental* theoretical objection in quantum mechanics. So, where is the particle now? Hiding on Mars? Hiding on Venus?

Orthodox quantum mechanics says: *neither*. It will pop up on one of the two if circumstances change to force it to reveal its presence. But until that moment, it is just as ready to pop up on Mars as on Venus, at an instant’s notice. If it was hiding on Mars, it could not possibly

pop up on Venus on an instant's notice; the fastest it would be allowed to move is at the speed of light.

Of course, quantum mechanics is largely a matter of inference. The wave function cannot be directly observed. But I am not sure that that is as strong an argument against quantum mechanics as it may seem. After almost a century, quantum mechanics is still standing, with no real “more reasonable” competitors, ones that stay closer to the Newtonian picture. And the best minds in physics have tried.

### Key Points

- ◊ According to quantum mechanics, particles do not have definite values of position or velocity when examined closely enough.
- ◊ What they do have is a “wave function” that depends on position.
- ◊ Larger values of the absolute value of the wave function, (indicated in this book by darker regions,) correspond to regions where the particle is more likely to be found if a location measurement is done.
- ◊ Such a measurement changes the wave function; the measurement itself creates the reduced uncertainty in position that exists immediately after the measurement.
- ◊ In other words, the wave function is all there is; we cannot identify a hidden position in a *given* wave function, just create a *new* wave function that more precisely locates the particle.
- ◊ The creation of such a more localized wave function during a position measurement is governed by laws of chance: the more localized wave function is more likely to end up in regions where the initial wave function had a larger magnitude.
- ◊ Proper wave functions are normalized.

## 2.2 The Heisenberg Uncertainty Principle

The Heisenberg uncertainty principle is a way of expressing the qualitative properties of quantum mechanics in an easy to visualize way.

Figure 2.2 is a combination plot of the position  $x$  of a particle and the corresponding linear momentum  $p_x = mu$ , (with  $m$  the mass and  $u$  the velocity in the  $x$ -direction):

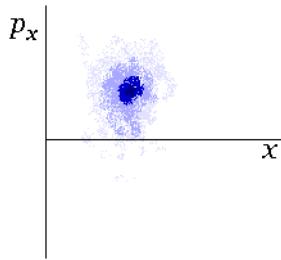


Figure 2.2: Combined plot of position and momentum components.

Figure 2.3 shows what happens if we squeeze down on the particle to try to restrict it to one position  $x$ : it stretches out in the momentum direction:

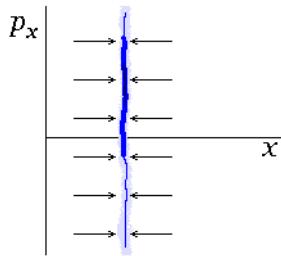


Figure 2.3: The uncertainty principle illustrated.

Heisenberg showed that according to quantum mechanics, the area of the blue “blob” cannot be contracted to a point. When we try to narrow down the position of a particle, we get into trouble with momentum. Conversely, if we try to pin down a precise momentum, we lose all hold on the position.

### Key Points

- ◊ The Heisenberg uncertainty principle says that there is always a minimum combined uncertainty in position and linear momentum.
- ◊ It implies that a particle cannot have a mathematically precise position, because that would require an infinite uncertainty in linear momentum.
- ◊ It also implies that a particle cannot have a mathematically precise linear momentum (velocity), since that would imply an infinite uncertainty in position.

## 2.3 The Operators of Quantum Mechanics

The numerical quantities that the old Newtonian physics uses, (position, momentum, energy, ...), are just “shadows” of what really describes nature: operators. The operators described in this section are the key to quantum mechanics.

As the first example, while a mathematically precise value of the position  $x$  of a particle never exists, we do have an *x-position operator*  $\hat{x}$ . It turns the wave function  $\Psi$  into  $x\Psi$ :

$$\Psi(x, y, z, t) \xrightarrow{\hat{x}} x\Psi(x, y, z, t) \quad (2.3)$$

The operators  $\hat{y}$  and  $\hat{z}$  are defined similarly as  $\hat{x}$ .

Instead of a linear momentum  $p_x = mu$ , we have an *x-momentum operator*

$$\boxed{\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}} \quad (2.4)$$

that turns  $\Psi$  into its *x*-derivative:

$$\Psi(x, y, z, t) \xrightarrow{\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}} \frac{\hbar}{i} \Psi_x(x, y, z, t) \quad (2.5)$$

The constant  $\hbar$  is called Planck’s constant. (Or rather, it is Planck’s original constant  $h$  divided by  $2\pi$ .) If it would have been zero, we would not have had all these troubles with quantum mechanics. The blobs would become points. Unfortunately,  $\hbar$  is very small, but nonzero. It is about  $10^{-34}$  kg m<sup>2</sup>/s.

The factor  $i$  in  $\hat{p}_x$  makes it a Hermitian operator (a proof of that is in note {4}). All operators reflecting our macroscopic physical quantities are Hermitian.

The operators  $\hat{p}_y$  and  $\hat{p}_z$  are defined similarly as  $\hat{p}_x$ .

The *kinetic energy operator*  $\hat{T}$  is:

$$\hat{T} = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} \quad (2.6)$$

Its shadow is the Newtonian notion that the kinetic energy equals:

$$T = \frac{1}{2}m(u^2 + v^2 + w^2) = \frac{(mu)^2 + (mv)^2 + (mw)^2}{2m}$$

This is an example of the “Newtonian analogy”: the relationships between the different operators in quantum mechanics are in general the same as those between the corresponding numerical values in Newtonian physics. But since the momentum *operators* are gradients, the actual kinetic energy operator is:

$$\hat{T} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right). \quad (2.7)$$

Mathematicians call the set of second order derivative operators in the kinetic energy operator the “Laplacian”, and indicate it by  $\nabla^2$ :

$$\boxed{\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}} \quad (2.8)$$

In those terms, the kinetic energy operator can be written more concisely as:

$$\boxed{\hat{T} = -\frac{\hbar^2}{2m}\nabla^2} \quad (2.9)$$

Following the Newtonian analogy once more, the total energy operator, indicated by  $H$ , is the sum of the kinetic energy operator above and the potential energy operator  $V(x, y, z, t)$ :

$$\boxed{H = -\frac{\hbar^2}{2m}\nabla^2 + V} \quad (2.10)$$

This total energy operator  $H$  is called the *Hamiltonian* and it is very important. Its eigenvalues are indicated by  $E$  (for energy), for example  $E_1, E_2, E_3, \dots$  with:

$$H\psi_n = E_n\psi_n \quad \text{for } n = 1, 2, 3, \dots \quad (2.11)$$

where  $\psi_n$  is eigenfunction number  $n$  of the Hamiltonian.

It is seen later that in many cases a more elaborate numbering of the eigenvalues and eigenvectors of the Hamiltonian is desirable instead of using a single counter  $n$ . For example, for the electron of the hydrogen atom, there is more than one eigenfunction for each different eigenvalue  $E_n$ , and additional counters  $l$  and  $m$  are used to distinguish them. It is usually best to solve the eigenvalue problem first and decide on how to number the solutions afterwards.

(It is also important to remember that in the literature, the Hamiltonian eigenvalue problem is commonly referred to as the “time-independent Schrödinger equation.” However, this book prefers to reserve the term Schrödinger equation for the unsteady evolution of the wave function.)

### Key Points

- ◊ Physical quantities correspond to operators in quantum mechanics.
- ◊ Expressions for various important operators were given.
- ◊ Kinetic energy is in terms of the so-called Laplacian operator.
- ◊ The important total energy operator, (kinetic plus potential energy,) is called the Hamiltonian.

## 2.4 The Orthodox Statistical Interpretation

In addition to the operators defined in the previous section, quantum mechanics requires rules on how to use them. This section gives those rules, along with a critical discussion what they really mean.

### 2.4.1 Only eigenvalues

According to quantum mechanics, the only “measurable values” of position, momentum, energy, etcetera, are the *eigenvalues* of the corresponding operator. For example, if the total energy of a particle is “measured”, the only numbers that can come out are the eigenvalues of the total energy Hamiltonian.

There is really no controversy that only the eigenvalues come out; this has been verified overwhelmingly in experiments, often to astonishingly many digits accuracy. It is the reason for the line spectra that allow us to recognize the elements, either on earth or halfway across the observable universe, for lasers, for the blackbody radiation spectrum, for the value of the speed of sound, for the accuracy of atomic clocks, for the properties of chemical bonds, for the fact that a Stern-Gerlach apparatus does not fan out a beam of atoms but splits it into discrete rays, and countless other basic properties of nature.

But the question *why and how* only the eigenvalues come out is much more tricky. In general the wave function that describes physics is a *combination* of eigenfunctions, not a single eigenfunction. (Even if the wave function was an eigenfunction of one operator, it would not be one of another operator.) If the wave function is a combination of eigenfunctions, then why is the measured value not a combination, (maybe some average), of eigenvalues, but a *single* eigenvalue? And what happens to the eigenvalues in the combination that do not come out? It is a question that has plagued quantum mechanics since the beginning.

The most generally given answer in the physics community is the “orthodox interpretation.” It is commonly referred to as the “Copenhagen Interpretation”, though that interpretation, as promoted by Niels Bohr, was actually much more circumspect than what is usually presented.

*The orthodox interpretation says that “measurement” causes the wave function  $\Psi$  to “collapse” into one of the eigenfunctions of the quantity being measured.*

Staying with energy measurements as the example, any total energy “measurement” will cause the wave function to collapse into one of the eigenfunctions  $\psi_n$  of the total energy Hamiltonian. The energy that is measured is the corresponding eigenvalue:

$$\left. \begin{array}{l} \Psi = c_1\psi_1 + c_2\psi_2 + \dots \\ \text{Energy is uncertain} \end{array} \right\} \xrightarrow{\text{energy measurement}} \left\{ \begin{array}{l} \Psi = c_n\psi_n \\ \text{Energy} = E_n \end{array} \right. \quad \text{for some } n$$

This story, of course, is nonsense. It makes a distinction between “nature” (the particle, say) and the “measurement device” supposedly producing an exact value. But the measurement device is a part of nature too, and therefore also uncertain. What measures the measurement device?

Worse, there is no definition at all of what “measurement” is or is not, so anything physicists, and philosophers, want to put there goes. Needless to say, theories have proliferated, many totally devoid of common sense. The more reasonable “interpretations of the interpretation” tend to identify measurements as interactions with macroscopic systems. Still, there is no indication how and when a system would be sufficiently macroscopic, and how that would produce a collapse or at least something approximating it.

If that is not bad enough, quantum mechanics *already has* a law, called the Schrödinger equation (chapter 6.1), that says how the wave function evolves. This equation contradicts the collapse, (chapter 7.6.1.)

The collapse in the orthodox interpretation is what the classical theater world would have called “Deus ex Machina”. It is a god that appears out of thin air to make things right. A god that has the power to distort the normal laws of nature at will. We mere humans may not question the god. In fact, physicists tend to actually get upset if you do.

However, it is a fact that after a real-life measurement has been made, further follow-up measurements have statistics that are consistent with a collapsed wave function, (which can be computed.) The orthodox interpretation does describe what happens practically in actual laboratory settings well. It just offers no practical help in circumstances that are not so clear cut, being phrased in terms that are essentially meaningless.

### Key Points

- ◊ Even if a system is initially in a combination of the eigenfunctions of a physical quantity, a measurement of that quantity pushes the measured system into a single eigenfunction.
- ◊ The measured value is the corresponding eigenvalue.

#### 2.4.2 Statistical selection

There is another hot potato besides the collapse itself; it is the selection of the eigenfunction to collapse to. If the wave function before a “measurement” is a combination of many different eigenfunctions, then *what* eigenfunction will the measurement produce? Will it be  $\psi_1$ ?  $\psi_2$ ?  $\psi_{10}$ ?

The answer of the orthodox interpretation is that nature contains a mysterious random number generator. If the wave function  $\Psi$  before the “measurement” equals, in terms of the eigenfunctions,

$$\Psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \dots$$

then this random number generator will, in Einstein’s words, “throw the dice” and select one of the eigenfunctions based on the result. It will collapse the wave function to eigenfunction  $\psi_1$  in on average a fraction  $|c_1|^2$  of the cases, it will collapse the wave function to  $\psi_2$  in a fraction  $|c_2|^2$  of the cases, etc.

*The orthodox interpretation says that the square magnitudes of the coefficients of the eigenfunctions give the probabilities of the corresponding eigenvalues.*

This too describes very well what happens practically in laboratory experiments, but offers again no insight into why and when. And the notion that nature would somehow come with, maybe not a physical random number generator, but certainly an endless sequence of *truly* random numbers seemed very hard to believe even for an early pioneer of quantum mechanics like Einstein. Many have proposed that the eigenfunction selections are not truly random, but reflect unobserved “hidden variables” that merely seem random to us humans. Yet, after almost a century, none of these theories have found convincing evidence or general acceptance. Physicists still tend to insist quite forcefully on a *literal* random number generator. Somehow, when belief is based on faith, rather than solid facts, tolerance of alternative views is much less, even among scientists.

Regardless of its popularity, I take the usual philosophy about the orthodox interpretation with a big grain of salt. The bottom line to remember is:

*random collapse of the wave function, with chances governed by the square magnitudes of the coefficients, is indeed the correct way for us humans to describe what happens in our observations.*

As explained in chapter 7.6.2, this is despite the fact that the wave function *does not* collapse: the collapse is an artifact produced by limitations in our capability to see the entire picture. We have no choice but to work within our limitations, and within these, the rules of the orthodox interpretation do apply.

### Key Points

- ◊ If a system is initially in a combination of the eigenfunctions of a physical quantity, a measurement of that quantity picks one of the eigenvalues at random.
- ◊ The chances of a given eigenvalue being picked are proportional to the square magnitude of the coefficient of the corresponding eigenfunction in the combination.

## 2.5 Schrödinger's Cat [Background]

Schrödinger, apparently not an animal lover, came up with an example illustrating what the conceptual difficulties of quantum mechanics really mean in everyday terms. This section describes the example, for those who are interested.

A cat is placed in a closed box. Also in the box is a Geiger counter and a tiny amount of radioactive material that will cause the Geiger counter to go off in a typical time of an hour. The Geiger counter has been rigged so that if it goes off, it releases a poison that kills the cat.

Now the decay of the radioactive material is a quantum-mechanical process; the different times for it to trigger the Geiger counter each have their own probability. According to the orthodox interpretation, “measurement” is needed to fix a single trigger time. If the box is left closed to prevent measurement, then at any given time, there is only a *probability* of the Geiger counter having been triggered. The cat is then alive, and also dead, each with a nonzero probability.

Of course no reasonable person is going to believe that she is looking at a box with a cat in it that is both dead and alive. The problem is obviously with what is to be called a “measurement” or “observation.” The countless trillions of air molecules are hardly going to miss “observing” that they no longer enter the cat’s nose. The biological machinery in the cat is not going to miss “observing” that the blood is no longer circulating. More directly, the Geiger counter is not going to miss “observing” that a decay has occurred; it is releasing the poison, isn’t it?

If we postulate that the Geiger counter is in this case doing the “measurement” that the orthodox interpretation so deviously leaves undefined, it agrees with our common sense. But of course, this Deus ex Machina only *rephrases* our common sense; it provides no explanation *why* the Geiger counter would cause quantum mechanics to apparently terminate its normal evolution, no proof or plausible reason that the Geiger counter is *able* to fundamentally change the normal evolution of the wave function, and not even a shred of hard evidence *that* it terminates the evolution, if the box is truly closed.

There is a strange conclusion to this story. The entire point Schrödinger was trying to make was that no sane person is going to believe that a cat can be both dead and kicking around alive at the same time. But when the equations of quantum mechanics are examined more closely, it is found that they require exactly that. The wave function evolves into describing a series of different *realities*. In our own reality, the cat dies at a specific, apparently random time, just as common sense tells us. Regardless whether the box is open or not. But, as discussed further in chapter 7.6.2, the mathematics of quantum mechanics extends beyond our reality. Other realities develop, which we are utterly unable to observe, and in each of those other realities, the cat dies at a different time.

## 2.6 A Particle Confined Inside a Pipe

This section demonstrates the general procedure for analyzing quantum systems using a very elementary example. The system to be studied is that of a particle, say an electron, confined to the inside of a narrow pipe with sealed end. This example will be studied in some detail, since if you understand it thoroughly, it becomes much easier not to get lost in the more advanced examples of quantum mechanics discussed later. And as subsection 2.6.9 shows, the particle in a pipe is really quite interesting despite its simplicity.

### 2.6.1 The physical system

The system that we want to study is shown in figure 2.4 as it would appear in classical nonquantum physics. A particle is bouncing around between the two ends of a pipe. It is



Figure 2.4: Classical picture of a particle in a closed pipe.

assumed that there is no friction, so the particle will keep bouncing back and forward forever. (Friction is a macroscopic effect that has no place in the sort of quantum-scale systems that we want to analyze here.) Typically, classical physics draws the particles that it describes as little spheres, so that is what figure 2.4 shows.

The actual quantum system to be analyzed is shown in figure 2.5. A particle like an electron



Figure 2.5: Quantum mechanics picture of a particle in a closed pipe.

has no (known) specific shape or size, but it does have a wave function “blob.” So in quantum mechanics the equivalent of a particle bouncing around is a wave function blob bouncing around between the ends of the pipe.

Please don’t ask what this impenetrable pipe is made off. It is obviously a crude idealization. You could imagine that the electron is a valence electron in a very tiny bar of copper. In that case the pipe walls would correspond to the surface of the copper bar, and we are assuming the electron cannot get off the bar.

But of course, a copper bar would have nuclei, and other electrons, and we really do not want to consider those. So maybe it is better to think of the particle as being a lone helium atom stuck inside a carbon nanotube.

---

### Key Points

- ◊ We will be looking at an idealized problem of a particle bouncing about in a pipe.
- 

## 2.6.2 Mathematical notations

The first step in the solution process is to describe the problem mathematically. To do so, we will use an  $x$ -coordinate that measures longitudinal position inside the pipe, as shown in figure 2.6. Also, we will call the length of the pipe  $\ell_x$ .

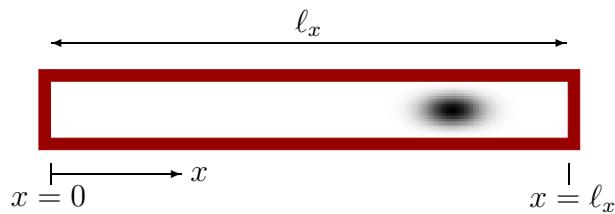


Figure 2.6: Definitions.

To make the problem as easy to solve as possible, we are going to pretend that *the only position coordinate that exists is this longitudinal position  $x$  along the pipe*. For now, we are just going to ignore the existence of any coordinates  $y$  and  $z$  that measure the location in cross section.

---

### Key Points

- ◊ The only position coordinate to be considered for now is  $x$ .
  - ◊ The notations have been defined.
- 

## 2.6.3 The Hamiltonian

To analyze a quantum system we must find the Hamiltonian. The Hamiltonian is the total energy operator, equal to the sum of kinetic plus potential energy.

The potential energy  $V$  is the easiest to find: since we assume that the particle does not experience forces inside the pipe, (until it hits the ends of the pipe, that is), the potential energy must be constant inside the pipe:

$$V = \text{constant}$$

(The force is the derivative of the potential energy, so a constant potential energy produces zero force.) Further, since the value of the constant does not make any difference physically, we may as well assume that it is zero and save some writing:

$$V = 0$$

Next, the kinetic energy operator  $\hat{T}$  is needed. We can just look up its precise form in section 2.3 and find it is:

$$\hat{T} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

Note that we just took the  $x$ -term; we are completely ignoring the existence of the other two coordinates  $y$  and  $z$ . The constant  $m$  is the mass of the particle, and  $\hbar$  is Planck's constant.

Since the potential energy is zero, the Hamiltonian  $H$  is just this kinetic energy:

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (2.12)$$

### Key Points

- ◊ The one-dimensional Hamiltonian (2.12) has been written down.

#### 2.6.4 The Hamiltonian eigenvalue problem

With the Hamiltonian  $H$  found, the next step is to formulate the Hamiltonian eigenvalue problem, (or “time-independent Schrödinger equation.”). This problem is always of the form

$$H\psi = E\psi$$

Any nonzero solution  $\psi$  of this equation is called an energy eigenfunction and the corresponding constant  $E$  is called the energy eigenvalue.

Substituting the Hamiltonian for the pipe as found in the previous subsection, the eigenvalue problem is:

$$-\frac{\hbar^2}{2m} \frac{\partial^2\psi}{\partial x^2} = E\psi \quad (2.13)$$

We are not done yet. We also need so called “boundary conditions”, conditions that say what happens at the *ends* of the  $x$  range. In this case, the ends of the  $x$  range are the ends of the pipe. Now recall that the square magnitude of the wave function gives the probability of finding the particle. So the wave function must be zero wherever there is no possibility of finding the particle. That is outside the pipe: we are assuming that the particle is confined

to the pipe. So the wave function is zero outside the pipe. And since the outside of the pipe starts at the ends of the pipe, that means that the wave function must be zero at the ends {5}:

$$\psi = 0 \text{ at } x = 0 \quad \text{and} \quad \psi = 0 \text{ at } x = \ell_x \quad (2.14)$$

### Key Points

- ◊ The Hamiltonian eigenvalue problem (2.13) has been found.
- ◊ It also includes the boundary conditions (2.14).

## 2.6.5 All solutions of the eigenvalue problem

The previous section found the Hamiltonian eigenvalue problem to be:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E\psi$$

Now we need to solve this equation. Mathematicians call an equation of this type an ordinary differential equation; “differential” because it has a derivative in it, and “ordinary” since there are no derivatives with respect to variables other than  $x$ .

If you do not know how to solve ordinary differential equations, it is no big deal. The best way is usually to look them up anyway. The equation above can be found in most mathematical table books, e.g. [5, item 19.7]. According to what it says there, (with changes in notation), if we assume that the energy  $E$  is negative, the solution is

$$\psi = C_1 e^{\kappa x} + C_2 e^{-\kappa x} \quad \kappa = \frac{\sqrt{-2mE}}{\hbar}$$

This solution may easily be checked by simply substituting it into the ordinary differential equation.

As far as the ordinary differential equation is concerned, the constants  $C_1$  and  $C_2$  could be any two numbers. But we also need to satisfy the two boundary conditions given in the previous subsection. The boundary condition that  $\psi = 0$  when  $x = 0$  produces, if  $\psi$  is as above,

$$C_1 e^0 + C_2 e^0 = 0$$

and since  $e^0 = 1$ , this can be used to find an expression for  $C_2$ :

$$C_2 = -C_1$$

The second boundary condition, that  $\psi = 0$  at  $x = \ell_x$ , produces

$$C_1 e^{\kappa \ell_x} + C_2 e^{-\kappa \ell_x} = 0$$

or, since we just found out that  $C_2 = -C_1$ ,

$$C_1 (e^{\kappa \ell_x} - e^{-\kappa \ell_x}) = 0$$

This equation spells trouble because the term between parentheses cannot be zero; the exponentials are not equal. Instead  $C_1$  will have to be zero; that is bad news since it implies that  $C_2 = -C_1$  is zero too, and then so is the wave function  $\psi$ :

$$\psi = C_1 e^{\kappa x} + C_2 e^{-\kappa x} = 0$$

A zero wave function is not acceptable, since there would be no possibility to find the particle anywhere!

We did everything right. So the problem must be our initial assumption that the energy is negative. Apparently, the energy cannot be negative. This can be understood from the fact that for this particle, the energy is all kinetic energy. Classical physics would say that the kinetic energy cannot be negative because it is proportional to the square of the velocity. We now see that quantum mechanics agrees that the kinetic energy cannot be negative, but says it is because of the boundary conditions on the wave function.

We try again, but now we assume that the energy  $E$  is zero instead of negative. In that case the solution of the ordinary differential equation is according to [5, item 19.7]

$$\psi = C_1 + C_2 x$$

The boundary condition that  $\psi = 0$  at  $x = 0$  now produces:

$$C_1 + C_2 0 = C_1 = 0$$

so  $C_1$  must be zero. The boundary condition that  $\psi = 0$  at  $x = \ell_x$  gives:

$$0 + C_2 \ell_x = 0$$

so  $C_2$  must be zero too. Once again we have failed to find a nonzero solution, so our assumption that the energy  $E$  can be zero must be wrong too.

Note that classically, it is perfectly OK for the energy to be zero: it would simply mean that the particle is sitting in the pipe at rest. But in quantum mechanics, zero kinetic energy is not acceptable, and it all has to do with Heisenberg's uncertainty principle. Since the particle is restricted to the inside of the pipe, its position is constrained, and so the uncertainty principle requires that the linear momentum must be uncertain. Uncertain momentum cannot be zero momentum; measurements will show a range of values for the momentum of the particle, implying that it is in motion and therefore has kinetic energy.

We try, try again. The only possibility left is that the energy  $E$  is positive. In that case, the solution of the ordinary differential equation is according to [5, item 19.7]:

$$\psi = C_1 \cos(kx) + C_2 \sin(kx) \quad k = \frac{\sqrt{2mE}}{\hbar}$$

The boundary condition that  $\psi = 0$  at  $x = 0$  is:

$$C_1 1 + C_2 0 = C_1 = 0$$

so  $C_1$  must be zero. The boundary condition  $\psi = 0$  at  $x = \ell_x$  is then:

$$0 + C_2 \sin(k\ell_x) = 0$$

We finally have a possibility to get a nonzero coefficient  $C_2$ : this equation can be satisfied if  $\sin(k\ell_x) = 0$  instead of  $C_2$ . In fact, there is not just one possibility for this to happen: a sine is zero when its argument equals  $\pi, 2\pi, 3\pi, \dots$ . So we have a nonzero solution for each of the following values of the positive constant  $k$ :

$$k = \frac{\pi}{\ell_x}, k = \frac{2\pi}{\ell_x}, k = \frac{3\pi}{\ell_x}, \dots$$

Each of these possibilities gives one solution  $\psi$ . We will distinguish the different solutions  $\psi$  by giving them a numeric subscript:

$$\psi_1 = C_2 \sin\left(\frac{\pi}{\ell_x}x\right), \psi_2 = C_2 \sin\left(\frac{2\pi}{\ell_x}x\right), \psi_3 = C_2 \sin\left(\frac{3\pi}{\ell_x}x\right), \dots$$

The generic solution can be written more concisely using a counter  $n$  as:

$$\psi_n = C_2 \sin\left(\frac{n\pi}{\ell_x}x\right) \quad \text{for } n = 1, 2, 3, \dots$$

Let's check the solutions. Clearly each is zero when  $x = 0$  and when  $x = \ell_x$ . Also, substitution of each of the solutions into the ordinary differential equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E\psi$$

shows that they all satisfy it, provided that their energy values are, respectively:

$$E_1 = \frac{\hbar^2 \pi^2}{2m\ell_x^2}, E_2 = \frac{2^2 \hbar^2 \pi^2}{2m\ell_x^2}, E_3 = \frac{3^2 \hbar^2 \pi^2}{2m\ell_x^2}, \dots$$

or generically:

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2m\ell_x^2} \quad \text{for } n = 1, 2, 3, \dots$$

There is one more condition that must be satisfied: each solution must be normalized so that the total probability of finding the particle integrated over all possible positions is 1 (certainty). That requires:

$$1 = \langle \psi_n | \psi_n \rangle = \int_{x=0}^{\ell_x} |C_2|^2 \sin^2\left(\frac{n\pi}{\ell_x}x\right) dx$$

which after integration fixes  $C_2$  (assuming we choose it to be a positive real number):

$$C_2 = \sqrt{\frac{2}{\ell_x}}$$

Summarizing the results of this subsection, we have found not just one energy eigenfunction and corresponding eigenvalue, but an infinite set of them:

$$\begin{aligned} \psi_1 &= \sqrt{\frac{2}{\ell_x}} \sin\left(\frac{\pi}{\ell_x}x\right) & E_1 &= \frac{\hbar^2\pi^2}{2m\ell_x^2} \\ \psi_2 &= \sqrt{\frac{2}{\ell_x}} \sin\left(\frac{2\pi}{\ell_x}x\right) & E_2 &= \frac{2^2\hbar^2\pi^2}{2m\ell_x^2} \\ \psi_3 &= \sqrt{\frac{2}{\ell_x}} \sin\left(\frac{3\pi}{\ell_x}x\right) & E_3 &= \frac{3^2\hbar^2\pi^2}{2m\ell_x^2} \\ &\vdots & &\vdots \end{aligned} \tag{2.15}$$

or in generic form:

$$\psi_n = \sqrt{\frac{2}{\ell_x}} \sin\left(\frac{n\pi}{\ell_x}x\right) \quad E_n = \frac{n^2\hbar^2\pi^2}{2m\ell_x^2} \quad \text{for } n = 1, 2, 3, 4, 5, \dots \tag{2.16}$$

The next thing will be to take a better look at these results.

### Key Points

- ◊ After a lot of grinding mathematics armed with table books, the energy eigenfunctions and eigenvalues have finally been found
- ◊ There are infinitely many of them.
- ◊ They are as listed in (2.16) above. The first few are also written out explicitly in (2.15).

#### 2.6.5 Review Questions

- 1 Write down eigenfunction number 6.
- 2 Write down eigenvalue number 6.

### 2.6.6 Discussion of the energy values

This subsection discusses the energy that the particle in the pipe can have. We have already discovered in the previous subsection that the particle cannot have negative energy, nor zero energy. In fact, according to the orthodox interpretation, the only values that the total energy of the particle can take are the energy eigenvalues

$$E_1 = \frac{\hbar^2\pi^2}{2m\ell_x^2}, \quad E_2 = \frac{2^2\hbar^2\pi^2}{2m\ell_x^2}, \quad E_3 = \frac{3^2\hbar^2\pi^2}{2m\ell_x^2}, \quad \dots$$

derived in the previous subsection.

Energy values are typically shown graphically in the form of an “energy spectrum”, as in figure 2.7. Energy is plotted upwards, so the vertical height of each energy level indicates the

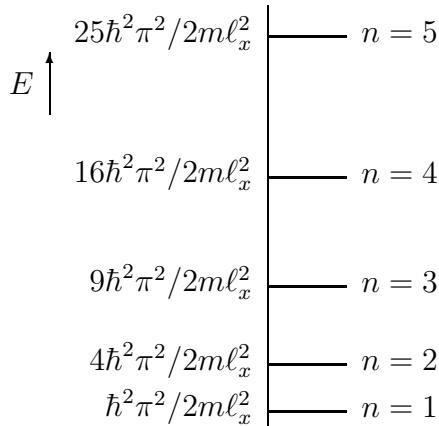


Figure 2.7: One-dimensional energy spectrum for a particle in a pipe.

amount of energy it has. To the right of each energy level, the solution counter, or “quantum number”,  $n$  is listed.

Classically, the total energy of the particle can have any nonnegative value. But according to quantum mechanics, that is not true: the total energy must be one of the levels shown in the energy spectrum figure 2.7. It should be noted that for a macroscopic particle, you would not know the difference; the spacing between the energy levels is macroscopically very fine, since Planck’s constant  $\hbar$  is so small. However, for a quantum-scale system, the discreteness of the energy values can make a major difference.

Another point: at absolute zero temperature, the particle will be stuck in the lowest possible energy level,  $E_1 = \hbar^2\pi^2/2m\ell_x^2$ , in the spectrum figure 2.7. This lowest possible energy level is called the “ground state.” Classically you would expect that at absolute zero the particle has no kinetic energy, so zero total energy. But quantum mechanics does not allow it. Heisenberg’s principle requires some momentum, hence kinetic energy to remain for a confined particle even at zero temperature.

---

### Key Points

- ◊ Energy values can be shown as an energy spectrum.
  - ◊ The possible energy levels are discrete.
  - ◊ But for a macroscopic particle, they are extremely close together.
  - ◊ The ground state of lowest energy has nonzero kinetic energy.
- 

---

### 2.6.6 Review Questions

- 1 Plug the mass of an electron,  $m = 9.10938 \cdot 10^{-31}$  kg, and the rough confinement size of an hydrogen atom, call it  $\ell_x = 2 \cdot 10^{-10}$  m, into the expression for the ground state kinetic energy and see how big it is. Note that  $\hbar = 1.05457 \cdot 10^{-34}$  J s. Express in units of eV, where one eV equals  $1.60218 \cdot 10^{-19}$  J.
  - 2 Just for fun, plug macroscopic values,  $m = 1$  kg and  $\ell_x = 1$  m, into the expression for the ground state energy and see how big it is. Note that  $\hbar = 1.05457 \cdot 10^{-34}$  J s.
  - 3 What is the eigenfunction number, or quantum number,  $n$  that produces a macroscopic amount of energy, 1 J, for macroscopic values  $m = 1$  kg and  $\ell_x = 1$  m? With that many energy levels involved, would you see the difference between successive ones?
- 

## 2.6.7 Discussion of the eigenfunctions

This subsection discusses the one-dimensional energy eigenfunctions of the particle in the pipe. The solution of subsection 2.6.5 found them to be:

$$\psi_1 = \sqrt{\frac{2}{\ell_x}} \sin\left(\frac{\pi}{\ell_x}x\right), \quad \psi_2 = \sqrt{\frac{2}{\ell_x}} \sin\left(\frac{2\pi}{\ell_x}x\right), \quad \psi_3 = \sqrt{\frac{2}{\ell_x}} \sin\left(\frac{3\pi}{\ell_x}x\right), \dots$$

Let's first look at the ground state eigenfunction

$$\psi_1 = \sqrt{\frac{2}{\ell_x}} \sin\left(\frac{\pi}{\ell_x}x\right).$$

It is plotted at the top of figure 2.8. As noted in section 2.1, it is the *square* magnitude of a wave function that gives the probability of finding the particle. So, the second graph in figure 2.8 shows the square of the ground state wave function, and the higher values of this function then give the locations where the particle is more likely to be found. This book shows regions where the particle is more likely to be found as darker regions, and in those terms the probability of finding the particle is as shown in the bottom graphic of figure 2.8. It is

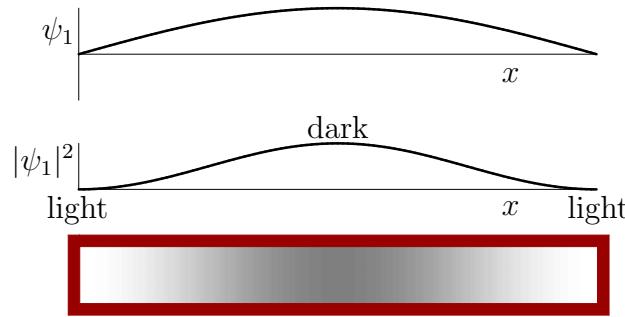


Figure 2.8: One-dimensional ground state of a particle in a pipe.

seen that in the ground state, the particle is much more likely to be found somewhere in the middle of the pipe than close to the ends.

Figure 2.9 shows the two next lowest energy states

$$\psi_2 = \sqrt{\frac{2}{\ell_x}} \sin\left(\frac{2\pi}{\ell_x}x\right) \text{ and } \psi_3 = \sqrt{\frac{2}{\ell_x}} \sin\left(\frac{3\pi}{\ell_x}x\right)$$

as grey tones. Regions where the particle is relatively likely to be found alternate with ones

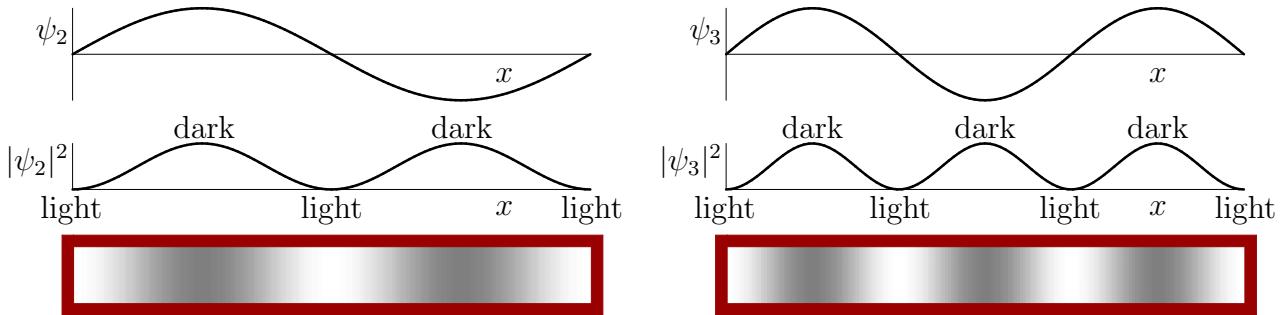


Figure 2.9: Second and third lowest one-dimensional energy states.

where it is less likely to be found. And the higher the energy, the more such regions there are. Also note that in sharp contrast to the ground state, for eigenfunction  $\psi_2$  there is almost no likelihood of finding the particle close to the center.

Needless to say, none of those energy states looks at all like the wave function blob bouncing around in figure 2.5. Moreover, it turns out that energy eigenstates are stationary states: the probabilities shown in figures 2.8 and 2.9 do not change with time.

In order to describe a localized wave function blob bouncing around, states of different energy must be combined. It will take until chapter 6.6.5 before we have the analytical tools to do so. For now, we must restrict ourselves to just finding the energy levels. And these are important enough by themselves anyway, sufficient for many practical applications of quantum mechanics.

---

### Key Points

- ◊ In the energy eigenfunctions, the particle is not localized to within any particular small region of the pipe.
  - ◊ In general there are regions where the particle may be found separated by regions in which there is little chance to find the particle.
  - ◊ The higher the energy level, the more such regions there are.
- 

---

### 2.6.7 Review Questions

- 1** So how does, say, the one-dimensional eigenstate  $\psi_6$  look?
  - 2** Generalizing the results above, for eigenfunction  $\psi_n$ , any  $n$ , how many distinct regions are there where the particle may be found?
  - 3** If you are up to a trick question, consider the following. There are no forces inside the pipe, so the particle has to keep moving until it hits an end of the pipe, then reflect backward until it hits the other side and so on. So, it has to cross the center of the pipe regularly. But in the energy eigenstate  $\psi_2$ , the particle has *zero* chance of ever being found at the center of the pipe. What gives?
- 

### 2.6.8 Three-dimensional solution

The solution for the particle stuck in a pipe that we obtained in the previous subsections cheated. It pretended that there was only one spatial coordinate  $x$ . Real life is three-dimensional. And yes, as a result, the solution as obtained is simply wrong.

Fortunately, it turns out that we can fix up the problem pretty easily if we assume that the pipe has a square cross section. There is a way of combining one-dimensional solutions for all three coordinates into full three-dimensional solutions. This is called the “separation of variables” idea: Solve each of the three variables  $x$ ,  $y$ , and  $z$  separately, then combine the results.

The full coordinate system for the problem is shown in figure 2.10: in addition to the  $x$  coordinate along the length of the pipe, there is also a  $y$ -coordinate giving the vertical position in cross section, and similarly a  $z$ -coordinate giving the position in cross section towards us.

Let’s first recall the one-dimensional solutions that we obtained assuming there is just an

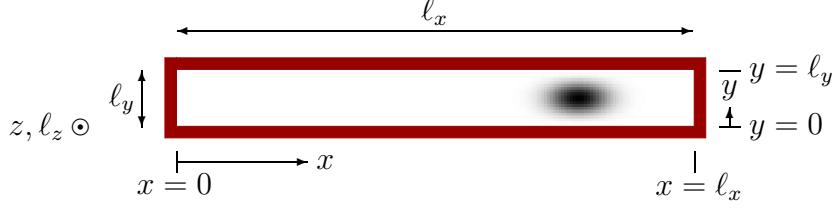


Figure 2.10: Definition of all variables.

$x$ -coordinate, but add subscripts “ $x$ ” to keep them apart from any solutions for  $y$  and  $z$ :

$$\begin{aligned}
 \psi_{x1} &= \sqrt{\frac{2}{\ell_x}} \sin\left(\frac{\pi}{\ell_x} x\right) & E_{x1} &= \frac{\hbar^2 \pi^2}{2m\ell_x^2} \\
 \psi_{x2} &= \sqrt{\frac{2}{\ell_x}} \sin\left(\frac{2\pi}{\ell_x} x\right) & E_{x2} &= \frac{2^2 \hbar^2 \pi^2}{2m\ell_x^2} \\
 \psi_{x3} &= \sqrt{\frac{2}{\ell_x}} \sin\left(\frac{3\pi}{\ell_x} x\right) & E_{x3} &= \frac{3^2 \hbar^2 \pi^2}{2m\ell_x^2} \\
 &\vdots & &\vdots
 \end{aligned} \tag{2.17}$$

or in generic form:

$$\psi_{xn_x} = \sqrt{\frac{2}{\ell_x}} \sin\left(\frac{n_x \pi}{\ell_x} x\right) \quad E_{xn_x} = \frac{n_x^2 \hbar^2 \pi^2}{2m\ell_x^2} \quad \text{for } n_x = 1, 2, 3, \dots \tag{2.18}$$

Since we assume that the cross section of the pipe is square or rectangular of dimensions  $\ell_y \times \ell_z$ , the  $y$  and  $z$  directions have *one-dimensional* solutions completely equivalent to the  $x$  direction:

$$\psi_{yn_y} = \sqrt{\frac{2}{\ell_y}} \sin\left(\frac{n_y \pi}{\ell_y} y\right) \quad E_{yn_y} = \frac{n_y^2 \hbar^2 \pi^2}{2m\ell_y^2} \quad \text{for } n_y = 1, 2, 3, \dots \tag{2.19}$$

and

$$\psi_{zn_z} = \sqrt{\frac{2}{\ell_z}} \sin\left(\frac{n_z \pi}{\ell_z} z\right) \quad E_{zn_z} = \frac{n_z^2 \hbar^2 \pi^2}{2m\ell_z^2} \quad \text{for } n_z = 1, 2, 3, \dots \tag{2.20}$$

After all, there is no fundamental difference between the three coordinate directions; each is along an edge of a rectangular box.

Now it turns out, {6}, that the full three-dimensional problem has eigenfunctions  $\psi_{n_x n_y n_z}$  that are simply *products* of the one dimensional ones:

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{\ell_x \ell_y \ell_z}} \sin\left(\frac{n_x \pi}{\ell_x} x\right) \sin\left(\frac{n_y \pi}{\ell_y} y\right) \sin\left(\frac{n_z \pi}{\ell_z} z\right) \tag{2.21}$$

There is one such three-dimensional eigenfunction for each *set* of three numbers  $(n_x, n_y, n_z)$ . These numbers are the three “quantum numbers” of the eigenfunction.

Further, the energy eigenvalues  $E_{n_x n_y n_z}$  of the three-dimensional problem are the *sum* of those of the one-dimensional problems:

$$E_{n_x n_y n_z} = \frac{n_x^2 \hbar^2 \pi^2}{2m\ell_x^2} + \frac{n_y^2 \hbar^2 \pi^2}{2m\ell_y^2} + \frac{n_z^2 \hbar^2 \pi^2}{2m\ell_z^2} \quad (2.22)$$

For example, the ground state of lowest energy occurs when all three quantum numbers are lowest,  $n_x = n_y = n_z = 1$ . The three-dimensional ground state wave function is therefore:

$$\psi_{111} = \sqrt{\frac{8}{\ell_x \ell_y \ell_z}} \sin\left(\frac{\pi}{\ell_x}x\right) \sin\left(\frac{\pi}{\ell_y}y\right) \sin\left(\frac{\pi}{\ell_z}z\right) \quad (2.23)$$

This ground state is shown in figure 2.11. The  $y$ - and  $z$ -factors ensure that the wave function is now zero at all the surfaces of the pipe.

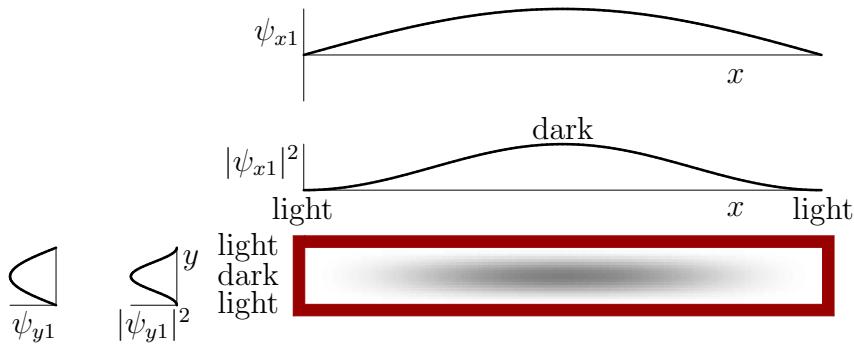


Figure 2.11: True ground state of a particle in a pipe.

The ground state energy is:

$$E_{111} = \frac{\hbar^2 \pi^2}{2m\ell_x^2} + \frac{\hbar^2 \pi^2}{2m\ell_y^2} + \frac{\hbar^2 \pi^2}{2m\ell_z^2} \quad (2.24)$$

Since the cross section dimensions  $\ell_y$  and  $\ell_z$  are small compared to the length of the pipe, the last two terms are large compared to the first one. They make the true ground state energy much larger than what we got in the one-dimensional case, which was just the first term.

The next two lowest energy levels occur for  $n_x = 2, n_y = n_z = 1$  respectively  $n_x = 3, n_y = n_z = 1$ . (The latter assumes that the cross section dimensions are small enough that the alternative possibilities  $n_y = 2, n_x = n_z = 1$  and  $n_z = 2, n_x = n_y = 1$  have more energy.) The energy eigenfunctions

$$\psi_{211} = \sqrt{\frac{8}{\ell_x \ell_y \ell_z}} \sin\left(\frac{2\pi}{\ell_x}x\right) \sin\left(\frac{\pi}{\ell_y}y\right) \sin\left(\frac{\pi}{\ell_z}z\right) \quad (2.25)$$

$$\psi_{311} = \sqrt{\frac{8}{\ell_x \ell_y \ell_z}} \sin\left(\frac{3\pi}{\ell_x}x\right) \sin\left(\frac{\pi}{\ell_y}y\right) \sin\left(\frac{\pi}{\ell_z}z\right) \quad (2.26)$$

are shown in figure 2.12. They have energy levels:



Figure 2.12: True second and third lowest energy states.

$$E_{211} = \frac{4\hbar^2\pi^2}{2m\ell_x^2} + \frac{\hbar^2\pi^2}{2m\ell_y^2} + \frac{\hbar^2\pi^2}{2m\ell_z^2} \quad E_{311} = \frac{9\hbar^2\pi^2}{2m\ell_x^2} + \frac{\hbar^2\pi^2}{2m\ell_y^2} + \frac{\hbar^2\pi^2}{2m\ell_z^2} \quad (2.27)$$

### Key Points

- ◊ Three-dimensional energy eigenfunctions can be found as products of one-dimensional ones.
- ◊ Three-dimensional energies can be found as sums of one-dimensional ones.
- ◊ Example three-dimensional eigenstates have been shown.

#### 2.6.8 Review Questions

- 1 If the cross section dimensions  $\ell_y$  and  $\ell_z$  are one tenth the size of the pipe length, how much bigger are the energies  $E_{y1}$  and  $E_{z1}$  compared to  $E_{x1}$ ? So, by what percentage is the one-dimensional ground state energy  $E_{x1}$  as an approximation to the three-dimensional one,  $E_{111}$ , then in error?
- 2 At what ratio of  $\ell_y/\ell_x$  does the energy  $E_{121}$  become higher than the energy  $E_{311}$ ?
- 3 Shade the regions where the particle is likely to be found in the  $\psi_{322}$  energy eigenstate.

#### 2.6.9 Quantum confinement

Normally, motion in physics occurs in three dimensions. Even in a narrow pipe, in classical physics a point particle of zero size would be able to move in all three directions. But in quantum mechanics, if the pipe gets very narrow, the motion becomes truly one-dimensional.

It all has to do with the fact that the energy levels in quantum mechanics are discrete. For example, the kinetic energy in the  $y$ -direction takes the possible values, according to the previous section,

$$E_{y1} = \frac{\hbar^2\pi^2}{2m\ell_y^2}, \quad E_{y2} = \frac{4\hbar^2\pi^2}{2m\ell_y^2}, \quad E_{y3} = \frac{9\hbar^2\pi^2}{2m\ell_y^2}, \quad \dots$$

That will be very large energies for a narrow pipe in which  $\ell_y$  is small. The particle will certainly have the large energy  $E_{y1}$  in the  $y$ -direction; if it is in the pipe at all it has at least that amount of energy. But it will probably not have enough *additional*, thermal, energy to reach the next level  $E_{y2}$ . The kinetic energy in the  $y$ -direction will therefore be stuck at the lowest possible level  $E_{y1}$ .

Note that the point is not that the particle is not “moving” in the  $y$ -direction; in fact,  $E_{y1}$  is a large amount of kinetic energy in that direction. The point is that this energy is frozen in a single state. The particle does not have other energy states in the  $y$ -direction available to “play around with” and do creative things like change its predominant position from one place to the other. (Such motion will be discussed in more detail much later in chapter 6.) The  $y$ -motion is large but trivial.

If the pipe is also narrow in the  $z$ -direction, the only interesting motion is in the  $x$ -direction, making the nontrivial physics truly one-dimensional. We have created a “quantum wire”. However, if the pipe size in the  $z$ -direction is relatively wide, the particle will have lots of different energy states in the  $z$ -direction available too and the motion will be two-dimensional, a “quantum well”. Conversely, if the pipe is narrow in all three directions, we get a zero-dimensional “quantum dot” in which the particle does nothing unless it gets a sizable chunk of energy.

An isolated atom can be regarded as an example of a quantum dot; the electrons are confined to a small region around the nucleus and will be at a single energy level unless they are given a sufficient amount of energy. But note that when people talk about quantum confinement, they are normally talking about semi-conductors, for which similar effects occur at significantly larger scales, maybe tens of times as large, making them much easier to manufacture. An actual quantum dot is often referred to as an “artificial atom”, and has similar properties as a real atom.

It may give you a rough idea of all the interesting things you can do in nanotechnology when you restrict the motion of particles, in particular of electrons, in various directions. You truly change the dimensionality of our normal three-dimensional world into a lower dimensional one. Only quantum mechanics can explain why, by making the energy levels discrete instead of continuously varying. And the lower dimensional worlds can have your choice of topology (a ring, a letter 8, a sphere, a cylinder, a Möbius strip?, . . .) to make things really exciting.

---

### Key Points

- 
- ◊ Quantum mechanics allows us to create lower-dimensional worlds for our particles.
-

## 2.7 The Harmonic Oscillator

This section provides an in-depth discussion of a basic quantum system. The case to be analyzed is a particle constrained by forces to remain at approximately the same position. This can describe systems such as an atom in a solid or in a molecule. If the forces pushing the particle back to its nominal position are proportional to the distance that the particle moves away from it, we have what is called an harmonic oscillator. This is usually also a good approximation for other constrained systems as long as the distances from the nominal position remain small.

We will indicate the particle's displacement from the nominal position by  $(x, y, z)$ . The forces keeping the particle constrained can be modeled as springs, as sketched in figure 2.13. The

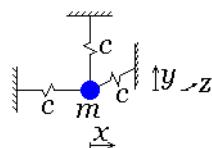


Figure 2.13: The harmonic oscillator.

stiffness of the springs is characterized by the so called “spring constant”  $c$ , giving the ratio between force and displacement. Note that we will assume that the three spring stiffnesses are equal.

According to classical Newtonian physics, the particle vibrates back and forth around its nominal position with a frequency

$$\omega = \sqrt{\frac{c}{m}}. \quad (2.28)$$

This frequency remains a convenient computational quantity in the quantum solution.

### Key Points

- ◊ The system to be described is that of a particle held in place by forces that increase proportional to the distance that the particle moves away from its equilibrium position.
- ◊ We assume the same relation between distance and force in all three coordinate directions.
- ◊ Number  $c$  is a measure of the strength of the forces and  $\omega$  is the frequency of vibration according to classical physics.

### 2.7.1 The Hamiltonian

In order to find the energy levels that the oscillating particle can have, we must first write down the total energy Hamiltonian.

As far as the potential energy is concerned, the spring in the  $x$ -direction holds an amount of potential energy equal to  $\frac{1}{2}cx^2$ , and similarly the ones in the  $y$ - and  $z$ -directions.

To this total potential energy, we need to add the kinetic energy operator  $\hat{T}$  from section 2.3 to get the Hamiltonian:

$$H = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + \frac{1}{2}c(x^2 + y^2 + z^2) \quad (2.29)$$

#### Key Points

- ◊ The Hamiltonian (2.29) has been found.

### 2.7.2 Solution using separation of variables

This section finds the energy eigenfunctions and eigenvalues of the harmonic oscillator using the Hamiltonian as found in the previous subsection. Every energy eigenfunction  $\psi$  and its eigenvalue  $E$  must satisfy the Hamiltonian eigenvalue problem, (or “time-independent Schrödinger equation”):

$$\left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + \frac{1}{2}c(x^2 + y^2 + z^2) \right] \psi = E\psi \quad (2.30)$$

The boundary condition is that  $\psi$  becomes zero at large distance from the nominal position. After all, the magnitude of  $\psi$  tells you the relative probability of finding the particle at that position, and because of the rapidly increasing potential energy, the chances of finding the particle very far from the nominal position should be vanishingly small.

Like for the particle in the pipe of the previous section, it will be assumed that each eigenfunction is a product of *one-dimensional* eigenfunctions, one in each direction:

$$\psi = \psi_x(x)\psi_y(y)\psi_z(z) \quad (2.31)$$

Finding the eigenfunctions and eigenvalues by making such an assumption is known in mathematics as the “method of separation of variables”.

Substituting the assumption in the eigenvalue problem above, and dividing everything by  $\psi_x(x)\psi_y(y)\psi_z(z)$  reveals that E consists of three parts that will be called  $E_x$ ,  $E_y$ , and  $E_z$ :

$$\begin{aligned} E &= E_x + E_y + E_z \\ E_x &= -\frac{\hbar^2}{2m} \frac{\psi''_x(x)}{\psi_x(x)} + \frac{1}{2}cx^2 \\ E_y &= -\frac{\hbar^2}{2m} \frac{\psi''_y(y)}{\psi_y(y)} + \frac{1}{2}cy^2 \\ E_z &= -\frac{\hbar^2}{2m} \frac{\psi''_z(z)}{\psi_z(z)} + \frac{1}{2}cz^2 \end{aligned} \quad (2.32)$$

where the primes indicate derivatives. The three parts represent the  $x$ ,  $y$ , and  $z$ -dependent terms.

By the definition above, the quantity  $E_x$  can only depend on  $x$ ; variables  $y$  and  $z$  do not appear in its definition. But actually,  $E_x$  cannot depend on  $x$  either, since  $E_x = E - E_y - E_z$ , and none of those quantities depends on  $x$ . The inescapable conclusion is that  $E_x$  must be a constant, independent of all three variables  $(x, y, z)$ . The same way  $E_y$  and  $E_z$  must be constants.

If now in the definition of  $E_x$  above, both sides are multiplied by  $\psi_x(x)$ , a one-dimensional eigenvalue problem results:

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2}cx^2 \right] \psi_x = E_x \psi_x \quad (2.33)$$

The operator within the square brackets here, call it  $H_x$ , involves only the  $x$ -related terms in the full Hamiltonian. Similar problems can be written down for  $E_y$  and  $E_z$ . We have obtained separate problems in each of the three variables  $x$ ,  $y$ , and  $z$ , explaining why this mathematical method is called separation of variables.

Solving the one dimensional problem for  $\psi_x$  can be done by fairly elementary means {7}, but we will skip the elaborate details and just give the results. Like for the particle in the pipe of the previous section, there is again an infinite number of different solutions for  $E_x$  and  $\psi_x$ :

$$\begin{aligned} E_{x0} &= \frac{1}{2}\hbar\omega \quad \psi_{x0}(x) = h_0(x) \\ E_{x1} &= \frac{3}{2}\hbar\omega \quad \psi_{x1}(x) = h_1(x) \\ E_{x2} &= \frac{5}{2}\hbar\omega \quad \psi_{x2}(x) = h_2(x) \\ &\vdots \quad \vdots \end{aligned} \quad (2.34)$$

Unlike for the particle in the pipe, by convention the solutions here are numbered starting from 0, rather than from 1. So the first eigenvalue is  $E_{x0}$  and the first eigenfunction  $\psi_{x0}$ . That is just how people choose to do it.

Also, the eigenfunctions are not sines like for the particle in the pipe; instead, as table 2.1 shows, they take the form of some polynomial times an exponential. But you will probably really not care much about what kind of functions they are anyway unless you end up writing a textbook on quantum mechanics and have to plot them. In that case, the following generic expression is useful:

$$h_n = \frac{1}{(\pi\ell^2)^{1/4}} \frac{H_n(\xi)}{\sqrt{2^n n!}} e^{-\xi^2/2} \quad n = 0, 1, 2, 3, 4, 5, \dots$$

where the  $H_n$  are the “Hermite polynomials” whose details you can find in [5, pp, 167-168]. They are readily evaluated on a computer using the “recurrence relation” you can find there, for as far as computer round-off error allows (up to  $n$  about 70.)

$h_0(x) = \frac{1}{(\pi\ell^2)^{1/4}} e^{-\xi^2/2}$	
$h_1(x) = \frac{2\xi}{(4\pi\ell^2)^{1/4}} e^{-\xi^2/2}$	$\omega = \sqrt{\frac{c}{m}}$
$h_2(x) = \frac{2\xi^2 - 1}{(4\pi\ell^2)^{1/4}} e^{-\xi^2/2}$	$\ell = \sqrt{\frac{\hbar}{m\omega}}$
$h_3(x) = \frac{2\xi^3 - 3\xi}{(9\pi\ell^2)^{1/4}} e^{-\xi^2/2}$	$\xi = \frac{x}{\ell}$
$h_4(x) = \frac{4\xi^4 - 12\xi^2 + 3}{(576\pi\ell^2)^{1/4}} e^{-\xi^2/2}$	

Table 2.1: One-dimensional eigenfunctions of the harmonic oscillator, [3, p. 56].

But it are the eigenvalues that you may want to remember from this solution. According to the orthodox interpretation, these are the measurable values of the total energy in the  $x$ -direction (potential energy in the  $x$ -spring plus kinetic energy of the motion in the  $x$ -direction.) Instead of writing them all out as we did above, they can be described using the generic expression:

$$E_{xn_x} = \frac{2n_x + 1}{2}\hbar\omega \quad \text{for } n_x = 0, 1, 2, 3, \dots \quad (2.35)$$

We have now solved the eigenvalue problem, because the equations for  $Y$  and  $Z$  are mathematically the same and must therefore have corresponding solutions:

$$E_{yn_y} = \frac{2n_y + 1}{2}\hbar\omega \quad \text{for } n_y = 0, 1, 2, 3, \dots \quad (2.36)$$

$$E_{zn_z} = \frac{2n_z + 1}{2}\hbar\omega \quad \text{for } n_z = 0, 1, 2, 3, \dots \quad (2.37)$$

The total energy  $E$  of the complete system is the sum of  $E_x$ ,  $E_y$ , and  $E_z$ . Any nonnegative choice for number  $n_x$ , combined with any nonnegative choice for number  $n_y$ , and for  $n_z$ , produces *one* combined total energy value  $E_{xn_x} + E_{yn_y} + E_{zn_z}$ , which we will indicate by  $E_{n_x n_y n_z}$ . Putting in the expressions for the three partial energies above, these total energy eigenvalues become:

$$E_{n_x n_y n_z} = \frac{2n_x + 2n_y + 2n_z + 3}{2} \hbar\omega \quad (2.38)$$

where the “quantum numbers”  $n_x$ ,  $n_y$ , and  $n_z$  may each have any value in the range 0, 1, 2, 3, ...

The corresponding eigenfunction of the complete system is:

$$\psi_{n_x n_y n_z} = h_{n_x}(x)h_{n_y}(y)h_{n_z}(z) \quad (2.39)$$

where the functions  $h_0, h_1, \dots$  are in table 2.1.

Note that the  $n_x, n_y, n_z$  numbering system for the solutions arose naturally from the solution process; it was not imposed a priori.

### Key Points

- ◊ The eigenvalues and eigenfunctions have been found, skipping a lot of tedious math that you can check when the weather is bad during spring break.
- ◊ Generic expressions for the eigenvalues are above in (2.38) and for the eigenfunctions in (2.39).

### 2.7.2 Review Questions

- 1** Write out the ground state energy.
- 2** Write out the ground state wave function fully.
- 3** Write out the energy  $E_{100}$ .
- 4** Write out the eigenstate  $\psi_{100}$  fully.

### 2.7.3 Discussion of the eigenvalues

As the previous subsection showed, for every set of three nonnegative whole numbers  $n_x, n_y, n_z$ , there is one unique energy eigenfunction, or eigenstate, (2.39) and a corresponding energy

eigenvalue (2.38). The “quantum numbers”  $n_x$ ,  $n_y$ , and  $n_z$  correspond to the numbering system of the one-dimensional solutions that make up the full solution.

This section will examine the energy eigenvalues. These are of great physical importance, because according to the orthodox interpretation, they are the only measurable values of the total energy, the only energy levels that the oscillator can ever be found at.

The energy levels can be plotted in the form of a so-called “energy spectrum”, as in figure 2.14. The energy values are listed along the vertical axis, and the sets of quantum numbers  $n_x, n_y, n_z$  for which they occur are shown to the right of the plot.

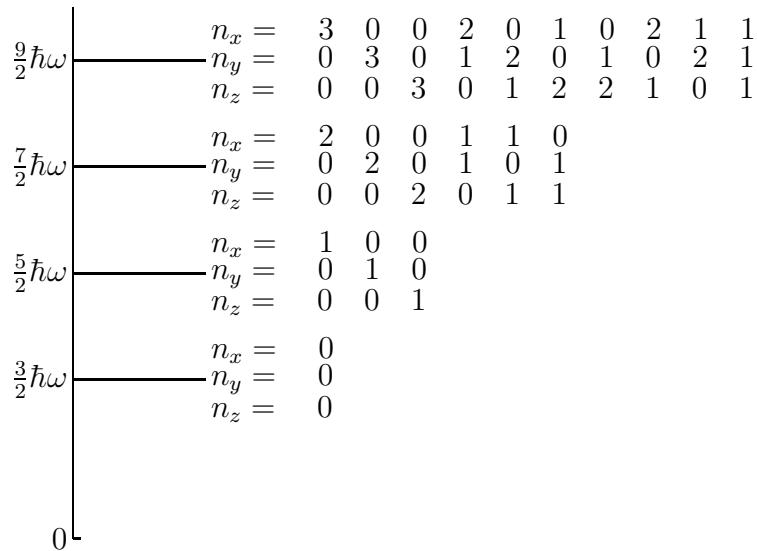


Figure 2.14: The energy spectrum of the harmonic oscillator.

The first point of interest illustrated by the energy spectrum is that the energy of the oscillating particle cannot take on any arbitrary value, but only certain discrete values. Of course, that is just like for the particle in the pipe of the previous section, but for the harmonic oscillator, the energy levels are evenly spaced. In particular the energy value is always an odd multiple of  $\frac{1}{2}\hbar\omega$ . It contradicts the Newtonian notion that a harmonic oscillator can have any energy level. But since  $\hbar$  is so small, about  $10^{-34}$  kg m<sup>2</sup>/s, macroscopically the different energy levels are extremely close together. Though the old Newtonian theory is strictly speaking incorrect, it remains an excellent approximation for macroscopic oscillators.

Also note that the energy levels have no largest value; however high the energy of the particle in a true harmonic oscillator may be, it will never escape. The further it tries to go, the larger the forces that pull it back. It can't win.

Another striking feature of the energy spectrum is that the lowest possible energy is again nonzero. The lowest energy occurs for  $n_x = n_y = n_z = 0$  and has a value:

$$E_{000} = \frac{3}{2}\hbar\omega \tag{2.40}$$

So, even at absolute zero temperature, the particle is not completely at rest at its nominal position; it still has  $\frac{3}{2}\hbar\omega$  worth of kinetic and potential energy left that it can never get rid of. This lowest energy state is the ground state.

The reason that the energy cannot be zero can be understood from the uncertainty principle. To get the potential energy to be zero, the particle would have to be at its nominal position for certain. But the uncertainty principle does not allow a certain position. Also, to get the kinetic energy to be zero, the linear momentum would have to be zero for certain, and the uncertainty relationship does not allow that either.

The actual ground state is a compromise between uncertainties in momentum and position that make the total energy as small as Heisenberg's relationship allows. There is enough uncertainty in momentum to keep the particle near the nominal position, minimizing potential energy, but there is still enough uncertainty in position to keep the momentum low, minimizing kinetic energy. In fact, the compromise results in potential and kinetic energies that are exactly equal, {8}.

For energy levels above the ground state, figure 2.14 shows that there is a rapidly increasing number of different sets of quantum numbers  $n_x$ ,  $n_y$ , and  $n_z$  that all produce that energy. Since each set represents one eigenstate, it means that multiple states produce the same energy.

### Key Points

- ◊ Energy values can be graphically represented as an energy spectrum.
- ◊ The energy values of the harmonic oscillator are equally spaced, with a constant energy difference of  $\hbar\omega$  between successive levels.
- ◊ The ground state of lowest energy has nonzero kinetic and potential energy.
- ◊ For any energy level above the ground state, there is more than one eigenstate that produces that energy.

#### 2.7.3 Review Questions

- 1** Verify that the sets of quantum numbers shown in the spectrum figure 2.14 do indeed produce the indicated energy levels.
- 2** Verify that there are no sets of quantum numbers missing in the spectrum figure 2.14; the listed ones are the only ones that produce those energy levels.

### 2.7.4 Discussion of the eigenfunctions

This section takes a look at the energy eigenfunctions of the harmonic oscillator to see what can be said about the position of the particle at various energy levels.

At absolute zero temperature, the particle will be in the ground state of lowest energy. The eigenfunction describing this state has the lowest possible numbering  $n_x = n_y = n_z = 0$ , and is according to (2.39) of subsection 2.7.2 equal to

$$\psi_{000} = h_0(x)h_0(y)h_0(z) \quad (2.41)$$

where function  $h_0$  is in table 2.1. The wave function in the ground state must be equal to the eigenfunction to within a constant:

$$\Psi_{\text{GS}} = c_{000}h_0(x)h_0(y)h_0(z) \quad (2.42)$$

where the magnitude of the constant  $c_{000}$  must be one. Using the expression for function  $h_0$  from table 2.1, the properties of the ground state can be explored.

As noted earlier in section 2.1, it is useful to plot the square magnitude of  $\Psi$  as grey tones, because the darker regions will be the ones where the particle is more likely to be found. Such a plot for the ground state is shown in figure 2.15. It shows that in the ground state, the particle is most likely to be found near the nominal position, and that the probability of finding the particle falls off quickly to zero beyond a certain distance from the nominal position.

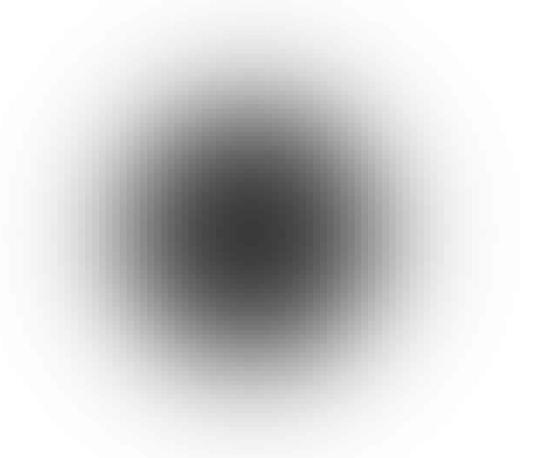


Figure 2.15: Ground state  $\psi_{000}$  of the harmonic oscillator

The region in which the particle is likely to be found extends, roughly speaking, about a distance  $\ell = \sqrt{\hbar/m\omega}$  from the nominal position. For a macroscopic oscillator, this will be a very small distance because of the smallness of  $\hbar$ . That is somewhat comforting, because macroscopically, we would expect an oscillator to be able to be at rest at the nominal position.

While quantum mechanics does not allow it, at least the distance  $\ell$  from the nominal position, and the energy  $\frac{3}{2}\hbar\omega$  are extremely small.

But obviously, the bad news is that the ground state probability density of figure 2.15 does not at all resemble the classical Newtonian picture of a localized particle oscillating back and forwards. In fact, the probability density does not even depend on time: the chances of finding the particle in any given location are the same for all times. The probability density is also spherically symmetric; it only depends on the distance from the nominal position, and is the same at all angular orientations. To get something that can start to resemble a Newtonian spring-mass oscillator, one requirement is that the energy is well above the ground level.

Turning now to the second lowest energy level, this energy level is achieved by three different energy eigenfunctions,  $\psi_{100}$ ,  $\psi_{010}$ , and  $\psi_{001}$ . The probability distribution of each of the three takes the form of two separate ‘‘blobs’’; figure 2.16 shows  $\psi_{100}$  and  $\psi_{010}$  when seen along the  $z$ -direction. In case of  $\psi_{001}$ , one blob hides the other, so this eigenfunction was not shown.

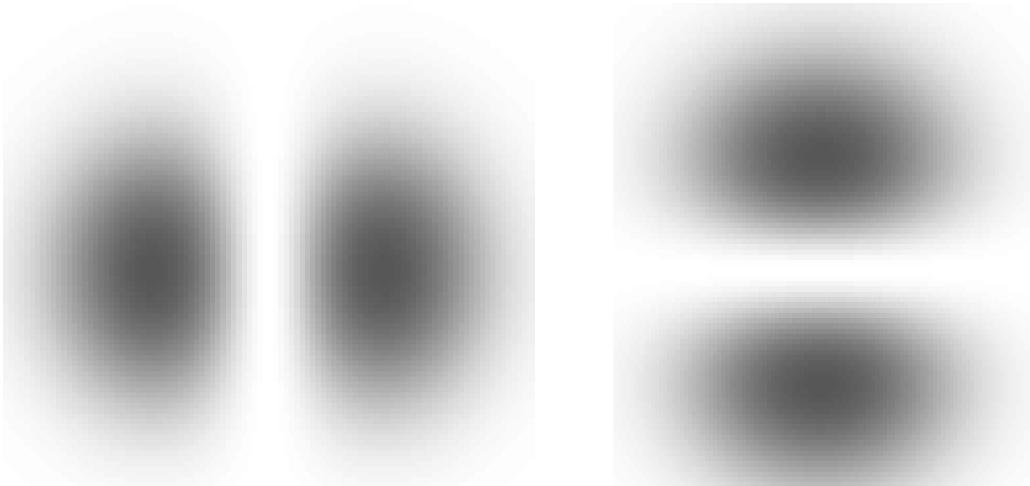


Figure 2.16: Wave functions  $\psi_{100}$  and  $\psi_{010}$ .

Obviously, these states too do not resemble a Newtonian oscillator at all. The probability distributions once again stay the same at all times. (This is a consequence of energy conservation, as discussed later in chapter 6.1.2.) Also, while in each case there are two blobs occupied by a single particle, the particle will never be caught on the symmetry plane in between the blobs, which naively could be taken as a sign of the particle moving from one blob to the other.

The eigenfunctions for still higher energy levels show similar lack of resemblance to the classical motion. As an arbitrary example, figure 2.17 shows eigenfunction  $\psi_{213}$  when looking along the  $z$ -axis. To resemble a classical oscillator, the particle would need to be restricted to, maybe not an exact moving point, but at most a very small moving region. Instead, all energy

eigenfunctions have steady probability distributions and the locations where the particle may be found extend over large regions. It turns out that there is an uncertainty principle involved here: in order to get some localization of the position of the particle, we need to allow some uncertainty in its energy. This will have to wait until much later, in chapter 6.6.5.

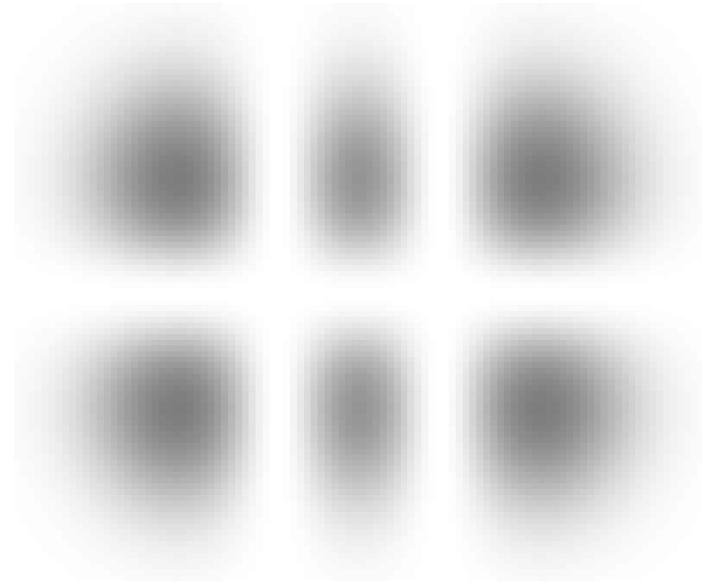


Figure 2.17: Energy eigenfunction  $\psi_{213}$ .

The basic reason that quantum mechanics is so slow is simple. To analyze, say the  $x$ -motion, classical physics says: “the *value* of the total energy  $E_x$  is

$$E_x = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}cx^2,$$

now let's go analyze the motion!”. Quantum mechanics says: “the total energy *operator*  $H_x$  is

$$H_x = \frac{1}{2}m \left( \frac{\hbar}{im} \frac{\partial}{\partial x} \right)^2 + \frac{1}{2}c\hat{x}^2,$$

now let's first go figure out the possible energy *values*  $E_{x0}, E_{x1}, \dots$  before we can even start thinking about analyzing the motion.”

### Key Points

- ◊ The ground state wave function is spherically symmetric: it looks the same seen from any angle.
- ◊ In energy eigenstates the particle position is uncertain.

#### 2.7.4 Review Questions

- 1 Write out the ground state wave function and show that it is indeed spherically symmetric.
  - 2 Show that the ground state wave function is maximal at the origin and, like all the other energy eigenfunctions, becomes zero at large distances from the origin.
  - 3 Write down the explicit expression for the eigenstate  $\psi_{213}$  using table 2.1, then verify that it looks like figure 2.17 when looking along the  $z$ -axis, with the  $x$ -axis horizontal and the  $y$ -axis vertical.
- 

### 2.7.5 Degeneracy

As the energy spectrum figure 2.14 illustrated, the only energy level for which there is only a single energy eigenfunction is the ground state. All higher energy levels are what is called “degenerate”; there is more than one eigenfunction that produces them. (In other words, more than one set of three quantum numbers  $n_x$ ,  $n_y$ , and  $n_z$ .)

It turns out that degeneracy always results in nonuniqueness of the eigenfunctions. That is important for a variety of reasons. For example, in the quantum mechanics of molecules, chemical bonds often select among nonunique theoretical solutions those that best fit the given conditions. Also, to find specific mathematical or numerical solutions for the eigenfunctions of a quantum system, the nonuniquenesses will somehow have to be resolved.

Nonuniqueness also poses problems for advanced analysis. For example, suppose you try to analyze the effect of various small perturbations that a harmonic oscillator might experience in real life. Analyzing the effect of small perturbations is typically a relatively easy mathematical problem: the perturbation will slightly change an eigenfunction, but it can still be approximated by the unperturbed one. So, if you know the unperturbed eigenfunction you are in business; unfortunately, if the unperturbed eigenfunction is not unique, you may not know which is the right one to use in the analysis.

The nonuniqueness arises from the fact that:

*linear combinations of eigenfunctions at the same energy level produce alternative eigenfunctions that still have that same energy level.*

For example, the eigenfunctions  $\psi_{100}$ , and  $\psi_{010}$  of the harmonic oscillator have the same energy  $E_{100} = E_{010} = \frac{5}{2}\hbar\omega$  (as does  $\psi_{001}$ , but we will restrict this example to two eigenfunctions.) Any linear combination of the two has that energy too, so we could replace eigenfunctions  $\psi_{100}$  and  $\psi_{010}$  by two alternative ones such as:

$$\frac{\psi_{100} + \psi_{010}}{\sqrt{2}} \quad \text{and} \quad \frac{\psi_{010} - \psi_{100}}{\sqrt{2}}$$

It is readily verified these linear combinations are indeed still eigenfunctions with eigenvalue  $E_{100} = E_{010}$ : applying the Hamiltonian  $H$  to either one will multiply each term by  $E_{100} = E_{010}$ , hence the entire combination by that amount. How do these alternative eigenfunctions look? Exactly like  $\psi_{100}$  and  $\psi_{010}$  in figure 2.16, except that they are rotated over 45 degrees. Clearly then, they are just as good as the originals, just seen under a different angle.

Which raises the question, how come we ended up with the ones that we did in the first place? The answer is in the method of separation of variables that was used in subsection 2.7.2. It produced eigenfunctions of the form  $h_{n_x}(x)h_{n_y}(y)h_{n_z}(z)$  that were not just eigenfunctions of the full Hamiltonian  $H$ , but also of the partial Hamiltonians  $H_x$ ,  $H_y$ , and  $H_z$ , being the  $x$ -,  $y$ -, and  $z$ -parts of it.

For example,  $\psi_{100} = h_1(x)h_0(y)h_0(z)$  is an eigenfunction of  $H_x$  with eigenvalue  $E_{x1} = \frac{3}{2}\hbar\omega$ , of  $H_y$  with eigenvalue  $E_{y0} = \frac{1}{2}\hbar\omega$ , and of  $H_z$  with eigenvalue  $E_{z0} = \frac{1}{2}\hbar\omega$ , as well as of  $H$  with eigenvalue  $E_{100} = \frac{5}{2}\hbar\omega$ .

The alternative eigenfunctions are still eigenfunctions of  $H$ , but no longer of the partial Hamiltonians. For example,

$$\frac{\psi_{100} + \psi_{010}}{\sqrt{2}} = \frac{h_1(x)h_0(y)h_0(z) + h_0(x)h_1(y)h_0(z)}{\sqrt{2}}$$

is not an eigenfunction of  $H_x$ : taking  $H_x$  times this eigenfunction would multiply the first term by  $E_{x1}$  but the second term by  $E_{x0}$ .

So, the obtained eigenfunctions were really made determinate by ensuring that they are simultaneously eigenfunctions of  $H$ ,  $H_x$ ,  $H_y$ , and  $H_z$ . The nice thing about them is that they can answer questions not just about the total energy of the oscillator, but also about how much of that energy is in each of the three directions.

### Key Points

- ◊ Degeneracy occurs when different eigenfunctions produce the same energy.
- ◊ It causes nonuniqueness: alternative eigenfunctions will exist.
- ◊ That can make various analysis a lot more complex.

### 2.7.5 Review Questions

- 1 Just to check that this book is not lying, (you cannot be too careful), write down the analytical expression for  $\psi_{100}$  and  $\psi_{010}$  using table 2.1, then  $(\psi_{100} + \psi_{010})/\sqrt{2}$  and  $(\psi_{010} - \psi_{100})/\sqrt{2}$ . Verify that the latter two are the functions  $\psi_{100}$  and  $\psi_{010}$  in a coordinate system  $(\bar{x}, \bar{y}, z)$  that is rotated 45 degrees counter-clockwise around the  $z$ -axis compared to the original  $(x, y, z)$  coordinate system.

### 2.7.6 Non-eigenstates

It should not be thought that the harmonic oscillator only exists in energy eigenstates. The opposite is more like it. Anything that somewhat localizes the particle will produce an uncertainty in energy. This section explores the procedures to deal with states that are not energy eigenstates.

First, even if the wave function is not an energy eigenfunction, it can still always be written as a combination of the eigenfunctions:

$$\Psi(x, y, z, t) = \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} c_{n_x n_y n_z} \psi_{n_x n_y n_z} \quad (2.43)$$

That this is always possible is a consequence of the completeness of the eigenfunctions of Hermitian operators such as the Hamiltonian. An arbitrary example of such a combination state is shown in figure 2.18.

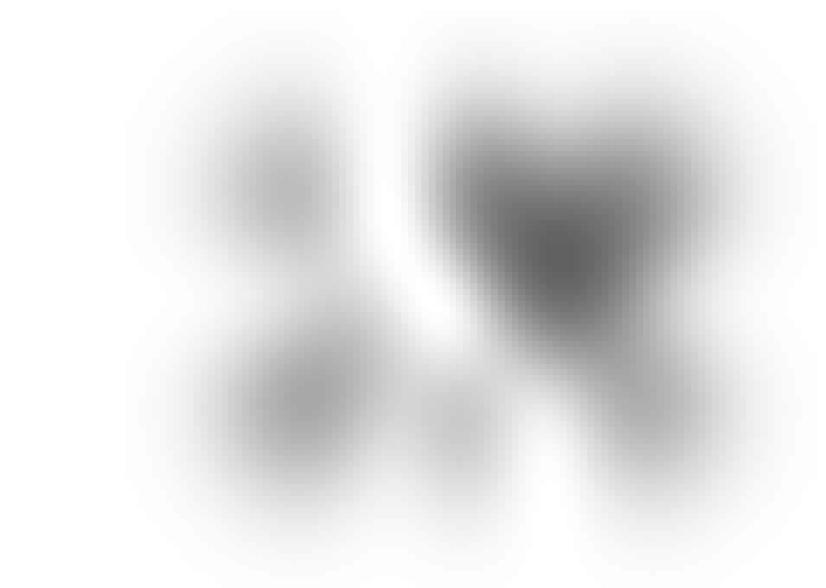


Figure 2.18: Arbitrary wave function (not an energy eigenfunction).

The coefficients  $c_{n_x n_y n_z}$  in the combination are important: according to the orthodox statistical interpretation, their square magnitude gives the probability to find the energy to be the corresponding eigenvalue  $E_{n_x n_y n_z}$ . For example,  $|c_{000}|^2$  gives the probability of finding that the oscillator is in the ground state of lowest energy.

If the wave function  $\Psi$  is in a known state, (maybe because the position of the particle was fairly accurately measured), then each coefficient  $c_{n_x n_y n_z}$  can be found by computing an inner product:

$$c_{n_x n_y n_z} = \langle \psi_{n_x n_y n_z} | \Psi \rangle \quad (2.44)$$

The reason this works is orthonormality of the eigenfunctions. As an example, consider the case of coefficient  $c_{100}$ :

$$c_{100} = \langle \psi_{100} | \Psi \rangle = \langle \psi_{100} | c_{000}\psi_{000} + c_{100}\psi_{100} + c_{010}\psi_{010} + c_{001}\psi_{001} + c_{200}\psi_{200} + \dots \rangle$$

Now proper eigenfunctions of Hermitian operators are orthonormal, which means that the inner product between different eigenfunctions is zero, and between identical eigenfunctions is one:

$$\langle \psi_{100} | \psi_{000} \rangle = 0 \quad \langle \psi_{100} | \psi_{100} \rangle = 1 \quad \langle \psi_{100} | \psi_{010} \rangle = 0 \quad \langle \psi_{100} | \psi_{001} \rangle = 0 \quad \dots$$

So, the inner product above must indeed produce  $c_{100}$ .

Later, in chapter 6.1, we will discuss another reason why the coefficients are important: they determine the time evolution of the wave function. It may be recalled that the Hamiltonian, and hence the eigenfunctions derived from it, did not involve time. However, the coefficients do.

Even if the wave function is initially in a state involving many eigenfunctions, such as the one in figure 2.18, the orthodox interpretation says that energy “measurement” will collapse it into a single eigenfunction. For example, assume that the energies in all three coordinate directions are measured and that they return the values:

$$E_{x2} = \frac{5}{2}\hbar\omega \quad E_{y1} = \frac{3}{2}\hbar\omega \quad E_{z3} = \frac{7}{2}\hbar\omega$$

for a total energy  $E = \frac{15}{2}\hbar\omega$ . Quantum mechanics could not exactly predict that this was going to happen, but it did predict that the energies had to be odd multiples of  $\frac{1}{2}\hbar\omega$ . Also, quantum mechanics gave the probability of measuring the given values to be whatever  $|c_{213}|^2$  was. Or in other words, what  $|\langle \psi_{213} | \Psi \rangle|^2$  was.

After the example measurement, the predictions become much more specific, because the wave function is now collapsed into the measured one:

$$\Psi^{\text{new}} = c_{213}^{\text{new}} \psi_{213}$$

This eigenfunction was shown earlier in figure 2.17.

If another measurement of the energies is now done, the only values that can come out are  $E_{x2}$ ,  $E_{y1}$ , and  $E_{z3}$ , the same as in the first measurement. There is now certainty of getting those values; the probability  $|c_{213}^{\text{new}}|^2 = 1$ . This will continue to be true for energy measurements until the system is disturbed, maybe by a position measurement.

### Key Points

- ◊ The basic ideas of quantum mechanics were illustrated using an example.
- ◊ The energy eigenfunctions are not the only game in town. Their seemingly lowly coefficients are important too.

- ◊ When the wave function is known, the coefficient of any eigenfunction can be found by taking an inner product of the wave function with that eigenfunction.
-

# Chapter 3

## Single-Particle Systems

### 3.1 Angular Momentum

Before we can solve the important electronic structure of the hydrogen atom, the basis for the description of all the other elements and chemical bonds, we first need to look at angular momentum. Like in the classical Newtonian case, angular momentum is essential for the analysis, and in quantum mechanics, angular momentum is also essential for describing the final solution. Moreover, the quantum properties of angular momentum turn out to be quite unexpected and important for practical applications.

#### 3.1.1 Definition of angular momentum

The old Newtonian physics defines *angular* momentum  $\vec{L}$  as the vectorial product  $\vec{r} \times \vec{p}$ , where  $\vec{r}$  is the position of the particle in question and  $\vec{p}$  is its *linear* momentum.

Following the Newtonian analogy, quantum mechanics substitutes the gradient operator  $\hbar\nabla/\text{i}$  for the linear momentum, so the angular momentum operator becomes:

$$\hat{\vec{L}} = \frac{\hbar}{\text{i}} \hat{\vec{r}} \times \nabla \quad \hat{\vec{r}} \equiv (\hat{x}, \hat{y}, \hat{z}) \quad \nabla \equiv \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \quad (3.1)$$

Unlike the Hamiltonian, the angular momentum operator is not specific to a given system. All observations about angular momentum will apply regardless of the physical system being studied.

- ◊ The angular momentum operator (3.1) has been identified.
- 

### 3.1.2 Angular momentum in an arbitrary direction

The intent in this subsection is to find the operator for the angular momentum in an arbitrary direction and its eigenfunctions and eigenvalues.

For convenience, we take the direction in which we want to know the angular momentum as the  $z$ -axis of our coordinate system. In fact, much of the mathematics that you do in quantum mechanics requires you to select some arbitrary direction as your  $z$ -axis, even if the physics itself does not have any preferred direction. It is further conventional in the quantum mechanics of atoms to draw the chosen  $z$ -axis horizontal, (though not in [3] or [6]), so that is what we will do.

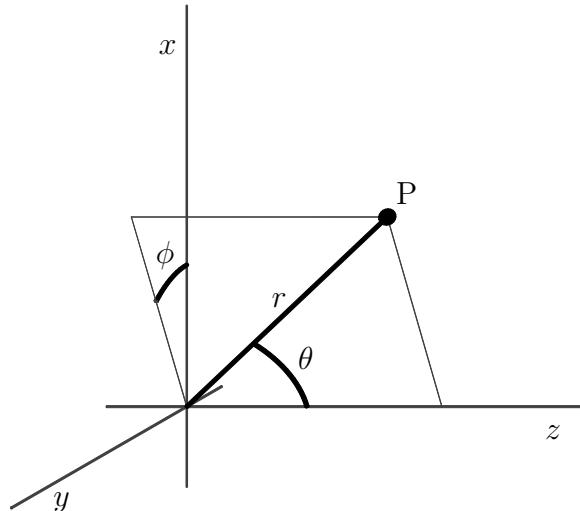


Figure 3.1: Spherical coordinates of an arbitrary point P.

Things further simplify greatly if we switch from Cartesian coordinates  $x$ ,  $y$ , and  $z$  to “spherical coordinates”  $r$ ,  $\theta$ , and  $\phi$ , as shown in figure 3.1. The coordinate  $r$  is the distance from the chosen origin,  $\theta$  is the angular position away from the chosen  $z$ -axis, and  $\phi$  is the angular position around the  $z$ -axis, measured from the chosen  $x$ -axis.

In terms of these spherical coordinates, the  $z$ -component of angular momentum simplifies to:

$$\boxed{\hat{L}_z \equiv \frac{\hbar}{i} \frac{\partial}{\partial \phi}} \quad (3.2)$$

This can be verified by looking up the gradient operator  $\nabla$  in spherical coordinates in [5, pp. 124-126] and then taking the component of  $\vec{r} \times \nabla$  in the  $z$ -direction.

In any case, with a bit of thought, it clearly makes sense: the  $z$ -component of linear momentum classically describes the motion in the *direction* of the  $z$ -axis, while the  $z$ -component of angular momentum describes the motion *around* the  $z$ -axis. So if in quantum mechanics the  $z$ -linear momentum is  $\hbar/i$  times the derivative with respect the coordinate  $z$  along the  $z$ -axis, then surely the logical equivalent for  $z$ -angular momentum is  $\hbar/i$  times the derivative with respect to the angle  $\phi$  around the  $z$ -axis?

Anyway, the eigenfunctions of the operator  $\hat{L}_z$  above turn out to be exponentials in  $\phi$ . More precisely, the eigenfunctions are of the form

$$C(r, \theta)e^{im\phi} \quad (3.3)$$

where  $m$  is a constant and  $C(r, \theta)$  can be any arbitrary function of  $r$  and  $\theta$ . The number  $m$  is called the “magnetic quantum number”. It must be an integer, one of  $\dots, -2, -1, 0, 1, 2, 3, \dots$ . The reason is that if we increase the angle  $\phi$  by  $2\pi$ , we make a complete circle around the  $z$ -axis and return to the same point. Then the eigenfunction (3.3) must again be the same, but that is only the case if  $m$  is an integer, as can be verified from the Euler identity (1.5).

The above solution is easily verified directly, and the eigenvalue  $L_z$  identified, by substitution into the eigenvalue problem  $\hat{L}_z C e^{im\phi} = L_z C e^{im\phi}$  using the expression for  $\hat{L}_z$  above:

$$\frac{\hbar}{i} \frac{\partial C e^{im\phi}}{\partial \phi} = L_z C e^{im\phi} \implies \frac{\hbar}{i} i m C e^{im\phi} = L_z C e^{im\phi}$$

It follows that every eigenvalue is of the form:

$$L_z = m\hbar \text{ for } m \text{ an integer} \quad (3.4)$$

So the angular momentum in a given direction cannot just take on any value: it must be a whole multiple  $m$ , (possibly negative), of Planck’s constant  $\hbar$ .

Compare that with the linear momentum component  $p_z$  which can take on any value, within the accuracy that the uncertainty principle allows.  $L_z$  can only take discrete values, but they will be precise. And since the  $z$ -axis was arbitrary, this is true in any direction we choose.

### Key Points

- ◊ Even if the physics that you want to describe has no preferred direction, you usually need to select some arbitrary  $z$ -axis to do the mathematics of quantum mechanics.
- ◊ Spherical coordinates based on the chosen  $z$ -axis are needed in this and subsequent analysis. They are defined in figure 3.1.
- ◊ The operator for the  $z$ -component of angular momentum is (3.2), where  $\phi$  is the angle around the  $z$ -axis.
- ◊ The eigenvalues, or measurable values, of angular momentum in any arbitrary direction are whole multiples  $m$ , possibly negative, of  $\hbar$ .

- 
- ◊ The whole multiple  $m$  is called the magnetic quantum number.
- 

### 3.1.2 Review Questions

- 1 If the angular momentum in a given direction is a whole multiple of  $\hbar = 1.05457 \cdot 10^{-34}$  J s, then  $\hbar$  should have units of angular momentum. Verify that.
  - 2 What is the magnetic quantum number of a macroscopic, 1 kg, particle that is encircling the  $z$ -axis at a distance of 1 m at a speed of 1 m/s? Write out as an integer, and show digits you are not sure about as a question mark.
  - 3 Actually, based on the derived eigenfunction,  $C(r, \theta) e^{im\phi}$ , would any macroscopic particle ever be at a single magnetic quantum number in the first place? In particular, what can you say about where the particle can be found in an eigenstate?
- 

### 3.1.3 Square angular momentum

Besides the angular momentum in an arbitrary direction, the other quantity of primary importance is the magnitude of the angular momentum. This is the length of the angular momentum vector,  $\sqrt{\vec{L} \cdot \vec{L}}$ . The square root is awkward, though; it is easier to work with the square angular momentum:

$$L^2 \equiv \vec{L} \cdot \vec{L}$$

This subsection discusses the  $\hat{L}^2$  operator and its eigenvalues.

Like the  $\hat{L}_z$  operator of the previous subsection,  $\hat{L}^2$  can be written in terms of spherical coordinates. To do so, note first that, {9},

$$\hat{\vec{L}} \cdot \hat{\vec{L}} = \frac{\hbar}{i} (\vec{r} \times \nabla) \cdot \frac{\hbar}{i} (\vec{r} \times \nabla) = -\hbar^2 \vec{r} \cdot (\nabla \times (\vec{r} \times \nabla))$$

and then look up the gradient and the curl in [5, pp. 124-126]. The result is:

$$\hat{L}^2 \equiv -\frac{\hbar^2}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) - \frac{\hbar^2}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (3.5)$$

Obviously, this result is not as intuitive as the  $\hat{L}_z$ -operator of the previous subsection, but once again, it only involves the spherical coordinate angles. The measurable values of square angular momentum will be the eigenvalues of this operator. However, that eigenvalue problem is not easy to solve. In fact the solution is not even unique.

I will just state the solution. First, the nonuniqueness is removed by demanding that the eigenfunctions are *also* eigenfunctions of  $\hat{L}_z$ , the operator of angular momentum in the  $z$ -direction. This makes the problem solvable, {10}, and the resulting eigenfunctions are called

$Y_0^0 = \sqrt{\frac{1}{4\pi}}$	$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos(\theta)$	$Y_2^0 = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$
	$Y_1^1 = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$	$Y_2^1 = -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi}$
	$Y_1^{-1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi}$	$Y_2^{-1} = \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{-i\phi}$
		$Y_2^2 = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{2i\phi}$
		$Y_2^{-2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{-2i\phi}$

Table 3.1: The first few spherical harmonics, from [3, p. 139].

the “spherical harmonics”  $Y_l^m(\theta, \phi)$ . The first few are given explicitly in table 3.1. In case you need more of them for some reason, the generic expression is

$$Y_l^m(\theta, \phi) = (-1)^{\max(m, 0)} \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} P_l^{|m|}(\cos \theta) e^{im\phi} \quad (3.6)$$

where  $P_l^{|m|}$  is the “associated Legendre function of the first kind” whose properties you can find in table books like [5, pp. 162-166].

These eigenfunctions can additionally be multiplied by any arbitrary function of the distance from the origin  $r$ . They are normalized to be orthonormal on the surface of the unit sphere:

$$\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} Y_l^m(\theta, \phi)^* Y_{\lambda}^{\mu}(\theta, \phi) \sin \theta d\theta d\phi = \begin{cases} 1 & \text{if } l = \lambda \text{ and } m = \mu \\ 0 & \text{otherwise} \end{cases} \quad (3.7)$$

The spherical harmonics  $Y_l^m$  are sometimes symbolically written in “ket notation” as  $|l m\rangle$ .

What to say about them, except that they are in general a mess? Well, at least every one is proportional to  $e^{im\phi}$ , as any eigenfunction of  $\hat{L}_z$  should be. More importantly, the very first one,  $Y_0^0$  is independent of angular position compared to the origin (it is the same for all  $\theta$  and  $\phi$  angular positions.) This eigenfunction corresponds to the state in which there is no angular momentum around the origin at all. If a particle has no angular momentum around the origin, it can be found at all angular locations relative to it with equal probability.

Far more important than the details of the eigenfunctions themselves are the eigenvalues that come rolling out of the analysis. A spherical harmonic  $Y_l^m$  has an angular momentum in the

$z$ -direction

$$L_z = m\hbar \quad (3.8)$$

where the integer  $m$  is called the magnetic quantum number, as noted in the previous subsection. That is no surprise, because we demanded that they take that form. The new result is that a spherical harmonic has a square angular momentum

$$L^2 = l(l+1)\hbar^2 \quad (3.9)$$

where  $l$  is also an integer, and is called the “azimuthal quantum number”. It is maybe a weird result, (why not simply  $l^2\hbar^2$ ?) but that is what square angular momentum turns out to be.

The azimuthal quantum number is at least as large as the magnitude of the magnetic quantum number  $m$ :

$$l \geq |m| \quad (3.10)$$

The reason is that  $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$  must be at least as large as  $\hat{L}_z^2$ ; in terms of eigenvalues,  $l(l+1)\hbar^2$  must be at least as large as  $m^2\hbar^2$ . As it is, with  $l \geq |m|$ , either the angular momentum is completely zero, for  $l = m = 0$ , or  $L^2$  is always greater than  $L_z^2$ .

### Key Points

- ◊ The operator for square angular momentum is (3.5).
- ◊ The eigenfunctions of both square angular momentum and angular momentum in the chosen  $z$ -direction are called the spherical harmonics  $Y_l^m$ .
- ◊ If a particle has no angular momentum around the origin, it can be found at all angular locations relative to it with equal probability.
- ◊ The eigenvalues for square angular momentum take the counter-intuitive form  $L^2 = l(l+1)\hbar^2$  where  $l$  is a nonnegative integer, one of  $0, 1, 2, 3, \dots$ , and is called the azimuthal quantum number.
- ◊ The azimuthal quantum number  $l$  is always at least as big as the absolute value of the magnetic quantum number  $m$ .

#### 3.1.3 Review Questions

- 1 The general wave function of a state with azimuthal quantum number  $l$  and magnetic quantum number  $m$  is  $\Psi = R(r)Y_l^m(\theta, \phi)$ , where  $R(r)$  is some further arbitrary function of  $r$ . Show that the condition for this wave function to be normalized, so that the total probability of finding the particle integrated over all possible positions is one, is that

$$\int_{r=0}^{\infty} R(r)^* R(r) r^2 dr = 1.$$

- 2** Can we invert the statement about zero angular momentum and say: if a particle can be found at all angular positions compared to the origin with equal probability, it will have zero angular momentum?
- 3** What is the minimum amount that the total square angular momentum is larger than the square angular  $z$ -momentum only for a given value of  $l$ ?
- 

### 3.1.4 Angular momentum uncertainty

Rephrasing the final results of the previous subsection, if there is nonzero angular momentum, the angular momentum in the  $z$ -direction is always less than the total angular momentum. There is something funny going on here. The  $z$ -direction can be chosen arbitrarily, and if we choose it in the same direction as the angular momentum vector, then the  $z$ -component should be the entire vector. So, how can it always be less?

The answer of quantum mechanics is that the looked-for angular momentum vector *does not exist*. No axis, however arbitrarily chosen, can align with a nonexisting vector.

There is an uncertainty principle here, similar to the one of Heisenberg for position and linear momentum. For angular momentum, it turns out that if the component of angular momentum in a given direction, here taken to be  $z$ , has a definite value, then the components in both the  $x$  and  $y$  directions will be uncertain. (This will be shown later in chapter 7.1.1). The wave function will be in a state where  $L_x$  and  $L_y$  have a range of possible values  $m_1\hbar, m_2\hbar, \dots$ , each with some probability. Without definite  $x$  and  $y$  components, there simply is no angular momentum vector.

It is tempting to think of quantities that have not been measured, such as the angular momentum vector in this example, as being merely “hidden.” However, the impossibility for the  $z$ -axis to ever align with any angular momentum vector shows that there is a fundamental difference between “being hidden” and “not existing”.

---

#### Key Points

- ◊ According to quantum mechanics, an exact nonzero angular momentum vector will never exist. If one component of angular momentum has a value, then the other two components will be uncertain.
-

## 3.2 The Hydrogen Atom

This section examines the critically important case of the hydrogen atom. The hydrogen atom consists of a nucleus which is just a single proton, and an electron encircling that nucleus. The nucleus, being much heavier than the electron, can be assumed to be at rest, and only the motion of the electron needs concern us.

The energy levels of the electron determine the photons that the atom will absorb or emit, allowing the powerful scientific tool of spectral analysis. The electronic structure is also very important for understanding the properties of the other elements and of chemical bonds.

### 3.2.1 The Hamiltonian

The first step is to find the Hamiltonian of the electron. The electron experiences an electrostatic Coulomb attraction to the oppositely charged nucleus. The corresponding potential energy is

$$V = -\frac{e^2}{4\pi\epsilon_0 r} \quad (3.11)$$

with  $r$  the distance from the nucleus. The constant

$$e = 1.6 \cdot 10^{-19} \text{ C} \quad (3.12)$$

is the magnitude of the electric charges of the electron and proton, and the constant

$$\epsilon_0 = 8.85 \cdot 10^{-12} \text{ C}^2/\text{J m} \quad (3.13)$$

is called the “permittivity of space.”

Unlike for the harmonic oscillator discussed earlier, this potential energy cannot be split into separate parts for Cartesian coordinates  $x$ ,  $y$ , and  $z$ . To do the analysis for the hydrogen atom, we must put the nucleus at the origin of the coordinate system and use spherical coordinates  $r$  (the distance from the nucleus),  $\theta$  (the angle from an arbitrarily chosen  $z$ -axis), and  $\phi$  (the angle around the  $z$ -axis); see figure 3.1. In terms of spherical coordinates, the potential energy above depends on just the single coordinate  $r$ .

To get the Hamiltonian, we need to add to this potential energy the kinetic energy operator  $\hat{T}$  of chapter 2.3, which involves the Laplacian. The Laplacian in spherical coordinates is readily available in table books, [5, p. 126], and the Hamiltonian is thus found to be:

$$H = -\frac{\hbar^2}{2m_e r^2} \left\{ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} - \frac{e^2}{4\pi\epsilon_0 r} \quad (3.14)$$

where

$$m_e = 9.109 \cdot 10^{-31} \text{ kg} \quad (3.15)$$

is the mass of the electron.

It may be noted that the small proton motion can be corrected for by slightly adjusting the mass of the electron to be an effective  $9.1044 \times 10^{-31}$  kg. This makes the solution exact, except for extremely small effects due to relativity and spin.

### Key Points

- ◊ To analyze the hydrogen atom, we will have to use spherical coordinates.
- ◊ The Hamiltonian in spherical coordinates has been written down. It is (3.14).

### 3.2.2 Solution using separation of variables

The solution process to find the energy eigenfunctions and eigenvalues follows similar lines as the one for the harmonic oscillator. We will look for eigenfunctions  $\psi$  that take the form of a product of functions of each of the three coordinates:  $\psi = R(r)\Theta(\theta)\Phi(\phi)$ , or more concisely,  $\psi = R\Theta\Phi$ . Substituting this assumption into the Hamiltonian eigenvalue problem  $H\psi = E\psi$ , with  $E$  the energy eigenvalue of the prospective eigenfunction  $\psi$ , we get:

$$\left[ -\frac{\hbar^2}{2m_e r^2} \left\{ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} - \frac{e^2}{4\pi\epsilon_0 r} \right] R\Theta\Phi = ER\Theta\Phi$$

To reduce this problem, multiply first by  $2m_e r^2 / R\Theta\Phi$  and then split the terms:

$$\begin{aligned} & -\frac{\hbar^2}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{1}{\Theta\Phi} \left\{ -\frac{\hbar^2}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) - \frac{\hbar^2}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} \Theta\Phi - \frac{2m_e r^2 e^2}{4\pi\epsilon_0} \frac{1}{r} \\ & = 2m_e r^2 E \end{aligned} \quad (3.16)$$

Next collect the terms involving the angular derivatives and name them  $E_{\theta\phi}$ . They are:

$$\frac{1}{\Theta\Phi} \left[ -\frac{\hbar^2}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) - \frac{\hbar^2}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \Theta\Phi = E_{\theta\phi}$$

By this definition,  $E_{\theta\phi}$  only depends on  $\theta$  and  $\phi$ , not  $r$ . But it cannot depend on  $\theta$  or  $\phi$  either, since none of the other terms in the original equation (3.16) depends on them. So  $E_{\theta\phi}$  must be a constant, independent of all three coordinates. Multiplying by  $\Theta\Phi$ , we have obtained a reduced eigenvalue problem involving  $\Theta\Phi$  only, with eigenvalue  $E_{\theta\phi}$ :

$$\left[ -\frac{\hbar^2}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) - \frac{\hbar^2}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \Theta\Phi = E_{\theta\phi} \Theta\Phi$$

Repeat the game with this reduced eigenvalue problem. Multiply by  $\sin^2 \theta / \Theta \Phi$ , and name the only  $\phi$ -dependent term  $E_\phi$ . It is:

$$-\frac{1}{\Phi} \hbar^2 \left( \frac{\partial^2}{\partial \phi^2} \right) \Phi = E_\phi$$

By definition  $E_\phi$  only depends on  $\phi$ , but since the other two terms in the equation it came from did not depend on  $\phi$ ,  $E_\phi$  can neither, so it must be another constant. We now have a simple eigenvalue problem just involving  $\Phi$ :

$$-\hbar^2 \left( \frac{\partial^2}{\partial \phi^2} \right) \Phi = E_\phi \Phi$$

In fact, we already know how to solve it, since the operator involved is just the square of the angular momentum operator  $\hat{L}_z$  of section 3.1.2:

$$-\hbar^2 \left( \frac{\partial^2}{\partial \phi^2} \right) \Phi = \left( \frac{\hbar}{i} \frac{\partial}{\partial \phi} \right)^2 \Phi = \hat{L}_z^2 \Phi$$

So this equation must have the same eigenfunctions as the operator  $\hat{L}_z$ ,

$$\Phi_m = e^{im\phi}$$

and must have the square eigenvalues

$$E_\phi = (m\hbar)^2$$

(each application of  $\hat{L}_z$  multiplies the eigenfunction by  $m\hbar$ ). It may be recalled that the magnetic quantum number  $m$  must be an integer.

The eigenvalue problem for  $\Theta \Phi$  is even easier; it is exactly the one for the square angular momentum  $L^2$  of section 3.1.3. Its eigenfunctions are the spherical harmonics,

$$\Theta \Phi = Y_l^m(\theta, \phi)$$

and its eigenvalues are

$$E_{\theta\phi} = l(l+1)\hbar^2$$

It may be recalled that the azimuthal quantum number  $l$  must be an integer greater than or equal to  $|m|$ .

Returning now to the solution of the original eigenvalue problem (3.16), replacement of the angular terms by  $l(l+1)\hbar^2$  turns it into an ordinary differential equation problem for the radial factor  $R(r)$  in the energy eigenfunction. As usual, this problem is a pain to solve, {11}, so we will once again skip the details and just give the solution.

The solutions of the radial problem can be numbered using a third quantum number,  $n$ , called the “principal quantum number”. It is larger than the azimuthal quantum number  $l$ , which in turn must be at least as large as the absolute value of the magnetic quantum number:

$$n > l \geq |m| \quad (3.17)$$

so the principal quantum number must be at least 1. And if  $n = 1$ , then  $l = m = 0$ .

In terms of these three quantum numbers, the final energy eigenfunctions of the hydrogen atom are:

$$\psi_{nlm} = R_{nl}(r)Y_l^m(\theta, \phi) \quad (3.18)$$

where the spherical harmonics  $Y_l^m$  were described in section 3.1.3. The additional radial wave functions  $R_{nl}$  can be found written out in table 3.2 for small values of  $n$  and  $l$ . They are in terms of a scaled radial distance from the nucleus  $\rho = r/a_0$ , where the length  $a_0$  is called the “Bohr radius” and has the value

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}, \quad (3.19)$$

or about half an Ångstrom. The Bohr radius is a really good length scale to describe atoms in terms of. The Ångstrom itself is a good choice too, it is  $10^{-10}$  m, or one tenth of a nanometer.

If you need the wave functions for larger values of the quantum numbers than tabulated, the generic expression is, drums please, (do not for a second think that I am really enjoying this):

$$\psi_{nlm} = -\frac{2}{n^2} \sqrt{\frac{(n-l-1)!}{[(n+l)!a_0]^3}} \left(\frac{2\rho}{n}\right)^l L_{n+l}^{2l+1} \left(\frac{2\rho}{n}\right) e^{-\rho/n} Y_l^m(\theta, \phi) \quad (3.20)$$

I can see that you cannot wait for a rainy afternoon to check it all out. The functions  $L_{n+l}^{2l+1}(2\rho/n)$  are, of course, the “associated Laguerre polynomials.” If you forgot one or two of their properties, you can refresh your memory in table books like [5, pp. 169-172]. Do keep in mind that different references have contradictory definitions of the associated Laguerre polynomials, {12}. Combine the spherical harmonics of section 3.1.3 and the uncertain definition of the Laguerre polynomials in the formulae for the hydrogen energy eigenfunctions  $\psi_{nlm}$  above, and there is of course a possibility of getting an eigenfunction wrong if you are not careful.

The energy eigenvalues are much simpler and more interesting than the eigenfunctions; they are

$$E_n = -\frac{\hbar^2}{2m_e a_0^2} \frac{1}{n^2} \quad n = 1, 2, 3, \dots \quad (3.21)$$

You may wonder why the energy only depends on the principal quantum number  $n$ , and not also on the azimuthal quantum number  $l$  and the magnetic quantum number  $m$ . Well, the choice of  $z$ -axis was arbitrary, so it should not seem strange that the physics would not depend on the angular momentum in that direction. But that the energy does not depend on  $l$  is

$R_{10} = \frac{2}{\sqrt{a_0^3}} e^{-\rho}$	$R_{20} = \frac{2 - \rho}{2\sqrt{2a_0^3}} e^{-\rho/2}$	$R_{30} = \frac{54 - 36\rho + 4\rho^2}{81\sqrt{3a_0^3}} e^{-\rho/3}$
	$R_{21} = \frac{\rho}{2\sqrt{6a_0^3}} e^{-\rho/2}$	$R_{31} = \frac{24\rho - 4\rho^2}{81\sqrt{6a_0^3}} e^{-\rho/3}$
$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$ $\rho = \frac{r}{a_0}$		

Table 3.2: The first few radial wave functions for hydrogen, from [3, p. 154].

nontrivial; if you solve the similar problem of a particle stuck inside an impenetrable sphere, the energy values depend on both  $n$  and  $l$ . So, that is just the way it is. (It stops being true anyway if you include relativistic effects in the Hamiltonian.)

Since the lowest possible value of the quantum number  $n$  is one, the ground state of lowest energy  $E_1$  is eigenfunction  $\psi_{100}$ .

### Key Points

- ◊ Skipping a lot of math, energy eigenfunctions  $\psi_{nlm}$  and their energy eigenvalues  $E_n$  have been found.
- ◊ There is one eigenfunction for each set of three integer quantum numbers  $n$ ,  $l$ , and  $m$  satisfying  $n > l \geq |m|$ . The number  $n$  is called the principal quantum number.
- ◊ The typical length scale in the solution is called the Bohr radius  $a_0$ , which is about half an Ångstrom.
- ◊ The derived eigenfunctions  $\psi_{nlm}$  are eigenfunctions of
  - $z$ -angular momentum, with eigenvalue  $L_z = m\hbar$ ;
  - square angular momentum, with eigenvalue  $L^2 = l(l+1)\hbar^2$ ;
  - energy, with eigenvalue  $E_n = -\hbar^2/2m_e a_0^2 n^2$ .
- ◊ The energy values only depend on the principal quantum number  $n$ .
- ◊ The ground state is  $\psi_{100}$ .

### 3.2.2 Review Questions

- 1** Use the tables for the radial wave functions and the spherical harmonics to write down the wave function

$$\psi_{nlm} = R_{nl}(r)Y_l^m(\theta, \phi)$$

for the case of the ground state  $\psi_{100}$ .

Check that the state is normalized. Note:  $\int_0^\infty e^{-2u}u^2 du = \frac{1}{4}$ .

- 2** Use the generic expression

$$\psi_{nlm} = -\frac{2}{n^2} \sqrt{\frac{(n-l-1)!}{[(n+l)!a_0]^3}} \left(\frac{2\rho}{n}\right)^l L_{n+l}^{2l+1} \left(\frac{2\rho}{n}\right) e^{-\rho/n} Y_l^m(\theta, \phi)$$

with  $\rho = r/a_0$  and  $Y_l^m$  from the spherical harmonics table to find the ground state wave function  $\psi_{100}$ . Note: the Laguerre polynomial  $L_1(x) = 1 - x$  and for any  $p$ ,  $L_1^p$  is just its  $p$ -th derivative.

- 3** Plug numbers into the generic expression for the energy eigenvalues,

$$E_n = -\frac{\hbar^2}{2m_e a_0^2} \frac{1}{n^2},$$

where  $a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$ , to find the ground state energy. Express in eV, where 1 eV equals  $1.6022 \cdot 10^{-19}$  J. Values for the physical constants can be found at the start of this section and in the notations section.

---

### 3.2.3 Discussion of the eigenvalues

The only energy levels that the electron in the hydrogen atom can have are the energy eigenvalues derived in the previous subsection:

$$E_n = -\frac{\hbar^2}{2m_e a_0^2} \frac{1}{n^2} \quad n = 1, 2, 3, \dots$$

This subsection discusses the physical consequences of this result.

To aid the discussion, the allowed energies are plotted in the form of an energy spectrum in figure 3.2. To the right of the lowest three energy levels the values of the quantum numbers that give rise to those energy levels are listed.

The first thing that the energy spectrum illustrates is that the energy levels are all negative, unlike the ones of the harmonic oscillator, which were all positive. However, that does not mean much; it results from defining the potential energy of the harmonic oscillator to be zero at the nominal position of the particle, while the hydrogen potential is instead defined to be zero at large distance from the nucleus. (It will be shown later, chapter 6.1.4, that the average potential energy is twice the value of the total energy, and the average kinetic energy is minus the total energy, making the average kinetic energy positive as it should be.)

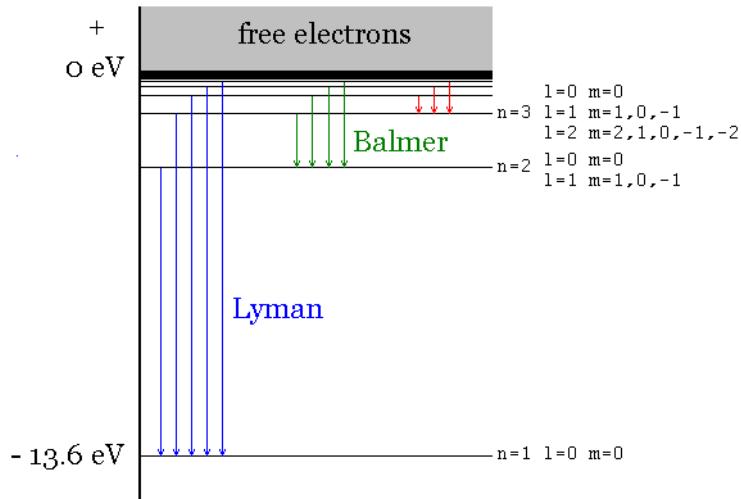


Figure 3.2: Spectrum of the hydrogen atom.

A more profound difference is that the energy levels of the hydrogen atom have a maximum value, namely zero, while those of the harmonic oscillator went all the way to infinity. It means physically that while the particle can never escape in a harmonic oscillator, in a hydrogen atom, the electron escapes if its total energy is greater than zero. Such a loss of the electron is called “ionization” of the atom.

There is again a ground state of lowest energy; it has total energy

$$E_1 = -13.6 \text{ eV} \quad (3.22)$$

(an eV or “electron volt” is  $1.6 \cdot 10^{-19}$  J). The ground state is the state in which the hydrogen atom will be at absolute zero temperature. In fact, it will still be in the ground state at room temperature, since even then the energy of heat motion is unlikely to raise the energy level of the electron to the next higher one,  $E_2$ .

The ionization energy of the hydrogen atom is 13.6 eV; this is the minimum amount of energy that must be added to raise the electron from the ground state to the state of a free electron.

If the electron is excited from the ground state to a higher but still bound energy level, (maybe by passing a spark through hydrogen gas), it will in time again transition back to a lower energy level. Discussion of the reasons and the time evolution of this process will have to wait until chapter 6.2. For now, it can be pointed out that different transitions are possible, as indicated by the arrows in figure 3.2. They are named by their final energy level to be Lyman, Balmer, or Paschen series transitions.

The energy lost by the electron during a transition is emitted as electromagnetic radiation in the form of a photon. The most energetic photons, in the ultraviolet range, are emitted by Lyman transitions. Balmer transitions emit visible light and Paschen ones infrared.

The emitted photons of isolated atoms at rest must have an energy very precisely equal to the difference in energy eigenvalues; anything else would violate the requirement of the orthodox interpretation that only the eigenvalues are observable. And according to the Planck formula, the natural frequency of the electromagnetic radiation is simply the photon's energy divided by  $\hbar$ . Thus the spectrum of the emitted light is very distinctive and can be identified to great accuracy. Different elements have different spectra, and so do molecules. It all allows atoms and molecules to be correctly recognized in a lab or out in space.

Atoms and molecules may also absorb electromagnetic energy of the same frequencies to enter an excited state and eventually emit it again in a different direction, chapter 6.2. In this way, they can remove these frequencies from light that passes them on its way to earth, resulting in an absorption spectrum. Since hydrogen is so prevalent in the universe, its energy levels as derived here are particularly important in astronomy.

---

### Key Points

- ◊ The energy levels of the electron in a hydrogen atom have a highest value. This energy is by convention taken to be the zero level.
  - ◊ The ground state has a energy 13.6 eV below this zero level.
  - ◊ If the electron in the ground state is given an additional amount of energy that exceeds the 13.6 eV, it has enough energy to escape from the nucleus. This is called ionization of the atom.
  - ◊ If the electron transitions from a higher bound energy state to a lower one, it emits radiation with a natural frequency given by the difference between the energy levels divided by  $\hbar$ .
  - ◊ Similarly, atoms may absorb electromagnetic energy of such a frequency.
- 

---

### 3.2.3 Review Questions

- 1 If there are infinitely many energy levels  $E_1, E_2, E_3, E_4, E_5, E_6, E_7, E_8, \dots$ , where did they all go in the energy spectrum?
  - 2 What is the value of energy level  $E_2$ ? And  $E_3$ ?
  - 3 Based on the results on the previous question, what is the color of the light emitted in a Balmer transition from energy  $E_3$  to  $E_2$ ? The Planck formula says that the natural frequency  $\omega$  of the emitted photon is its energy divided by  $\hbar$ , and the wave length of light is  $2\pi c/\omega$  where  $c$  is the speed of light. Typical wave lengths of visible light are: violet 400 nm, indigo 445 nm, blue 475 nm, green 510 nm, yellow 570 nm, orange 590 nm, red 650 nm.
  - 4 What is the color of the light emitted in a Balmer transition from an energy level  $E_n$  with a high value of  $n$  to  $E_2$ ?
-

### 3.2.4 Discussion of the eigenfunctions

The appearance of the energy eigenstates will be of great interest in understanding the heavier elements and chemical bonds. In this subsection, we describe the most important of them.

It may be recalled from subsection 3.2.2 that there is one eigenfunction  $\psi_{nlm}$  for each set of three integer quantum numbers. They are the principal quantum number  $n$  (determining the energy of the state), the azimuthal quantum number  $l$  (determining the square angular momentum), and the magnetic quantum number  $m$  (determining the angular momentum in the chosen  $z$ -direction.) They must satisfy the requirements that

$$n > l \geq |m|$$

For the ground state, with the lowest energy  $E_1$ , we have  $n = 1$  and hence according to the conditions above both  $l$  and  $m$  must be zero. So the ground state eigenfunction is  $\psi_{100}$ ; it is unique.

The expression for the wave function of the ground state is (from the results of subsection 3.2.2):

$$\psi_{100}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \quad (3.23)$$

where  $a_0$  is called the “Bohr radius”,

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.53 \times 10^{-10} \text{ m} \quad (3.24)$$

The square magnitude of the energy states will again be displayed as grey tones, darker regions corresponding to regions where the electron is more likely to be found. The ground state is shown this way in figure 3.3; the electron may be found within a blob size that is about thrice the Bohr radius, or roughly an Ångstrom, ( $10^{-10}$  m), in diameter.

Figure 3.3: Ground state wave function  $\psi_{100}$  of the hydrogen atom.

It is the quantum mechanical refusal of electrons to restrict themselves to a single location that gives atoms their size. If Planck’s constant  $\hbar$  would have been zero, so would have been

the Bohr radius, and the electron would have been in the nucleus. It would have been a very different world.

The ground state probability distribution is spherically symmetric: the probability of finding the electron at a point depends on the distance from the nucleus, but not on the angular orientation relative to it.

The excited energy levels  $E_2, E_3, \dots$  are all degenerate; as the spectrum figure 3.2 indicated, there is more than one eigenstate producing each level. Let's have a look at the states at energy level  $E_2$  now.

Figure 3.4 shows energy eigenfunction  $\psi_{200}$ . Like  $\psi_{100}$ , it is spherically symmetric. In fact, all eigenfunctions  $\psi_{n00}$  are spherically symmetric. However, the wave function has blown up a lot, and now separates into a small, more or less spherical region in the center, surrounded by a second region that forms a spherical shell. Separating the two is a radius at which there is zero probability of finding the electron.

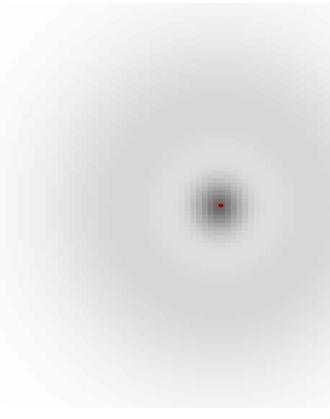


Figure 3.4: Eigenfunction  $\psi_{200}$ .

The state  $\psi_{200}$  is commonly referred to as the “2s” state. The 2 indicates that it is a state with energy  $E_2$ . The “s” indicates that the azimuthal quantum number is zero; just think “spherically symmetric.” Similarly, the ground state  $\psi_{100}$  is commonly indicated as “1s”, having the lowest energy  $E_1$ .

States which have azimuthal quantum number  $l = 1$  are called “p” states, for some historical reason. In particular, the  $\psi_{21m}$  states are called “2p” states. As first example of such a state, figure 3.5 shows  $\psi_{210}$ . This wave function squeezes itself close to the  $z$ -axis, which is plotted horizontally by convention. There is zero probability of finding the electron at the vertical  $x, y$ -symmetry plane, and maximum probability at two symmetric points on the  $z$ -axis. Since the wave function squeezes close to the  $z$  axis, this state is often more specifically referred to as the “ $2p_z$ ” state. Think “points along the  $z$ -axis.”

Figure 3.6 shows the other two “2p” states,  $\psi_{211}$  and  $\psi_{21-1}$ . These two states look exactly the

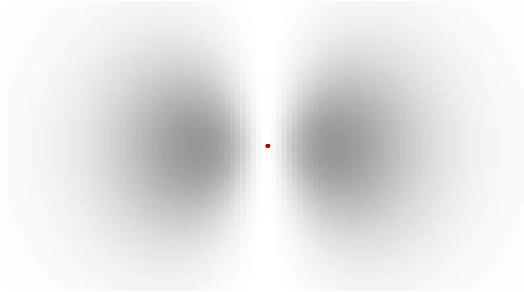


Figure 3.5: Eigenfunction  $\psi_{210}$ , or  $2p_z$ .

same as far as the probability density is concerned. It is somewhat hard to see in the figure, but they really take the shape of a torus around the horizontal  $z$ -axis.

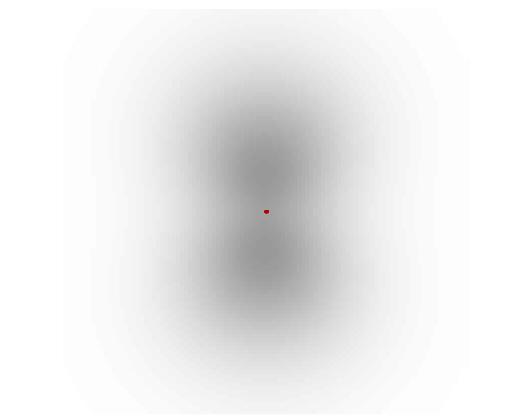


Figure 3.6: Eigenfunction  $\psi_{211}$  (and  $\psi_{21-1}$ ).

Eigenfunctions  $\psi_{200}$ ,  $\psi_{210}$ ,  $\psi_{211}$ , and  $\psi_{21-1}$  are degenerate: they all four have the same energy  $E_2 = -3.4$  eV. The consequence is that they are not unique. Combinations of them can be formed that have the same energy. These combination states may be more important physically than the original eigenfunctions.

In particular, the torus-shaped eigenfunctions  $\psi_{211}$  and  $\psi_{21-1}$  are usually not very relevant to descriptions of heavier elements and chemical bonds. Two states that are more likely to be relevant here are called  $2p_x$  and  $2p_y$ ; they are the combination states:

$$2p_x: \frac{1}{\sqrt{2}}(-\psi_{211} + \psi_{21-1}) \quad 2p_y: \frac{i}{\sqrt{2}}(\psi_{211} + \psi_{21-1}) \quad (3.25)$$

These two states are shown in figure 3.7; they look exactly like the “pointer” state  $2p_z$  of figure 3.5, except that they squeeze along the  $x$ -axis, respectively the  $y$ -axis, instead of along the  $z$ -axis. (Since the  $y$ -axis is pointing towards us,  $2p_y$  looks rotationally symmetric. Seen from the side, it would look like  $p_z$  in figure 3.5.)

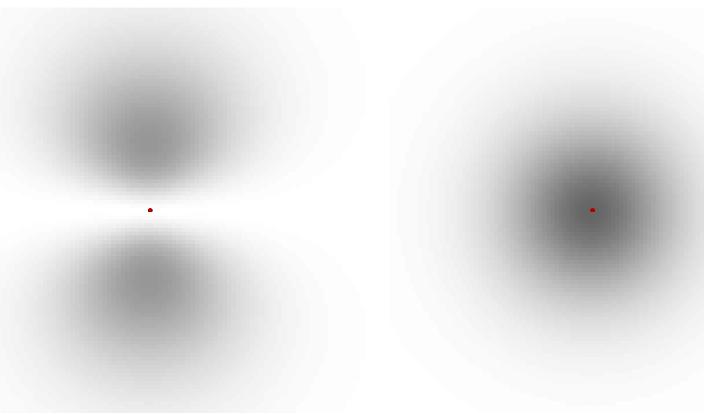


Figure 3.7: Eigenfunctions  $2p_x$ , left, and  $2p_y$ , right.

Note that unlike the two original states  $\psi_{211}$  and  $\psi_{21-1}$ , the states  $2p_x$  and  $2p_y$  do not have a definite value of the  $z$ -component of angular momentum; the  $z$ -component has a 50/50 uncertainty of being either  $+\hbar$  or  $-\hbar$ . But that is not important in most circumstances. What is important is that when multiple electrons occupy the p states, mutual repulsion effects tend to push them into the  $p_x$ ,  $p_y$ , and  $p_z$  states.

So, the four independent eigenfunctions at energy level  $E_2$  are best thought of as consisting of one spherically symmetrical 2s state, and three directional states,  $2p_x$ ,  $2p_y$ , and  $2p_z$ , pointing along the three coordinate axes.

But even that is not always ideal; as discussed in chapter 5.2.4, for many chemical bonds, especially those involving the important element carbon, still different combination states called “hybrids” show up. They involve combinations of the 2s and the 2p states and therefore have uncertain square angular momentum as well.

### Key Points

- ◊ The typical size of eigenstates is given by the Bohr radius, making the size of the atom of the order of a Å.
- ◊ The ground state  $\psi_{100}$ , or 1s state, is nondegenerate: no other set of quantum numbers  $n, l, m$  produces energy  $E_1$ .
- ◊ All higher energy levels are degenerate, there is more than one eigenstate producing that energy.
- ◊ All states of the form  $\psi_{n00}$ , including the ground state, are spherically symmetric, and are called s states. The ground state  $\psi_{100}$  is the 1s state,  $\psi_{200}$  is the 2s state, etcetera.
- ◊ States of the form  $\psi_{n1m}$  are called p states. The basic 2p states are  $\psi_{21-1}$ ,  $\psi_{210}$ , and  $\psi_{211}$ .
- ◊ The state  $\psi_{210}$  is more specifically called the  $2p_z$  state, since it squeezes itself around the  $z$ -axis.

- ◊ There are similar  $2p_x$  and  $2p_y$  states that squeeze around the  $x$  and  $y$  axes. Each is a combination of  $\psi_{21-1}$  and  $\psi_{211}$ .
  - ◊ The four spatial states at the  $E_2$  energy level can therefore be thought of as one spherically symmetric  $2s$  state and three  $2p$  pointer states along the axes.
  - ◊ However, since the  $E_2$  energy level is degenerate, eigenstates of still different shapes are likely to show up in applications.
- 

### 3.2.4 Review Questions

**1** At what distance from the nucleus  $r$ , expressed as a multiple of the Bohr radius  $a_0$ , becomes the square of the ground state wave function less than one percent of its value at the nucleus? What is that expressed in Å?

**2** Check from the conditions

$$n > l \geq |m|$$

that  $\psi_{200}$ ,  $\psi_{211}$ ,  $\psi_{210}$ , and  $\psi_{21-1}$  are the only states of the form  $\psi_{nlm}$  that have energy  $E_2$ . (Of course, all their combinations, like  $2p_x$  and  $2p_y$ , have energy  $E_2$  too, but they are not simply of the form  $\psi_{nlm}$ , but combinations of the “basic” solutions  $\psi_{200}$ ,  $\psi_{211}$ ,  $\psi_{210}$ , and  $\psi_{21-1}$ .)

**3** Check that the states

$$2p_x = \frac{1}{\sqrt{2}}(-\psi_{211} + \psi_{21-1}) \quad 2p_y = \frac{i}{\sqrt{2}}(\psi_{211} + \psi_{21-1})$$

are properly normalized.

---

## 3.3 Expectation Value and Standard Deviation

It is a striking consequence of quantum mechanics that physical quantities may not have a value. This occurs whenever the wave function is not an eigenfunction of the quantity of interest. For example, the ground state of the hydrogen atom is not an eigenfunction of the position operator  $\hat{x}$ , so the  $x$ -position of the electron does not have a value. According to the orthodox interpretation, it cannot be predicted with certainty what a measurement of such a quantity will produce.

However, it is possible to say something if the same measurement is done on a large number of systems that are all the same before the measurement. An example would be  $x$ -position measurements on a large number of hydrogen atoms that are all in the ground state before the measurement. In that case, it is relatively straightforward to predict what the average, or “expectation value,” of all the measurements will be.

The expectation value is certainly not a replacement for the classical value of physical quantities. For example, for the hydrogen atom in the ground state, the expectation position of the electron is in the nucleus by symmetry. Yet because the nucleus is so small, measurements will never find it there! (The typical measurement will find it a distance comparable to the Bohr radius away.) Actually, that is good news, because if the electron would be in the nucleus as a classical particle, its potential energy would be almost minus infinity instead of the correct value of about -27 eV. It would be: goodbye, world as we know it. Still, having an expectation value is of course better than having no information at all.

The average discrepancy between the expectation value and the actual measurements is called the “standard deviation.”. In the hydrogen atom example, where typically the electron is found a distance comparable to the Bohr radius away from the nucleus, the standard deviation in the  $x$ -position turns out to be exactly one Bohr radius.

In general, the standard deviation is the quantitative measure for how much uncertainty there is in a physical value. If the standard deviation is very small compared to what we are interested in, it is probably OK to use the expectation value as a classical value. It is perfectly fine for me to say that the electron of the hydrogen atom that you are measuring is in your lab, instead of mine, but it is not OK for me to say that it has countless electron volts of negative potential energy because it is in the nucleus.

This section discusses how to find expectation values and standard deviations after a brief introduction to the underlying ideas of statistics.

---

### Key Points

- ◊ The expectation value is the average value obtained by doing a large number of measurements on initially identical systems. It is as close as quantum mechanics can come to having classical values for uncertain physical quantities.
  - ◊ The standard deviation is how far the individual measurements on average deviate from the expectation value. It is the quantitative measure of uncertainty in quantum mechanics.
- 

### 3.3.1 Statistics of a die

Since it seems to us humans as if, in Einstein’s words, God is playing dice with the universe, it may be a worthwhile idea to examine the statistics of a die first.

For a fair die, each of the six numbers will, on average, show up a fraction  $1/6$  of the number of throws. In other words, each face has a probability of  $1/6$ .

The average value of a large number of throws is called the expectation value. For a fair die,

the expectation value is 3.5. After all, number 1 will show up in about 1/6 of the throws, as will numbers 2 through 6, so the average is

$$\frac{(\text{number of throws}) \times (\frac{1}{6}1 + \frac{1}{6}2 + \frac{1}{6}3 + \frac{1}{6}4 + \frac{1}{6}5 + \frac{1}{6}6)}{\text{number of throws}} = 3.5$$

The general rule to get the expectation value is to sum the probability for each value times the value. In this example:

$$\frac{1}{6}1 + \frac{1}{6}2 + \frac{1}{6}3 + \frac{1}{6}4 + \frac{1}{6}5 + \frac{1}{6}6 = 3.5$$

Note that the name “expectation value” is very poorly chosen. Even though the *average* value of a lot of throws will be 3.5, you would surely not *expect* to throw 3.5. We just have to live with it, too late to change it now.

The maximum possible deviation from the expectation value does of course occur when you throw a 1 or a 6; the absolute deviation is then  $|1 - 3.5| = |6 - 3.5| = 2.5$ . It means that the possible values produced by a throw can deviate as much as 2.5 from the expectation value.

However, the maximum possible deviation from the average is not a useful concept for quantities like position, or for the energy levels of the harmonic oscillator, where the possible values extend all the way to infinity. So, instead of the *maximum* deviation from the expectation value, some *average* deviation is better. The most useful of those is called the “standard deviation”, denoted by  $\sigma$ . It is found in two steps: first the average *square* deviation from the expectation value is computed, and then a square root is taken of that. For the die that works out to be:

$$\begin{aligned}\sigma &= [\frac{1}{6}(1 - 3.5)^2 + \frac{1}{6}(2 - 3.5)^2 + \frac{1}{6}(3 - 3.5)^2 + \\ &\quad \frac{1}{6}(4 - 3.5)^2 + \frac{1}{6}(5 - 3.5)^2 + \frac{1}{6}(6 - 3.5)^2]^{1/2} \\ &= 1.71\end{aligned}$$

On average then, the throws are 1.71 points off from 3.5.

### Key Points

- ◊ The expectation value is obtained by summing the possible values times their probabilities.
- ◊ To get the standard deviation, first find the average square deviation from the expectation value, then take a square root of that.

#### 3.3.1 Review Questions

- 1 Suppose we toss a coin a large number of times, and count heads as one, tails as two. What will be the expectation value?

- 2** Continuing this example, what will be the maximum deviation?
- 3** Continuing this example, what will be the standard deviation?
- 4** Have I got a die for you! By means of a small piece of lead integrated into its light-weight structure, it does away with that old-fashioned uncertainty. It comes up six every time! What will be the expectation value of your throws? What will be the standard deviation?
- 

### 3.3.2 Statistics of quantum operators

The expectation values of the operators of quantum mechanics are defined in the same way as those for the die.

Consider an arbitrary physical quantity, call it  $a$ , and assume it has an associated operator  $A$ . For example, if the physical quantity  $a$  is the total energy  $E$ ,  $A$  will be the Hamiltonian  $H$ .

The equivalent of the face values of the die are the values that the quantity  $a$  can take, and according to the orthodox interpretation, that are the eigenvalues

$$a_1, a_2, a_3, \dots$$

of the operator  $A$ .

Next, the probabilities of getting those values are according to quantum mechanics the square magnitudes of the coefficients when the wave function is written in terms of the eigenfunctions of  $A$ . In other words, if  $\alpha_1, \alpha_2, \alpha_3, \dots$  are the eigenfunctions of operator  $A$ , and the wave function is

$$\Psi = c_1\alpha_1 + c_2\alpha_2 + c_3\alpha_3 + \dots$$

then  $|c_1|^2$  is the probability of value  $a_1$ ,  $|c_2|^2$  the probability of value  $a_2$ , etcetera.

The expectation value is written as  $\langle a \rangle$ , or as  $\langle A \rangle$ , whatever is more appealing. Like for the die, it is found as the sum of the probability of each value times the value:

$$\langle a \rangle = |c_1|^2 a_1 + |c_2|^2 a_2 + |c_3|^2 a_3 + \dots$$

Of course, the eigenfunctions might be numbered using multiple indices; that does not really make a difference. For example, the eigenfunctions  $\psi_{nlm}$  of the hydrogen atom are numbered with three indices. In that case, if the wave function of the hydrogen atom is

$$\Psi = c_{100}\psi_{100} + c_{200}\psi_{200} + c_{210}\psi_{210} + c_{211}\psi_{211} + c_{21-1}\psi_{21-1} + c_{300}\psi_{300} + c_{310}\psi_{310} + \dots$$

then the expectation value for energy will be, noting that  $E_1 = -13.6$  eV,  $E_2 = -3.4$  eV, ...:

$$\langle E \rangle = -|c_{100}|^2 13.6 \text{ eV} - |c_{200}|^2 3.4 \text{ eV} - |c_{210}|^2 3.4 \text{ eV} - |c_{211}|^2 3.4 \text{ eV} - \dots$$

Also, the expectation value of the square angular momentum will be, recalling that its eigenvalues are  $l(l+1)\hbar^2$ ,

$$\langle L^2 \rangle = |c_{100}|^2 0 + |c_{200}|^2 0 + |c_{210}|^2 2\hbar^2 + |c_{211}|^2 2\hbar^2 + |c_{21-1}|^2 2\hbar^2 + |c_{300}|^2 0 + |c_{310}|^2 2\hbar^2 + \dots$$

Also, the expectation value of the  $z$ -component of angular momentum will be, recalling that its eigenvalues are  $m\hbar$ ,

$$\langle L_z \rangle = |c_{100}|^2 0 + |c_{200}|^2 0 + |c_{210}|^2 0 + |c_{211}|^2 \hbar - |c_{21-1}|^2 \hbar + |c_{300}|^2 0 + |c_{310}|^2 0 + \dots$$

### Key Points

- ◊ The expectation value of a physical quantity is found by summing its eigenvalues times the probability of measuring that eigenvalue.
- ◊ To find the probabilities of the eigenvalues, the wave function  $\Psi$  can be written in terms of the eigenfunctions of the physical quantity. The probabilities will be the square magnitudes of the coefficients of the eigenfunctions.

### 3.3.2 Review Questions

- 1** The  $2p_x$  pointer state of the hydrogen atom was defined as

$$\frac{1}{\sqrt{2}} (-\psi_{211} + \psi_{21-1}).$$

What are the expectation values of energy, square angular momentum, and  $z$ -angular momentum for this state?

- 2** Continuing the previous question, what are the standard deviations in energy, square angular momentum, and  $z$ -angular momentum?

### 3.3.3 Simplified expressions

The procedure described in the previous section to find the expectation value of a quantity is unwieldy: it requires that first the eigenfunctions of the quantity are found, and next that the wave function is written in terms of those eigenfunctions. There is a quicker way.

Assume that we want to find the expectation value,  $\langle a \rangle$  or  $\langle A \rangle$ , of some quantity  $a$  with associated operator  $A$ . The simpler way to do it is as an inner product:

$$\boxed{\langle A \rangle = \langle \Psi | A | \Psi \rangle.} \quad (3.26)$$

(Recall that  $\langle \Psi | A | \Psi \rangle$  is just the inner product  $\langle \Psi | A \Psi \rangle$ ; the additional separating bar is often visually convenient, though.) This formula for the expectation value is easily remembered as

“leaving out  $\Psi$ ” from the inner product bracket. The reason that  $\langle \Psi | A | \Psi \rangle$  works for getting the expectation value is given in note {13}.

The simplified expression for the expectation value can also be used to find the standard deviation,  $\sigma_A$  or  $\sigma_a$ :

$$\boxed{\sigma_A = \sqrt{\langle (A - \langle A \rangle)^2 \rangle}} \quad (3.27)$$

where  $\langle (A - \langle A \rangle)^2 \rangle$  is again the inner product  $\langle \Psi | (A - \langle A \rangle)^2 | \Psi \rangle$ .

### Key Points

- ◊ The expectation value of a quantity  $a$  with operator  $A$  can be found as  $\langle A \rangle = \langle \Psi | A | \Psi \rangle$ .
- ◊ Similarly, the standard deviation can be found as  $\sigma_A = \sqrt{\langle (A - \langle A \rangle)^2 \rangle}$ .

### 3.3.3 Review Questions

- 1** The  $2p_x$  pointer state of the hydrogen atom was defined as

$$\frac{1}{\sqrt{2}} (-\psi_{211} + \psi_{21-1}).$$

where  $\psi_{211}$  and  $\psi_{21-1}$  are eigenfunctions of the total energy Hamiltonian  $H$  with eigenvalue  $E_2$  and of square angular momentum  $\hat{L}^2$  with eigenvalue  $2\hbar^2$ , while  $\psi_{211}$  is an eigenfunction of  $z$ -angular momentum  $\hat{L}_z$  with eigenvalue  $\hbar$ , while  $\psi_{21-1}$  is one with eigenvalue  $-\hbar$ . Evaluate the expectation values of energy, square angular momentum, and  $z$ -angular momentum in the  $2p_x$  state using inner products. (Of course, since  $2p_x$  is already written out in terms of the eigenfunctions, there is no simplification in this case.)

- 2** Continuing the previous question, evaluate the standard deviations in energy, square angular momentum, and  $z$ -angular momentum in the  $2p_x$  state using inner products.

### 3.3.4 Some examples

This section gives some examples of expectation values and standard deviations for known wave functions.

Let us first look at the expectation value of the energy of the hydrogen atom in its ground state  $\psi_{100}$ . The ground state is an energy eigenfunction with the lowest possible energy level  $E_1 = -13.6$  eV as eigenvalue. So, according to the orthodox interpretation, energy measurements of the ground state can only return the value  $E_1$ , with 100% certainty.

Clearly, if all measurements return the value  $E_1$ , then the average value must be that value too. So the expectation value  $\langle E \rangle$  should be  $E_1$ . In addition, the measurements will never deviate from the value  $E_1$ , so the standard deviation  $\sigma_E$  should be zero.

Let us check those conclusions using the simplified expressions for expectation values and standard deviations from the previous subsection. The expectation value can be found as:

$$\langle E \rangle = \langle H \rangle = \langle \Psi | H | \Psi \rangle$$

In the ground state

$$\Psi = c_{100} \psi_{100}$$

where  $c_{100}$  is a constant of magnitude one, and  $\psi_{100}$  is the ground state eigenfunction of the Hamiltonian  $H$  with the lowest eigenvalue  $E_1$ . Substituting this  $\Psi$ , the expectation value of the energy becomes

$$\langle E \rangle = \langle c_{100} \psi_{100} | H c_{100} \psi_{100} \rangle = c_{100}^* c_{100} \langle \psi_{100} | E_1 \psi_{100} \rangle = c_{100}^* c_{100} E_1 \langle \psi_{100} | \psi_{100} \rangle$$

since  $H\psi_{100} = E_1\psi_{100}$  by the definition of eigenfunction. Note that constants come out of the inner product bra as their complex conjugate, but unchanged out of the ket. The final expression shows that  $\langle E \rangle = E_1$  as it should, since  $c_{100}$  has magnitude one, while  $\langle \psi_{100} | \psi_{100} \rangle = 1$  because proper eigenfunctions are normalized to one. So the expectation value checks out OK.

The standard deviation

$$\sigma_E = \sqrt{\langle (H - \langle E \rangle)^2 \rangle}$$

checks out OK too:

$$\sigma_E = \sqrt{\langle \psi_{100} | (H - E_1)^2 \psi_{100} \rangle}$$

and since  $H\psi_{100} = E_1\psi_{100}$ , we have that  $(H - E_1)\psi_{100}$  is zero, so  $\sigma_E$  is zero as it should be.

In general,

*if the wave function is an eigenfunction of the measured variable, the expectation value will be the eigenvalue, and the standard deviation will be zero.*

To get uncertainty, in other words, a nonzero standard deviation, the wave function should not be an eigenfunction of the quantity being measured.

For example, the ground state of the hydrogen atom is an energy eigenfunction, but not an eigenfunction of the position operators. So, let us examine what we get for the expectation value and standard deviation of the position of the electron.

The expectation value for  $x$  is

$$\langle x \rangle = \langle \psi_{100} | \hat{x} \psi_{100} \rangle = \int \int \int x |\psi_{100}|^2 dx dy dz$$

This integral is zero. The reason is that  $|\psi_{100}|^2$ , shown as grey scale in figure 3.3, is symmetric around  $x = 0$ ; it has the same value at a negative value of  $x$  as at the corresponding positive value. Since the factor  $x$  in the integrand changes sign, integration values at negative  $x$  cancel out against those at positive  $x$ . So  $\langle x \rangle = 0$ .

The position coordinates  $y$  and  $z$  go the same way, and it follows that the expectation value of position is at  $(x, y, z) = (0, 0, 0)$ ; the expectation position of the electron is in nucleus.

In fact, all basic energy eigenfunctions  $\psi_{nlm}$  of the hydrogen atom, like figures 3.3, 3.4, 3.5, 3.6, as well as the combination states  $2p_x$  and  $2p_y$  of figure 3.7, have a symmetric probability distribution, and all have the expectation value of position in the nucleus. (For the hybrid states discussed later, that is no longer true.)

But don't really expect to ever find the electron in the negligible small nucleus! You will find it at locations that are on average one standard deviation away from it. For example, in the ground state

$$\sigma_x = \sqrt{\langle (x - \langle x \rangle)^2 \rangle} = \sqrt{\langle x^2 \rangle} = \sqrt{\int \int \int x^2 |\psi_{100}(x, y, z)|^2 dx dy dz}$$

which is positive since the integrand is everywhere positive. So, the results of  $x$ -position measurements are uncertain, even though they average out to the nominal position  $x = 0$ . The negative experimental results for  $x$  average away against the positive ones. The same is true in the  $y$ - and  $z$ -directions. Thus the expectation position becomes the nucleus even though the electron will really never be found there.

If you actually do the integral above, (it is not difficult in spherical coordinates,) you find that the standard deviation in  $x$  equals the Bohr radius. So on average, the electron will be found at an  $x$ -distance equal to the Bohr radius away from the nucleus. Similar deviations will occur in the  $y$  and  $z$  directions.

The expectation value of linear momentum in the ground state can be found from the linear momentum operator  $\hat{p}_x = \hbar \partial / i \partial x$ :

$$\langle p_x \rangle = \langle \psi_{100} | \hat{p}_x \psi_{100} \rangle = \int \int \int \psi_{100} \frac{\hbar}{i} \frac{\partial \psi_{100}}{\partial x} dx dy dz = \frac{\hbar}{i} \int \int \int \frac{\partial^2 \psi_{100}^2}{\partial x^2} dx dy dz$$

This is again zero, since differentiation turns a symmetric function into an antisymmetric one, one which changes sign between negative and corresponding positive positions. Alternatively, just perform integration with respect to  $x$ , noting that the wave function is zero at infinity.

More generally, the expectation value for linear momentum is zero for all the energy eigenfunctions; that is a consequence of Ehrenfest's theorem covered in chapter 6.1. The standard deviations are again nonzero, so that linear momentum is uncertain like position is.

All these observations carry over in the same way to the eigenfunctions  $\psi_{n_x n_y n_z}$  of the harmonic

oscillator. They too all have the expectation values of position at the origin, in other words in the nucleus, and the expectation linear momenta equal to zero.

If combinations of energy eigenfunctions are considered, things change, though. Such combinations may have nontrivial expectation positions and linear momenta. A discussion will have to wait until chapter 6.

### Key Points

- ◊ Examples of certain and uncertain quantities were given for example wave functions.
- ◊ A quantity is certain when the wave function is an eigenfunction of that quantity.

## 3.4 The Commutator

As the previous section discussed, the standard deviation  $\sigma$  is a measure of the uncertainty of a property of a quantum system. The larger the standard deviation, the farther typical measurements stray from the expected average value. Quantum mechanics often requires a minimum amount of uncertainty when more than one quantity is involved, like position and linear momentum in Heisenberg's uncertainty principle. In general, this amount of uncertainty is related to an important mathematical object called the “commutator”, to be discussed in this section.

### 3.4.1 Commuting operators

First, note that in many cases there is no fundamental prohibition against more than one quantity having a definite value at the same time. For example, if the electron of the hydrogen atom is in a  $\psi_{nlm}$  eigenstate, its total energy, square angular momentum, and  $z$ -component of angular momentum all have precise values at the same time.

More generally, two different quantities with operators  $A$  and  $B$  have precise values if the wave function is an eigenfunction of both  $A$  and  $B$ . So, the question whether two quantities can be certain at the same time is really whether their operators  $A$  and  $B$  have common eigenfunctions. And it turns out that the answer has to do with whether these operators “commute”, in other words, on whether their order can be reversed as in  $AB = BA$ .

It turns out that, {14}:

*iff two Hermitian operators commute, there is a complete set of eigenfunctions that is common to them both.*

For example, the operators  $H_x$  and  $H_y$  of the harmonic oscillator of chapter 2.7.2 commute:

$$\begin{aligned} H_x H_y \Psi &= \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} cx^2 \right] \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + \frac{1}{2} cy^2 \right] \Psi \\ &= \left( \frac{\hbar^2}{2m} \right)^2 \frac{\partial^4 \Psi}{\partial x^2 \partial y^2} - \frac{\hbar^2}{2m} \frac{\partial^2 \frac{1}{2} cy^2 \Psi}{\partial x^2} - \frac{1}{2} cx^2 \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial y^2} + \frac{1}{2} cx^2 \frac{1}{2} cy^2 \Psi \\ &= H_y H_x \Psi \end{aligned}$$

This is true since it makes no difference whether you differentiate  $\Psi$  first with respect to  $x$  and then with respect to  $y$  or vice versa, and since the  $\frac{1}{2}cy^2$  can be pulled in front of the  $x$ -differentiations and the  $\frac{1}{2}cx^2$  can be pushed inside the  $y$ -differentiations, and since multiplications can always be done in any order.

The same way,  $H_z$  commutes with  $H_x$  and  $H_y$ , and that means that  $H$  commutes with them all, since  $H$  is just their sum. So, these four operators should have a common set of eigenfunctions, and they do: it are the eigenfunctions  $\psi_{n_x n_y n_z}$  derived in chapter 2.7.2.

Similarly, for the hydrogen atom, the total energy Hamiltonian  $H$ , the square angular momentum operator  $\hat{L}^2$  and the  $z$ -component of angular momentum  $\hat{L}_z$  all commute, and they have the common set of eigenfunctions  $\psi_{nlm}$ .

Note that such eigenfunctions are not necessarily the only game in town. As a counter-example, for the hydrogen atom  $H$ ,  $\hat{L}^2$ , and the  $x$ -component of angular momentum  $\hat{L}_x$  also all commute, and they too have a common set of eigenfunctions. But that will *not* be the  $\psi_{nlm}$ , since  $\hat{L}_x$  and  $\hat{L}_z$  do not commute. (It will however be the  $\psi_{nlm}$  after you rotate them all 90 degrees around the  $y$ -axis.) It would certainly be simpler mathematically if each operator had just one unique set of eigenfunctions, but nature does not cooperate.

### Key Points

- ◊ Operators commute if you can change their order, as in  $AB = BA$ .
- ◊ For commuting operators, a common set of eigenfunctions exists.
- ◊ For those eigenfunctions, the physical quantities corresponding to the commuting operators all have precise values at the same time.

#### 3.4.1 Review Questions

1 The pointer state

$$2p_x = \frac{1}{\sqrt{2}} (-\psi_{211} + \psi_{21-1}).$$

is one of the eigenstates that  $H$ ,  $\hat{L}^2$ , and  $\hat{L}_x$  have in common. Check that it is not an eigenstate that  $H$ ,  $\hat{L}^2$ , and  $\hat{L}_z$  have in common.

### 3.4.2 Noncommuting operators and their commutator

Two quantities with operators that do not commute cannot in general have definite values at the same time. If one has a value, the other is in general uncertain.

The qualification “in general” is needed because there may be exceptions. The angular momentum operators do not commute, but it is still possible for the angular momentum to be zero in all three directions. But as soon as the angular momentum in any direction is nonzero, only one component of angular momentum can have a definite value.

A measure for the amount to which two operators  $A$  and  $B$  do not commute is the difference between  $AB$  and  $BA$ ; this difference is called their “commutator”  $[A, B]$ :

$$[A, B] \equiv AB - BA \quad (3.28)$$

A nonzero commutator  $[A, B]$  demands a minimum amount of uncertainty in the corresponding quantities  $a$  and  $b$ . It can be shown, {15}, that the uncertainties, or standard deviations,  $\sigma_a$  in  $a$  and  $\sigma_b$  in  $b$  are at least so large that:

$$\sigma_a \sigma_b \geq \frac{1}{2} | \langle [A, B] \rangle | \quad (3.29)$$

This equation is called the “generalized uncertainty relationship”.

#### Key Points

- ◊ The commutator of two operators  $A$  and  $B$  equals  $AB - BA$  and is written as  $[A, B]$ .
- ◊ The product of the uncertainties in two quantities is at least one half the magnitude of the expectation value of their commutator.

### 3.4.3 The Heisenberg uncertainty relationship

In this section, we will work out the uncertainty relationship of the previous subsection for the position and linear momentum in an arbitrary direction. The result will be a precise mathematical statement of the Heisenberg uncertainty principle.

To be specific, we will take the arbitrary direction as the  $x$ -axis, so the position operator will be  $\hat{x}$ , and the linear momentum operator  $\hat{p}_x = \hbar \partial / i\partial x$ . These two operators do not commute,  $\hat{p}_x \hat{x} \Psi$  is simply not the same as  $\hat{x} \hat{p}_x \Psi$ :  $\hat{p}_x \hat{x} \Psi$  means multiply function  $\Psi$  by  $x$  to get the product function  $x\Psi$  and then apply  $\hat{p}_x$  on that, while  $\hat{x} \hat{p}_x \Psi$  means apply  $\hat{p}_x$  on  $\Psi$  and then multiply the resulting function by  $x$ . The difference is:

$$\hat{p}_x \hat{x} \Psi = \frac{\hbar}{i} \frac{\partial x \Psi}{\partial x} = \frac{\hbar}{i} \Psi + \frac{\hbar}{i} x \frac{\partial \Psi}{\partial x} = -i\hbar \Psi + \hat{x} \hat{p}_x \Psi$$

Comparing start and end shows that the difference between  $\hat{x}\hat{p}_x$  and  $\hat{p}_x\hat{x}$  is not zero, but  $i\hbar$ . By definition, this difference is their commutator:

$$[\hat{x}, \hat{p}_x] = i\hbar \quad (3.30)$$

This important result is called the “canonical commutation relation.” The commutator of position and linear momentum in the same direction is the nonzero constant  $i\hbar$ .

Because the commutator is nonzero, there must be nonzero uncertainty involved. Indeed, the generalized uncertainty relationship of the previous subsection becomes in this case:

$$\sigma_x \sigma_{p_x} \geq \frac{1}{2}\hbar \quad (3.31)$$

This is the uncertainty relationship as first formulated by Heisenberg.

It implies that when the uncertainty in position  $\sigma_x$  is narrowed down to zero, the uncertainty in momentum  $\sigma_{p_x}$  must become infinite to keep their product nonzero, and vice versa. More generally, you can narrow down the position of a particle and you can narrow down its momentum. But you can never reduce the product of the uncertainties  $\sigma_x$  and  $\sigma_{p_x}$  below  $\frac{1}{2}\hbar$ , whatever you do.

It should be noted that the uncertainty relationship is often written as  $\Delta p \Delta x \geq \frac{1}{2}\hbar$  or even as  $\Delta p \Delta x \approx \hbar$  where  $\Delta p$  and  $\Delta x$  are taken to be vaguely described “uncertainties” in momentum and position, rather than rigorously defined standard deviations. And people write a corresponding uncertainty relationship for time,  $\Delta E \Delta t \geq \frac{1}{2}\hbar$ , because relativity suggests that we should treat time just like space. But note that unlike the linear momentum operator, the Hamiltonian is not at all universal. So, you might guess that the definition of the “uncertainty”  $\Delta t$  in time would not be universal either, and you would be right. One common definition will be given later in chapter 6.1.4.

### Key Points

- ◊ The canonical commutator  $[\hat{x}, \hat{p}_x]$  equals  $i\hbar$ .
- ◊ If either the uncertainty in position in a given direction or the uncertainty in linear momentum in that direction is narrowed down to zero, the other uncertainty blows up.
- ◊ The product of the two uncertainties is at least the constant  $\frac{1}{2}\hbar$ .

#### 3.4.3 Review Questions

- 1 This sounds serious! If I am driving my car, the police requires me to know my speed (linear momentum). Also, I would like to know where I am. But neither is possible according to quantum mechanics.

### 3.4.4 Commutator reference [Reference]

It is a fact of life in quantum mechanics that commutators pop up all over the place. Not just in uncertainty relations, but also in the time evolution of average quantities, and in angular momentum. This section can make your life easier dealing with them. Browse through it to see what is there. Then come back when you need it.

Recall the definition of the commutator  $[A, B]$  of any two operators  $A$  and  $B$ :

$$[A, B] = AB - BA \quad (3.32)$$

By this very definition, the commutator is zero for any two operators  $A_1$  and  $A_2$  that commute, (whose order can be interchanged):

$$[A_1, A_2] = 0 \quad \text{if } A_1 \text{ and } A_2 \text{ commute; } A_1 A_2 = A_2 A_1. \quad (3.33)$$

If operators all commute, all their products commute too:

$$[A_1 A_2 \dots A_k, A_n A_{n+1} \dots A_m] = 0 \quad \text{if } A_1, A_2, \dots, A_k, A_n, A_{n+1}, \dots, A_m \text{ all commute.} \quad (3.34)$$

Everything commutes with itself, of course:

$$[A, A] = 0, \quad (3.35)$$

and everything commutes with a numerical constant; if  $A$  is an operator and  $a$  is some number, then:

$$[A, a] = [a, A] = 0. \quad (3.36)$$

The commutator is “antisymmetric”; or in simpler words, if you interchange the sides; it will change the sign {16}:

$$[B, A] = -[A, B]. \quad (3.37)$$

For the rest however, linear combinations multiply out just like you would expect:

$$[aA + bB, cC + dD] = ac[A, C] + ad[A, D] + bc[B, C] + bd[B, D], \quad (3.38)$$

(in which it is assumed that  $A$ ,  $B$ ,  $C$ , and  $D$  are operators, and  $a$ ,  $b$ ,  $c$ , and  $d$  numerical constants.)

To deal with commutators that involve products of operators, the rule to remember is: “the first factor comes out at the front of the commutator, the second at the back”. More precisely:

$$\underbrace{[AB, \dots]}_{\leftarrow \rightarrow} = A[B, \dots] + [A, \dots]B, \quad \underbrace{[\dots, AB]}_{\leftarrow \rightarrow} = A[\dots, B] + [\dots, A]B. \quad (3.39)$$

So, if  $A$  or  $B$  commutes with the other side of the operator, it can simply be taken out at its side; (the second commutator will be zero.) For example,

$$[A_1 B, A_2] = A_1 [B, A_2], \quad [B A_1, A_2] = [B, A_2] A_1$$

if  $A_1$  and  $A_2$  commute.

Turning now from the general to the specific, position operators all mutually commute:

$$[\hat{x}, \hat{y}] = [\hat{y}, \hat{z}] = [\hat{z}, \hat{x}] = 0 \quad (3.40)$$

as do position-dependent operators such as a potential energy  $V(x, y, z)$ :

$$[\hat{x}, V(x, y, z)] = [\hat{y}, V(x, y, z)] = [\hat{z}, V(x, y, z)] = 0 \quad (3.41)$$

This illustrates that if a set of operators all commute, then all combinations of those operators commute too.

The linear momentum operators all mutually commute:

$$[\hat{p}_x, \hat{p}_y] = [\hat{p}_y, \hat{p}_z] = [\hat{p}_z, \hat{p}_x] = 0 \quad (3.42)$$

However, position operators and linear momentum operators in the same direction do *not* commute; instead:

$$[\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = [\hat{z}, \hat{p}_z] = i\hbar \quad (3.43)$$

As seen in the previous subsection, this lack of commutation causes the Heisenberg uncertainty principle. Position and linear momentum operators in different directions do commute:

$$[\hat{x}, \hat{p}_y] = [\hat{x}, \hat{p}_z] = [\hat{y}, \hat{p}_z] = [\hat{y}, \hat{p}_x] = [\hat{z}, \hat{p}_x] = [\hat{z}, \hat{p}_y] = 0 \quad (3.44)$$

A generalization that is frequently very helpful is:

$$[f, \hat{p}_x] = i\hbar \frac{\partial f}{\partial x} \quad [f, \hat{p}_y] = i\hbar \frac{\partial f}{\partial y} \quad [f, \hat{p}_z] = i\hbar \frac{\partial f}{\partial z} \quad (3.45)$$

where  $f$  is any function of  $x$ ,  $y$ , and  $z$ .

Unlike linear momentum operators, angular momentum operators do *not* mutually commute:

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \quad [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x \quad [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y \quad (3.46)$$

However, they do all commute with the square angular momentum operator:

$$[\hat{L}_x, \hat{L}^2] = [\hat{L}_y, \hat{L}^2] = [\hat{L}_z, \hat{L}^2] = 0 \quad \text{where } \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \quad (3.47)$$

### Key Points

- ◊ Rules for evaluating commutators were given.
- ◊ Return to this subsection if you need to figure out some commutator or the other.

## 3.5 The Hydrogen Molecular Ion

The hydrogen atom studied earlier is where full theoretical analysis stops. Larger systems are just too difficult to solve analytically. Yet, it is often quite possible to understand the solution of such systems using approximate arguments. As an example, this section considers the  $\text{H}_2^+$ -ion. This ion consists of two protons and a single electron circling them. We will show that a chemical bond forms that holds the ion together. The bond is a “covalent” one, in which the protons share the electron.

The general approach will be to compute the energy of the ion, and to show that the energy is less when the protons are sharing the electron as a molecule than when they are far apart. This must mean that the molecule is stable: energy must be expended to take the protons apart.

The approximate technique to be used to find the state of lowest energy is a simple example of what is called a “variational method”.

### 3.5.1 The Hamiltonian

We first need the Hamiltonian. Since the protons are so much heavier than the electron, to good approximation they can be considered fixed points in the energy computation. This is called the “Born-Oppenheimer approximation”. In this approximation, only the Hamiltonian of the electron is needed. It makes things a lot simpler, which is why the Born-Oppenheimer approximation is a common assumption in applications of quantum mechanics.

Compared to the Hamiltonian of the hydrogen atom of section 3.2.1, there are now two terms to the potential energy, the electron experiencing attraction to both protons:

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_L} - \frac{e^2}{4\pi\epsilon_0 r_R} \quad (3.48)$$

where  $r_L$  and  $r_R$  are the distances from the electron to the left and right protons,

$$r_L \equiv |\vec{r} - \vec{r}_{Lp}| \quad r_R \equiv |\vec{r} - \vec{r}_{Rp}| \quad (3.49)$$

with  $\vec{r}_{Lp}$  the position of the left proton and  $\vec{r}_{Rp}$  that of the right one.

The hydrogen ion in the Born-Oppenheimer approximation can be solved analytically using “prolate spheroidal coordinates.” However, we will use approximations here. For one thing, you learn more about the physics that way.

- ◊ In the Born-Oppenheimer approximation, the electronic structure is computed assuming that the nuclei are at fixed positions.
  - ◊ The Hamiltonian in the Born-Oppenheimer approximation has been found. It is above.
- 

### 3.5.2 Energy when fully dissociated

The fully dissociated state is when the protons are very far apart and there is no coherent molecule, as in figure 3.8. The best the electron can do under those circumstances is to combine with either proton, let's assume the left one, and form a hydrogen atom in the ground state of lowest energy. In that case the right proton will be alone. According to the solution for the



Figure 3.8: Hydrogen atom plus free proton far apart.

hydrogen atom, the electron loses 13.6 eV of energy by going in the ground state around the left proton. Of course, it would lose the same energy going into the ground state around the right proton, but for now, assume that it is around the left proton.

The wave function describing this state is just the ground state  $\psi_{100}$  derived for the hydrogen atom, equation (3.23), but the distance should be measured from the position of the left proton instead of from the origin:

$$\psi_{100}(|\vec{r} - \vec{r}_{Lp}|)$$

To shorten the notations, we will denote this wave function by  $\psi_L$ :

$$\psi_L(\vec{r}) \equiv \psi_{100}(|\vec{r} - \vec{r}_{Lp}|) \quad (3.50)$$

Similarly the wave function that would describe the electron as being in the ground state around the right proton will be denoted as  $\psi_R$ , with

$$\psi_R(\vec{r}) \equiv \psi_{100}(|\vec{r} - \vec{r}_{Rp}|) \quad (3.51)$$

---

#### Key Points

- ◊ When the protons are far apart, there are two lowest energy states,  $\psi_L$  and  $\psi_R$ , in which the electron is in the ground state around the left, respectively right, proton. In either case we have a hydrogen atom plus a free proton.
-

### 3.5.3 Energy when closer together

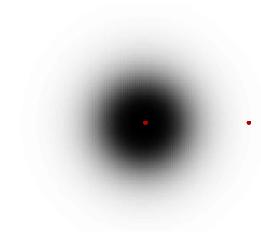


Figure 3.9: Hydrogen atom plus free proton closer together.

When the protons get a bit closer to each other, but still well apart, the distance  $r_R$  between the electron orbiting the left proton and the right proton decreases, as sketched in figure 3.9. The potential that the electron sees is now not just that of the left proton; the distance  $r_R$  to the right proton is no longer so large that the  $-e^2/4\pi\epsilon_0 r_R$  potential of subsection 3.5.1 can be completely neglected.

However, assuming that the right proton stays sufficiently clear of the electron wave function,  $r_R$  can still be averaged out as being the distance  $d$  between the two protons rather than between electron and right proton. Within that approximation, it simply adds the constant  $-e^2/4\pi\epsilon_0 d$  to the Hamiltonian of the electron. And adding a constant to a Hamiltonian does not change the eigenfunction; it only changes the eigenvalue, the energy, by that constant. So the ground state  $\psi_L$  of the left proton remains a good approximation to the lowest energy wave function.

Moreover, the decrease in energy of the electron is balanced by an increase in energy of the protons by their mutual repulsion, so the total energy of the ion remains the same. In other words, the right proton is to first approximation neither attracted nor repelled by the neutral hydrogen atom on the left. To second approximation the right proton does change the wave function of the electron a bit, resulting in some attraction, but we will ignore this effect.

So far, it has been assumed that the electron is circling the left proton. But the case that the electron is circling the right proton is of course physically equivalent. In particular the energy must be exactly the same by symmetry.

#### Key Points

- ◊ To first approximation, there is no attraction between the free proton and the neutral hydrogen atom, even somewhat closer together.

### 3.5.4 States that share the electron

Since the wave function  $\psi_L$  that describes the electron as being around the left proton, and  $\psi_R$  that describes it as being around the right one have the same energy, any linear combination of them,

$$\psi = a\psi_L + b\psi_R \quad (3.52)$$

is also an eigenfunction, with the same energy. In such combinations, the electron is shared by the protons, in ways that depend on the chosen values of  $a$  and  $b$ .

Note that the constants  $a$  and  $b$  are not independent: the wave function should be normalized,  $\langle \psi | \psi \rangle = 1$ . Since  $\psi_L$  and  $\psi_R$  are already normalized, and assuming that  $a$  and  $b$  are real, this works out to

$$a^2 + b^2 + 2ab\langle \psi_L | \psi_R \rangle = 1 \quad (3.53)$$

As a consequence, only the relative magnitude of the coefficients, say  $b/a$ , can be chosen freely.

A particularly interesting case is the “antisymmetric” one,  $b = -a$ . As figure 3.10 shows, in this state there is zero probability of finding the electron at the symmetry plane midway in between the protons. The reason is that  $\psi_L$  and  $\psi_R$  are equal at the symmetry plane, making

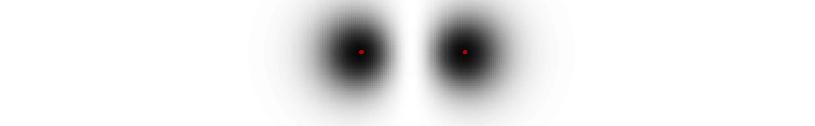


Figure 3.10: The electron being anti-symmetrically shared.

their difference zero.

This is actually a quite weird result. We combine two states, in both of which the electron has some probability of being at the symmetry plane, and in the combination the electron has *zero* probability of being there. The probability of finding the electron at any position, including the symmetry plane, in the first state is given by  $|\psi_L|^2$ . Similarly, the probability of finding the electron in the second state is given by  $|\psi_R|^2$ . But for the combined state nature does not do the logical thing of adding the two probabilities together to come up with  $\frac{1}{2}|\psi_L|^2 + \frac{1}{2}|\psi_R|^2$ .

Instead of adding physically *observable* probabilities, nature squares the *unobservable* wave function  $a\psi_L - a\psi_R$  to find the new probability distribution. The squaring adds a cross term,  $-2a^2\psi_L\psi_R$ , that simply adding probabilities does not have. This term has the physical effect of preventing the electron to be at the symmetry plane, but it does not have a normal physical explanation. There is no force repelling the electrons from the symmetry plane or anything like that. Yet it looks as if there is one in this state.

The most important combination of  $\psi_L$  and  $\psi_R$  is the “symmetric” one,  $b = a$ . In this case, there is increased probability for the electron to be at the symmetry plane, as shown in figure 3.11.

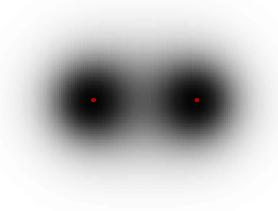


Figure 3.11: The electron being symmetrically shared.

A state in which the electron is shared is truly a case of the electron being in two different places at the same time. For if instead of sharing the electron, each proton would be given its own half an electron, the expression for the Bohr radius,  $a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$ , shows that the eigenfunctions  $\psi_L$  and  $\psi_R$  would have to blow up in radius by a factor four. That is simply not what happens. We get the physics of a complete electron being present around each proton with 50% probability, not the physics of half an electron being present for sure.

### Key Points

- ◊ This subsection brought home the physical weirdness arising from the mathematics of the unobservable wave function.
- ◊ In particular, within the approximations made, there exist states that all have the same minimal energy, but whose physical properties are dramatically different.
- ◊ The protons may “share the electron.”. In such states there is equal probability of finding the electron around either proton.
- ◊ Even if the protons share the electron equally as far as probability distribution is concerned, different physical states are still possible. It depends on differences in the sign of the wave function between the protons.
- ◊ In the symmetric case that the wave functions around the protons have the same sign, there is increased probability of the electron being found in between the protons. In the antisymmetric case of opposite sign, there is decreased probability of the electron being found in between the protons.

### 3.5.5 Comparative energies of the states

The previous two subsections described states of the hydrogen molecular ion in which the electron is around a single proton, as well as states in which it is shared between protons.

To the approximations made, all these states have the same energy. Yet, if the energy is more accurately examined, it turns out that there are differences when the protons get closer together. The symmetric state has the least energy, the antisymmetric state the highest, and the states where the electron is around a single proton have something in between.

It is not that easy to see physically why the symmetric state has the lowest energy. An argument can be made that in the symmetric case, the electron has increased probability of being in between the protons, where it is most effective in pulling them together. However, actually the potential energy of the symmetric state is higher than for the other states: putting the electron midway in between the two protons means having to pull it away from one of them.

Another argument that is sometimes made is that in the symmetric case, the electron is somewhat less constrained in position. According to the Heisenberg uncertainty relationship, that would allow it to have less variation in momentum, hence less kinetic energy. While the symmetric state does indeed have less kinetic energy, this is almost totally achieved at the cost of a corresponding increase in potential energy, rather than due to a larger area to move in at the same potential energy. And the kinetic energy is not really directly related to available area in any case.

### Key Points

- ◊ The energies of the discussed states are not the same when examined more closely.
- ◊ The symmetric state has the lowest energy, the antisymmetric one the highest.

#### 3.5.6 Variational approximation of the ground state

The objective of this subsection is to get an approximation to the ground state of the hydrogen molecular ion using the approximate combination wave functions  $\psi = a\psi_L + b\psi_R$  discussed in the previous subsections.

Since the ground state is the state of lowest energy among *all* wave functions, the best approximation to the ground state using  $a\psi_L + b\psi_R$  is the one with the lowest energy. Even that combination will still have too much energy, but it is the best we can do using only the functions  $\psi_L$  and  $\psi_R$ .

Note that the energy depends on the coefficients  $a$  and  $b$ , (or really just on the ratio  $b/a$  on account of the normalization requirements  $\langle\psi|\psi\rangle = 1$ ), as well as on the distance  $d$  between the protons. We want the combination of these parameters that produces the lowest energy.

This sort of method is called a “variational method” because at the minimum of energy, the

derivatives of the energy must be zero. That in turn means that the energy does not *vary* with infinitesimally small changes in the parameters  $b/a$  and  $d$ .

To briefly summarize the details of the computation, the way to evaluate the energy is as the expectation value of the Hamiltonian,  $\langle\psi|H|\psi\rangle$ :

$$\langle E \rangle = \langle a\psi_L + b\psi_R | H | a\psi_L + b\psi_R \rangle$$

This can be simplified by using the fact that  $\psi_L$  and  $\psi_R$  are eigenfunctions of the single-proton partial Hamiltonians. Also,  $a$  and  $b$  are related by the fact that  $\langle\psi|\psi\rangle = 1$ . The result of doing all the algebra is:

$$\langle E \rangle = E_1 - \frac{e^2}{4\pi\epsilon_0} \left[ \langle \psi_L | r_R^{-1} \psi_L \rangle - \frac{1}{d} + 2ab \langle \psi_L | \psi_R \rangle \left\{ \frac{\langle \psi_L | r_L^{-1} \psi_R \rangle}{\langle \psi_L | \psi_R \rangle} - \langle \psi_L | r_R^{-1} \psi_L \rangle \right\} \right] \quad (3.54)$$

which includes the proton to proton repulsion energy. The inner product integrals in this expression can be done analytically, {17}. The energy  $E_1$  is the  $-13.6$  eV amount of energy when the protons are far apart.

Putting the final result in a computer to see when the energy is lowest, it is found that the minimum energy occurs when  $a = b$ , the symmetric state, and at a separation distance between the protons equal to about  $1.3$  Å. This separation distance is called the “bond length”.

The minimum energy is found to be about  $1.8$  eV *below* the energy of  $-13.6$  eV when the protons are far apart. So it will take at least  $1.8$  eV to take the ground state with the protons at a distance of  $1.3$  Å completely apart into well separated protons. For that reason, the  $1.8$  eV is called the “binding energy”.

### Key Points

- ◊ The best approximation to the ground state using approximate wave functions is the one with the lowest energy. {18}.
- ◊ Making such an approximation is called a variational method.
- ◊ The energy should be evaluated as the expectation value of the Hamiltonian.
- ◊ Using our combinations of  $\psi_L$  and  $\psi_R$  as approximate wave functions, the approximate ground state turns out to be the one in which the electron is symmetrically shared between the protons.

### 3.5.6 Review Questions

- 1 The solution for the hydrogen molecular ion requires elaborate evaluations of inner product integrals and a computer evaluation of the state of lowest energy. Let's try

the variational method out on the much simpler one-dimensional case of a particle stuck inside a pipe, as discussed in chapter 2.6. Take the approximate wave function to be:

$$\psi = ax(\ell - x)$$

Find  $a$  from the normalization requirement that the total probability of finding the particle integrated over all possible positions is one. Then evaluate the energy  $\langle E \rangle$  as  $\langle \psi | H | \psi \rangle$ , where according to chapter 2.6.3, the Hamiltonian is

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

Compare the ground state energy with the exact value,  $E_1 = \hbar^2 \pi^2 / 2m\ell^2$ . (Hints:  $\int_0^\ell x(\ell - x) dx = \ell^3/6$  and  $\int_0^\ell x^2(\ell - x)^2 dx = \ell^5/30$ )

---

### 3.5.7 Comparison with the exact ground state

The variational solution derived in the previous subsection is only a crude approximation of the true ground state of the hydrogen molecular ion. In particular, the assumption that the molecular wave function can be approximated using the individual atom ground states is only valid when the protons are far apart, and is a bad one if they are 1.3 Å apart, as the solution says they are.

Yet, for such a poor wave function, the results are surprisingly good. For one thing, it leaves no doubt that a bound state really exists. The reason is that the true ground state must always have a lower energy than any approximate one. So, the binding energy must be *at least* the 1.8 eV found in the last subsection, though it could be more.

In fact, the experimental binding energy is 2.8 eV, which is indeed more. But the found approximate value is only a third less, pretty good for such a simplistic assumption for the wave function. It is really even better than that, since a fair comparison requires the absolute energies to be compared, rather than just the binding energy; the approximate solution has  $-15.4$  eV, rather than  $-16.4$ . This high accuracy for the energy using only marginal wave functions is one of the advantages of variational methods {19}.

The estimated bond length is not too bad either; experimentally the protons are 1.06 Å apart instead of 1.3 Å. (The analytical solution using spheroidal coordinates mentioned earlier gives 2.79 eV and 1.06 Å, in full agreement with the experimental values.)

The qualitative properties of the wave function are right too. For example, it can be seen that the exact ground state wave function must be real and positive {20}; the approximate wave function is real and positive too.

It can also be seen that the exact ground state must be symmetric around the symmetry

plane midway between the protons, and rotationally symmetric around the line connecting the protons,  $\{21\}$ . The approximate wave function has both those properties too.

Incidentally, the fact that the ground state wave function must be real and positive is a much more solid reason that the protons must share the electron symmetrically than the physical arguments given in subsection 3.5.5, even though it is more mathematical.

---

### Key Points

- ◊ The obtained approximate ground state is pretty good.
  - ◊ The protons really share the electron symmetrically in the ground state.
-

# Chapter 4

## Multiple-Particle Systems

### 4.1 Generalization to Multiple Particles

So far, we have looked at the wave functions for single particles. This section explains how the ideas generalize to more particles.

While a single particle is described by a wave function  $\Psi(\vec{r}; t)$ , a system of two particles, call them 1 and 2, is described by a wave function

$$\Psi(\vec{r}_1, \vec{r}_2; t) \tag{4.1}$$

depending on both particle positions. The value of  $|\Psi(\vec{r}_1, \vec{r}_2; t)|^2 d^3\vec{r}_1 d^3\vec{r}_2$  gives the probability of simultaneously finding particle 1 within a vicinity  $d^3\vec{r}_1$  of  $\vec{r}_1$  and particle 2 within a vicinity  $d^3\vec{r}_2$  of  $\vec{r}_2$ .

The wave function must be normalized to express that the electrons must be somewhere:

$$\langle \Psi | \Psi \rangle_6 = \int \int |\Psi(\vec{r}_1, \vec{r}_2; t)|^2 d^3\vec{r}_1 d^3\vec{r}_2 = 1 \tag{4.2}$$

where the subscript 6 of the inner product is just a reminder that the integration is over all six scalar position coordinates of  $\Psi$ .

The underlying idea of increasing system size is that of “every possible combination:” combine every possible state of particle 1 with every possible state of particle 2. For example, in one dimension, all possible  $x$ -positions of particle 1 geometrically form an  $x_1$ -axis. Similarly all possible  $x$ -positions of particle 2 form an  $x_2$ -axis. If every possible position  $x_1$  is combined with every possible position  $x_2$ , the result is an  $x_1, x_2$ -plane of possible positions of the combined system.

Similarly, in three dimensions the three-dimensional space of positions  $\vec{r}_1$  combines with the

three-dimensional space of positions  $\vec{r}_2$  into a six-dimensional space having all possible combinations of values for  $\vec{r}_1$  with all possible values for  $\vec{r}_2$ .

The increase in the number of dimensions when the system size increases is a major practical problem for quantum mechanics. For example, a *single* arsenic atom has 33 electrons, and each electron has 3 position coordinates. It follows that the wave function is a function of 99 scalar variables. (Not even counting the nucleus, spin, etcetera.) In a brute-force numerical solution of the wave function, maybe it would be enough to store the value of  $\Psi$  at 10 points along each axis, if no very high accuracy is desired. Even then,  $10^{99}$   $\Psi$  values must be stored, requiring maybe  $10^{91}$  Gigabytes of storage. To do a single multiplication on each of those numbers within a few years would require a computer with a speed of  $10^{82}$  Gigaflops. No need to take any of that arsenic to be long dead before an answer is obtained. (Imagine what it would take to compute a microgram of arsenic instead of an atom.) Obviously, more clever numerical procedures are needed.

## 4.2 The Hydrogen Molecule

This section uses similar approximations as for the hydrogen molecular ion of chapter 3.5 to examine the neutral  $H_2$  hydrogen molecule. This molecule has two electrons circling two protons. It is interesting to find that in the ground state, the protons share the two electrons, rather than each being assigned one. This is typical of covalent bonds.

### 4.2.1 The Hamiltonian

Just like for the hydrogen molecular ion earlier, for the neutral molecule the Born-Oppenheimer approximation will be made that the protons are fixed points. In the Hamiltonian for the electrons, following the Newtonian analogy the kinetic and potential energy operators simply add:

$$H = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{1L}} + \frac{1}{r_{1R}} + \frac{1}{r_{2L}} + \frac{1}{r_{2R}} - \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) \quad (4.3)$$

In this expression, the Laplacians of the first two kinetic energy terms are:

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \quad \nabla_2^2 = \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}$$

where  $\vec{r}_1 = (x_1, y_1, z_1)$  and  $\vec{r}_2 = (x_2, y_2, z_2)$  are the positions of electrons 1 and 2. The next four terms in (4.3) are the attractive potentials between the electrons and the protons, with  $r_{1L}$ ,  $r_{2L}$ ,  $r_{1R}$ , and  $r_{2R}$  being the distances between electrons 1 and 2 and the left, respectively right proton. The final term represents the repulsive potential between the two electrons.

### 4.2.2 Initial approximation to the lowest energy state

The first step is to obtain an approximate lowest energy state for the electrons. Following the same approach as in chapter 3.5, it will again be assumed that the protons are relatively far apart. One obvious approximate solution is then that of two neutral atoms, in which electron 1 is around the left proton in its ground state and electron 2 is around the right one.

To formulate the wave function for that, we define again the shorthand notations  $\psi_L$  for the wave function of a single electron that in the ground state around the left proton and  $\psi_R$  for one that is in the ground state around the right hand one:

$$\psi_L(\vec{r}) \equiv \psi_{100}(|\vec{r} - \vec{r}_{Lp}|) \quad \psi_R(\vec{r}) \equiv \psi_{100}(|\vec{r} - \vec{r}_{Rp}|)$$

where  $\psi_{100}$  is the hydrogen atom ground state (3.23).

The wave function that describes that electron 1 is in the ground state around the left proton and electron 2 around the right one will be taken to be the product of the single electron states:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_L(\vec{r}_1)\psi_R(\vec{r}_2)$$

Taking the combined wave function as a product of single electron states is really equivalent to an assumption that the two electrons are independent. Indeed, for the product state, the probability of finding electron 1 at position  $\vec{r}_1$  and electron 2 at  $\vec{r}_2$  is:

$$|\psi_L(\vec{r}_1)|^2 d^3\vec{r}_1 \times |\psi_R(\vec{r}_2)| d^3\vec{r}_2$$

or in words:

$$\begin{aligned} & [\text{probability of finding 1 at } \vec{r}_1 \text{ unaffected by where 2 is}] \\ & \times [\text{probability of finding 2 at } \vec{r}_2 \text{ unaffected by where 1 is}] \end{aligned}$$

Such product probabilities are characteristic of statistically independent quantities. As a simple example, the chances of getting a one in the first throw of a die and a two in the second throw are  $\frac{1}{6} \times \frac{1}{6}$  or 1 in 36.

### 4.2.3 The probability density

Showing the square magnitude of the wave function as grey tones no longer works since it is a function in six-dimensional space. However, at every spatial point  $\vec{r}$ , we can instead show the “probability density”  $n(\vec{r})$ , which is the probability per unit volume of finding *either* electron in a vicinity  $d^3\vec{r}$  of the point. This probability is found as

$$n(\vec{r}) = \int |\psi(\vec{r}, \vec{r}_2)|^3 d^3\vec{r}_2 + \int |\psi(\vec{r}_1, \vec{r})|^3 d^3\vec{r}_1 \quad (4.4)$$

since the first integral gives the probability of finding electron 1 at  $\vec{r}$ , regardless of where electron 2 is, and the second the probability of finding 2 at  $\vec{r}$ , regardless of where 1 is. Since  $d^3\vec{r}$  is vanishingly small, the chances of finding both particles in it at the same time are zero.

The probability density  $n(\vec{r})$  for state  $\psi_L(\vec{r}_1)\psi_R(\vec{r}_2)$  with electron 1 around the left proton and electron 2 around the right one is shown in figure 4.1.

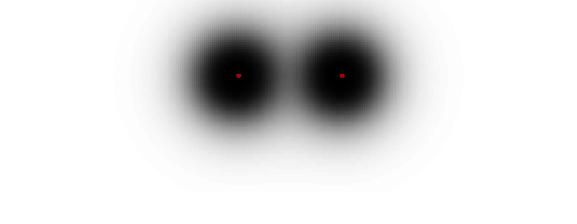


Figure 4.1: State with two neutral atoms.

#### 4.2.4 States that share the electron

In this section, we will examine the states where the protons share the two electrons.

The first thing is to shorten the notations a bit. So, the state  $\psi_L(\vec{r}_1)\psi_R(\vec{r}_2)$  which describes that electron 1 is around the left proton and electron 2 around the right one will be indicated by  $\psi_L\psi_R$ , using the convention that the first factor refers to electron 1 and the second to electron 2. In this convention, the state where electron 1 is around the right proton and electron 2 around the left one is  $\psi_R\psi_L$ . It is of course physically the same thing as  $\psi_L\psi_R$ ; the two electrons are identical.

The “every possible combination” idea of combining every possible state for electron 1 with every possible state for electron 2 would suggest that we also consider the combined states  $\psi_L\psi_L$  and  $\psi_R\psi_R$ , but these states have the electrons around the same proton, and this is not going to be energetically favorable due to the mutual repulsion of the electrons. So they are not relevant to finding the ground state of lowest energy.

States where the electrons are no longer assigned to a particular proton can be found as linear combinations of  $\psi_L\psi_R$  and  $\psi_R\psi_L$ :

$$\psi = a\psi_L\psi_R + b\psi_R\psi_L \quad (4.5)$$

The eigenfunction must be normalized,

$$\langle\psi|\psi\rangle_6 = \int \int |\psi(\vec{r}_1, \vec{r}_2)|^2 d^3\vec{r}_1 d^3\vec{r}_2 = 1 \quad (4.6)$$

Because  $\psi_L$  and  $\psi_R$  are real and normalized, and assuming that  $a$  and  $b$  are real too, this simplifies to:

$$a^2 + b^2 + 2ab\langle\psi_L|\psi_R\rangle^2 = 1 \quad (4.7)$$

The probability density of the combination is:

$$n(\vec{r}) = \psi_L^2 + \psi_R^2 + 2ab\langle\psi_L|\psi_R\rangle \left\{ 2\psi_L\psi_R - \langle\psi_L|\psi_R\rangle(\psi_L^2 + \psi_R^2) \right\} \quad (4.8)$$

The most important combination state is the one with  $b = a$ :

$$\psi(\vec{r}_1, \vec{r}_2) = a [\psi_L(\vec{r}_1)\psi_R(\vec{r}_2) + \psi_R(\vec{r}_1)\psi_L(\vec{r}_2)] \quad (4.9)$$

This state is called “symmetric” with respect to interchanging electron 1 with electron 2: such an interchange does not change this wave function at all. The wave function looks like figure 4.2. It has increased likelihood for electrons to be found in between the protons,

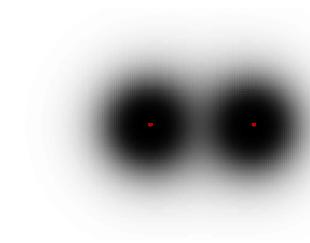


Figure 4.2: Symmetric state

The state with  $b = -a$ ,

$$\psi(\vec{r}_1, \vec{r}_2) = a [\psi_L(\vec{r}_1)\psi_R(\vec{r}_2) - \psi_R(\vec{r}_1)\psi_L(\vec{r}_2)] \quad (4.10)$$

is called “antisymmetric” with respect to interchanging electron 1 with electron 2: it changes the sign of wave function, but leaves it further unchanged. As seen in figure 4.3, the anti-symmetric state has decreased likelihood for electrons to be found in between the protons.

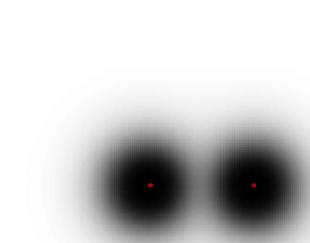


Figure 4.3: Antisymmetric state

### 4.2.5 Variational approximation of the ground state

We now want to find an approximation to the ground state of the hydrogen molecule using the approximate solutions described in the previous subsections.

The details of the analysis will only be briefly summarized. Like for the molecular ion, the best approximation to the ground state is given by the state that has the lowest expectation value of the energy. This expectation value can be evaluated as the inner product  $\langle \psi | H | \psi \rangle_6$ . Note that, for any arbitrary operator  $A(\vec{r})$ ,

$$\begin{aligned} \langle \psi | A(\vec{r}_1) + A(\vec{r}_2) | \psi \rangle_6 &= (\langle \psi_L | A | \psi_L \rangle + \langle \psi_R | A | \psi_R \rangle)(1 - 2ab\langle \psi_L | \psi_R \rangle^2) \\ &\quad + 2ab\langle \psi_L | \psi_R \rangle(\langle \psi_L | A | \psi_R \rangle + \langle \psi_R | A | \psi_L \rangle) \end{aligned} \quad (4.11)$$

Identifying the operator  $A$  as

$$-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_L} + \frac{1}{r_R} \right) \quad (4.12)$$

the energy becomes:

$$\begin{aligned} \langle E \rangle &= 2E_1 - \frac{e^2}{4\pi\epsilon_0} \left[ 2\langle \psi_L | r_R^{-1} \psi_L \rangle - \frac{1}{d} - \langle \psi_L | \psi_R | r_{12}^{-1} \psi_L | \psi_R \rangle_6 + 2ab\langle \psi_L | \psi_R \rangle^2 \right. \\ &\quad \left. \left( \frac{2\langle \psi_L | r_L^{-1} \psi_R \rangle}{\langle \psi_L | \psi_R \rangle} - 2\langle \psi_L | r_R^{-1} \psi_L \rangle - \frac{\langle \psi_L | \psi_R | r_{12}^{-1} \psi_R | \psi_L \rangle_6}{\langle \psi_L | \psi_R \rangle^2} + \langle \psi_L | \psi_R | r_{12}^{-1} \psi_L | \psi_R \rangle_6 \right) \right] \end{aligned}$$

Using the same integrations as for the hydrogen molecular ion, and numerical integration for the inner products involving  $r_{12} = |\vec{r}_1 - \vec{r}_2|$ , the minimum energy can again be found.

The binding energy turns out to be 3.2 eV, at a proton to proton spacing of 0.87 Å, and it occurs for the symmetric state  $a = b$ .

### 4.2.6 Comparison with the exact ground state

The solution for the ground state of the hydrogen molecule obtained in the previous subsection is, like the one for the molecular ion, pretty good. The approximate binding energy, 3.2 eV, is not too much different from the experimental value of 4.74 eV. Similarly, the bond length of 0.87 Å is not too far from the experimental value of 0.74 Å.

Qualitatively, the exact ground state wave function is real, positive and symmetric with respect to reflection around the symmetry plane and to rotations around the line connecting the protons, and so is the approximate one.

One issue that does not occur for the molecular ion, but only for the neutral molecule is the mutual repulsion between the two electrons. This repulsion is reduced when the electron clouds start to merge. (A similar effect is that the gravity force of the earth decreases when you go down below the surface.) The reduction in repulsion increases the binding energy significantly, from 1.8 eV to 3.2 eV. It also allows the protons to approach more closely.

## 4.3 Two-State Systems

The protons in the  $\text{H}_2^+$  hydrogen molecular ion of chapter 3.5 are held together by a single shared electron. However, in the  $\text{H}_2$  neutral hydrogen molecule of section 4.2, they are held together by a shared pair of electrons. The main purpose of this section is to shed some light on the reason that chemical bonds involving a single electron are relatively rare, while bonds involving pairs of shared electrons are common. The discussion is based on [2, chapters 8-11].

First it should be recognized that our models for the hydrogen molecular ion and the neutral hydrogen molecule were “two state systems,” systems involving two basic states  $\psi_1$  and  $\psi_2$ . For the hydrogen molecular ion, one state,  $\psi_1 = \psi_L$ , described that the electron was around the left proton, the other,  $\psi_2 = \psi_R$ , that it was around the right one.

For the hydrogen molecule,  $\psi_1 = \psi_L\psi_R$  had electron 1 around the left proton and electron 2 around the right one;  $\psi_2 = \psi_R\psi_L$  was the same, but with the electrons reversed.

There are many other physical situations that may be described as two state systems. Covalent chemical bonds involving atoms other than hydrogen would be an obvious example. Just substitute a positive ion for one or both protons.

A further example is provided by nuclear forces. Nuclear forces can be thought of as effects of nucleons sharing various particles, in particular  $\pi$ -mesons, just like the protons share the electron in the hydrogen molecular ion. (In fact, all four fundamental forces can be described in terms of “exchanges” of particles.)

In the benzene molecular ring, there are two ways the three double chemical bonds can distribute themselves between the carbon atoms. And for the ammonia molecule, the nitrogen can be at either side of its ring of hydrogen atoms.

In each case, there are two intuitive physical states  $\psi_1$  and  $\psi_2$ . The peculiarities of two state systems arise from states that are combinations of these two states, as in

$$\Psi = a\psi_1 + b\psi_2$$

Note that according to the ideas of quantum mechanics, the square magnitude of the first coefficient of the combined state,  $|a|^2$ , represents the probability of being in state  $\psi_1$  and  $|b|^2$

the probability of being in state  $\psi_2$ . Of course, the total probability of being in one of the states should be one:

$$|a|^2 + |b|^2 = 1$$

(This is only true if the  $\psi_1$  and  $\psi_2$  states are orthonormal. In the hydrogen cases, orthonormalizing the basic states would change them a bit, but their physical nature would remain much the same, especially if the protons are not too close.)

The key question is what combination of states has the lowest energy. The expectation value of energy is

$$\langle E \rangle = \langle a\psi_1 + b\psi_2 | H | a\psi_1 + b\psi_2 \rangle$$

This can be multiplied out as, (remember that the factors come out of the left of an inner product as complex conjugates,)

$$\langle E \rangle = a^*aH_{11} + a^*bH_{12} + b^*aH_{21} + b^*bH_{22}$$

where we use the shorthand notation

$$H_{11} = \langle \psi_1 | H \psi_1 \rangle, \quad H_{12} = \langle \psi_1 | H \psi_2 \rangle, \quad H_{21} = \langle \psi_2 | H \psi_1 \rangle, \quad H_{22} = \langle \psi_2 | H \psi_2 \rangle.$$

Note that  $H_{11}$  and  $H_{22}$  are real, (1.15), and we will order the states so that  $H_{11}$  is less or equal to  $H_{22}$ . Normally,  $H_{12}$  and  $H_{21}$  are not real but complex conjugates, (1.15), but we can always change the definition of, say,  $\psi_1$  by a factor of magnitude one to make  $H_{12}$  equal to a real and negative number, and then  $H_{21}$  will be that same negative number. Also note that  $a^*a = |a|^2$  and  $b^*b = |b|^2$ .

The above expression for the expectation energy consists of two kinds of terms, which we will call:

$$\text{the averaged energy: } |a|^2H_{11} + |b|^2H_{12} \quad (4.13)$$

$$\text{the exchange terms: } (a^*b + b^*a)H_{12} \quad (4.14)$$

We will discuss each of those contributions in turn.

The averaged energy is the energy that one would intuitively expect the combined wave function to have. It is a straightforward average of the energies of the two component states  $\psi_1$  and  $\psi_2$  times the probabilities of being in those states. In particular, in the important case that the two states have the same energy, the averaged energy is that energy. What is more logical than that any mixture of two states with the same energy would have that energy too?

But the exchange terms throw a monkey wrench in this simplistic thinking. It can be seen that they will always make the ground state energy lower than the energy  $H_{11}$  of the lowest component state. (To see that, just take  $a$  and  $b$  positive real numbers and  $b$  small enough that  $b^2$  can be neglected.) This lowering of the energy below the lowest component state comes out of the mathematics of combining states; absolutely no new physical forces are added to produce it. It produces more stable chemical bonds than you would expect.

Typically, the effect of the exchange terms is greatest if the two basic states  $\psi_1$  and  $\psi_2$  are physically equivalent and have the same energy. This is the case for the hydrogen examples and most of the others mentioned. For such states, the ground state will occur for an *equal* mixture of states,  $a = b = \sqrt{\frac{1}{2}}$ , because then the exchange terms are most negative. In that case, the lowest energy, call it  $E_L$ , is an amount  $H_{12}$  below the energy  $H_{11} = H_{22}$  of the component states.

On the other hand, if, say, state  $\psi_1$  has significantly less energy than state  $\psi_2$ , then the minimum energy will occur for  $|a| \approx 1$  and  $|b| \approx 0$ . (This assumes that the exchange terms are not big enough to dominate the energy.) In that case  $ab \approx 0$ , which pretty much takes the exchange terms (4.14) out of the picture completely.

This happens for the one-electron bond of the hydrogen molecular ion if the second proton is replaced by another ion, say a lithium ion. The energy in state  $\psi_1$  where the electron is around the proton will be less than that of state  $\psi_2$  where it is around the lithium ion. For such asymmetrical one-electron bonds, the exchange terms are not likely to help forge a strong bond. While it turns out that the  $\text{LiH}^+$  ion is stable, the binding energy is only 0.14 eV or so, compared to 2.8 eV for the  $\text{H}_2^+$  ion. Also, the  $\text{LiH}^+$  bond seems to be best described as polarization of the hydrogen atom by the lithium ion, instead of as a true chemical bond.

In contrast, for the two-electron bond of the neutral hydrogen molecule, if the second proton is replaced by a lithium ion, states  $\psi_1$  and  $\psi_2$  will still be the same: both have one electron around the proton and one around the lithium ion. The two states do have the electrons reversed, but the electrons are identical. Thus the exchange terms are still likely to be effective. Indeed neutral  $\text{LiH}$  lithium hydride exists as a stable molecule with a binding energy of about 2.5 eV at low pressures. It should be noted that the  $\text{LiH}$  bond is very ionic, with the “shared” electrons mostly at the hydrogen side, so the actual ground state is quite different from our model. But the model should be better when the nuclei are farther apart, so the analysis can at least justify the existence of a significant bond.

## 4.4 Spin

At this stage, we need to look somewhat closer at the various particles involved in quantum mechanics themselves. We have already used that particles have a property called mass, a quantity that special relativity has identified as being an internal amount of energy. It turns out that particles in addition have a fixed amount of “build-in” angular momentum, called “spin.” Spin reflects itself, for example, in how a charged particle such as an electron interacts with a magnetic field.

To distinguish it from spin, the angular momentum of a particle due to its motion will from now on be referred to as “orbital” angular momentum. As was discussed in chapter 3.1, the

square orbital angular momentum of a particle is given by

$$L^2 = l(l+1)\hbar^2$$

where the azimuthal quantum number  $l$  is a nonnegative integer.

The square spin angular momentum of a particle is given by a similar expression:

$$S^2 = s(s+1)\hbar^2 \quad (4.15)$$

but the “spin  $s$ ” is a fixed number for each type of particle. On the other hand, whereas  $l$  can only be an integer, the spin  $s$  can be any multiple of one half.

Particles with half integer spin are called fermions; for example, electrons, protons, and neutrons all three have spin  $s = \frac{1}{2}$  and are fermions.

Particles with integer spin are called bosons; for example, photons have spin  $s = 1$ . The  $\pi$ -mesons have spin  $s = 0$  and gravitons have spin  $s = 2$ .

The spin angular momentum in an arbitrarily chosen  $z$ -direction is

$$S_z = m\hbar \quad (4.16)$$

the same formula as for orbital angular momentum, and the values of  $m$  range again from  $-s$  to  $+s$  in integer steps. For example, photons can have spin in a given direction that is  $\hbar$ , 0, or  $-\hbar$ .

The common particles, (electrons, protons, neutrons), can only have spin angular momentum  $\frac{1}{2}\hbar$  or  $-\frac{1}{2}\hbar$  in any given direction. The positive sign state is called “spin up”, the negative one “spin down”.

Spin states are commonly shown in “ket notation” as  $|s\ m\rangle$ . For example, the spin up state for an electron is indicated by  $|\frac{1}{2} \frac{1}{2}\rangle$  and the spin down state as  $|\frac{1}{2} -\frac{1}{2}\rangle$ . More informally,  $\uparrow$  and  $\downarrow$  are often used.

## 4.5 Instantaneous Interactions [Background]

The existence of spin helped establish that nature really pulls weird tricks on us. In particular, special relativity has shown that we mere humans cannot transmit information at more than the speed of light. However, according to the orthodox interpretation, nature does not limit itself to the same silly restrictions that it puts on us. This section discusses why not, for those who still need convincing that our world may not be all that it seems.

Consider again the  $\text{H}_2^+$ -ion, with the single electron equally shared by the two protons. If we pull the protons apart, maintaining the symmetry, we get a wave function that looks like



Figure 4.4: Separating the hydrogen ion.

figure 4.4. We might send one proton off to our observer on Mars, the other to our observer on Venus. Where is our *electron*, on Mars or on Venus?

According to the orthodox interpretation, the answer is: *neither*. A position for the electron *does not exist*. The electron is not on Mars. It is not on Venus. Only when either observer makes a measurement to see whether the electron is there, nature throws its dice, and based on the result, might put the electron on Venus and zero the wave function on Mars. But regardless of the distance, it could just as well have put the electron on Mars, if the dice would have come up differently.

You might think that nature cheats, that when we take the protons apart, nature already decides where the electron is going to be. That the Venus proton secretly hides the electron “in its sleeve”, ready to make it appear if an observation is made. John Bell devised a clever test to force nature to reveal whether it has something hidden in its sleeve during a similar sort of trick.

The test case Bell used was a variant of an experiment proposed by Bohm. It involves spin measurements on an electron/positron pair, created by the decay of an  $\pi$ -meson. If we measure the spins of the electron and positron in any given direction, there is a 50/50% chance for each that it turns out to be positive or negative. However, if one is positive, the other must be negative. So there are only two different possibilities: (1) electron positive and positron negative, (2) electron negative and positron positive.

Now suppose Earth happens to be almost the same distance from Mars and Venus, and we shoot the positron out to Venus, and the electron to Mars, as shown in figure 4.5:

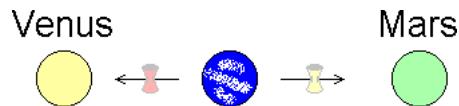


Figure 4.5: The Bohm experiment

We have observers on both planets waiting for the particles. According to quantum mechanics, the traveling electron and positron are both in an indeterminate state.

The positron reaches Venus a fraction of a second earlier, and the observer there measures its spin in the direction up from the ecliptic plane. According to the orthodox interpretation, nature now makes a random selection between the two possibilities, and let's assume it selects the positive spin value for the positron, corresponding to a spin that is up from the ecliptic plane, as shown in figure 4.6:



Figure 4.6: The Bohm experiment, after the Venus measurement.

Immediately, then, the spin state of the electron on Mars must also have collapsed; the observer on Mars is guaranteed to now measure negative spin, or spin down, for the electron. This too is sketched in figure 4.6.

The funny thing is, if we believe the orthodox interpretation, the information about the measurement of the positron has to reach the electron instantaneously, much faster than light can travel. This apparent problem in the orthodox interpretation was discovered by Einstein, Podolski, and Rosen. They doubted it could be true, and argued that it indicated that something must be missing in quantum mechanics.

In fact, instead of superluminal effects, it seems much more reasonable to assume that earlier on earth, when the particles were send on their way, nature attached a secret little “note” of some kind to the positron, saying the equivalent of “If your spin up is measured, give the positive value”, and that it attached a little note to the electron “If your spin up is measured, give the negative value.” The results of the measurements are still the same, and the little notes travel along with the particles, well below the speed of light, so all seems now fine. Of course, these would not be true notes, but some kind of additional information beyond the normal quantum mechanics. Such postulated additional information sources are called hidden variables.

Bell saw that there was a fundamental flaw in this idea if we do a large number of such measurements and we allow the observers to select from more than one measurement direction at random. He derived a neat little general formula, but we will restrict ourselves showing the contradiction in a single case, {22}. In particular, we will allow the observers on Venus and Mars to select randomly one of three measurement directions  $\vec{a}$ ,  $\vec{b}$ , and  $\vec{c}$  separated by 120 degrees:

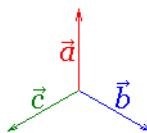


Figure 4.7: Spin measurement directions.

Let's see what the little notes attached to the electrons might say. They might say, for example, "Give the + value if  $\vec{a}$  is measured, give the - value if  $\vec{b}$  is measured, give the + value if  $\vec{c}$  is measured." Let's call the relative fractions of the various possible notes generated for the electrons  $f_1, f_2, \dots$ . There are 8 different possible notes:

	$f_1$	$f_2$	$f_3$	$f_4$	$f_5$	$f_6$	$f_7$	$f_8$
$\vec{a}$	+	+	+	+	-	-	-	-
$\vec{b}$	+	+	-	-	+	+	-	-
$\vec{c}$	+	-	+	-	+	-	+	-

The sum of the fractions  $f_1$  through  $f_8$  must be one. In fact, because of symmetry, each note will probably on average be generated for  $\frac{1}{8}$  of the electrons sent, but this will not be needed.

Of course, each note attached to the positron must always be just the opposite of the one attached to the electron, since the positron must measure + in a direction when the electron measures - in that direction and vice-versa.

Now consider those measurements in which the Venus observer measures direction  $\vec{a}$  and the Mars observer measures direction  $\vec{b}$ . In particular, we are interested in what fraction of such measurements the Venus observer measures the opposite sign from the Mars observer; call it  $f_{ab,\text{opposite}}$ . This is not that hard to figure out. First consider the case that Venus measures - and Mars +. If the Venus observer measures the - value for the positron, then the note attached to the electron must say "measure + for  $\vec{a}$ "; further, if the Mars observer measures the + value for  $\vec{b}$ , that one should say "measure +" too. So, looking at the table, the relative fraction where Venus measures - and Mars measures + is where the electron's note has a + for both  $\vec{a}$  and  $\vec{b}$ :  $f_1 + f_2$ .

Similarly, the fraction of cases where Venus finds + and Mars - is  $f_7 + f_8$ , and we get in total:

$$f_{ab,\text{opposite}} = f_1 + f_2 + f_7 + f_8 = 0.25$$

The value 0.25 is what quantum mechanics predicts; I will not derive it, but it has been verified in the experiments done after Bell's work. Those experiments also made sure that nature did not get the chance to do *subluminal* communication. The same way we get

$$f_{ac,\text{opposite}} = f_1 + f_3 + f_6 + f_8 = 0.25$$

and

$$f_{bc,\text{opposite}} = f_1 + f_4 + f_5 + f_8 = 0.25$$

We now have a problem, because the numbers add up to 0.75, but the fractions add up to at least 1: the sum of  $f_1$  through  $f_8$  is one. The conclusion is inescapable: attaching notes does not work. Information on what the observer on Venus decided to measure, the one thing that could not be put in the notes, must have been communicated *instantly* to the electron on Mars regardless of the distance.

We can also safely conclude that we humans will never be able to see inside quantum mechanics itself, instead of just observe the eigenvalues of operators. For, if we could see the wave function of the electron collapse, the observer on Venus could send the observer on Mars Morse signals faster than the speed of light by either measuring or not measuring the spin of the positron. Special relativity would then allow signals to be sent into the past, and that leads to logical contradictions such as you preventing your mother from having you.

While we can see the results of the spin measurements, they do not allow us to do superluminal communication. While the observer on Venus affects the results of the measurements of the observer on Mars, they will look completely random to that observer until the observer on Venus sends over the results of the Venus measurements, at a speed less than the speed of light, and the two sets of results are *compared*.

The Bell experiments are often used to argue that Nature must really make the collapse decision using a true random number generator, but that is of course crap. The experiments indicate that Nature instantaneously transmits the collapse decision on Venus to Mars, but say nothing about how that decision was reached.

Superluminal effects still cause paradoxes, of course. Figure 4.8 shows how a Bohm experiment appears to an observer on earth. The spins remain undecided until the measurement by the



Figure 4.8: Earth's view of events.

Venus observer causes both the positron and the electron spins to collapse.

However, for a moving observer, things would look very different. Assuming that the observer and the particles are all moving at speeds comparable to the speed of light, the same situation may look like in figure 4.9. In this case, the observer on *Mars* causes the wave function to



Figure 4.9: A moving observer's view of events.

collapse at a time that the positron has only just started moving towards Venus!

So the orthodox interpretation is not quite accurate. It should really have said that the measurement on Venus causes a *convergence* of the wave function, not an absolute collapse. What the observer of Venus really achieves in the orthodox interpretation is that after her measurement, *all* observers agree that the positron wave function is collapsed. Before that

time, some observers are perfectly correct in saying that the wave function is already collapsed, and that the Mars observer did it.

It should be noted that when the equations of quantum mechanics are correctly applied, the collapse and superluminal effects disappear. That is explained in chapter 7.6.2 after the necessary equations of quantum mechanics have been introduced. But, due to the fact that there are limits to our observational capabilities, as far as our own human experiences are concerned, the paradoxes remain real.

## 4.6 Multiple-Particle Systems Including Spin

Quantum mechanics as discussed so far must be generalized to account for particles that have spin. Just like there is a probability that a particle is at some position  $\vec{r}$ , there is the additional probability that it has some spin angular momentum  $S_z$  in an arbitrarily chosen  $z$ -direction, and this must be included in the wave function. This section discusses the various ways of doing so.

### 4.6.1 Wave function for a single particle with spin

First it needs to be determined how spin is included in the wave function of a single particle. If spin is ignored, a single particle has a wave function  $\Psi(\vec{r}; t)$ . Now, since the spin  $S_z$  is just some other scalar variable that describes the particle, in that respect no different from say the  $x$  position of the particle, the “every possible combination” idea of including all possible combinations of states implies that  $S_z$  needs to be added to the list of variables. So the complete wave function is:

$$\Psi(\vec{r}, S_z; t) \tag{4.17}$$

The value of  $|\Psi(\vec{r}, S_z; t)|^2 d^3\vec{r}$  gives the probability of finding the particle within a vicinity  $d^3\vec{r}$  of  $\vec{r}$  and with spin angular momentum in the  $z$ -direction  $S_z$ .

But note that there is a big difference between the spin “coordinate” and the position coordinates: while the position variables can take on any value, the values of  $S_z$  are highly limited. In particular, for the electron, proton, and neutron,  $S_z$  can only be  $\frac{1}{2}\hbar$  or  $-\frac{1}{2}\hbar$ , nothing else. We do not really have a full  $S_z$  “axis”, just two points. As a result, there are other meaningful ways of writing the wave function. The full wave function  $\Psi(\vec{r}, S_z; t)$  can be thought of as consisting of two parts  $\Psi_+$  and  $\Psi_-$  that only depend on position:

$$\Psi_+(\vec{r}; t) \equiv \Psi(\vec{r}, \frac{1}{2}\hbar; t) \quad \text{and} \quad \Psi_-(\vec{r}; t) \equiv \Psi(\vec{r}, -\frac{1}{2}\hbar; t)$$

These two parts can in turn be thought of as being the components of a two-dimensional

vector that only depends on position:

$$\vec{\Psi}(\vec{r}; t) \equiv \begin{pmatrix} \Psi_+(\vec{r}; t) \\ \Psi_-(\vec{r}; t) \end{pmatrix}$$

Remarkably, Dirac found that the wave function for particles like electrons *has* to be a vector, if we assume that the relativistic equations take a guessed simple and beautiful form, like the Schrödinger and all other basic equations of physics are simple and beautiful. Just like relativity reveals that particles should have build-in energy, it also reveals that particles like electrons have build-in angular momentum. A description of the Dirac equation is in chapter 7.2 if you are curious.

The wave function vector can also be written in terms of a magnitude times a unit vector:

$$\vec{\Psi}(\vec{r}; t) = \Psi_r(\vec{r}; t) \begin{pmatrix} \chi_1(\vec{r}; t) \\ \chi_2(\vec{r}; t) \end{pmatrix}$$

where the two-dimensional unit vector  $(\chi_1, \chi_2)$  is called “spinor.” (The name spinor indicates that its components do not change like ordinary physical vectors when the coordinate system is rotated.)

This document will just use the scalar wave function  $\Psi(\vec{r}, S_z; t)$ ; not a vector one. But it is often convenient to write the scalar wave function in a form equivalent to the vector one:

$$\Psi(\vec{r}, S_z; t) = \Psi_+(\vec{r}; t)\chi_+(S_z) + \Psi_-(\vec{r}; t)\chi_-(S_z) \quad (4.18)$$

where function  $\chi_+$  by definition equals 1 at  $\frac{1}{2}\hbar$  and 0 at  $-\frac{1}{2}\hbar$ , and the opposite for  $\chi_-$ . Note that now each function depends on space or on spin only. This tends to simplify analysis in many cases since spatial and spin effects are often not directly related. More informally,  $\Psi$  is commonly written as

$$\Psi(\vec{r}, S_z; t) = \Psi_+(\vec{r}; t)\uparrow + \Psi_-(\vec{r}; t)\downarrow \quad (4.19)$$

using arrows for functions  $\chi_+$  and  $\chi_-$ . This is the notation that will be used from now on.

### 4.6.2 Inner products including spin

Inner products are important: they are needed for finding expectation values, uncertainty, approximate ground states, etcetera. The additional spin coordinates add a new twist, since there is no way to integrate over the few discrete points on the spin “axis”. Instead, we must sum over these points.

In other words, the inner product of two arbitrary electron wave functions  $\Psi_1(\vec{r}, S_z, t)$  and  $\Psi_2(\vec{r}, S_z, t)$  is

$$\langle \Psi_1 | \Psi_2 \rangle = \sum_{S_z=\pm\frac{1}{2}\hbar} \int_{\vec{r}} \Psi_1(\vec{r}, S_z, t) \Psi_2(\vec{r}, S_z, t) d^3\vec{r}$$

or writing out the two-term sum,

$$\langle \Psi_1 | \Psi_2 \rangle = \int_{\vec{r}} \Psi_1(\vec{r}, \frac{1}{2}\hbar, t) \Psi_2(\vec{r}, \frac{1}{2}\hbar, t) d^3\vec{r} + \int_{\vec{r}} \Psi_1(\vec{r}, -\frac{1}{2}\hbar, t) \Psi_2(\vec{r}, -\frac{1}{2}\hbar, t) d^3\vec{r}$$

When written in terms of the spin basis functions  $\uparrow = \chi_+$  and  $\downarrow = \chi_-$ , inner products fall apart into separate spatial and spin inner products. For example, the inner product between two spin-up wave functions is:

$$\begin{aligned} & \langle \Psi_{1+} \uparrow | \Psi_{2+} \uparrow \rangle \\ &= \int_{\vec{r}} \Psi_{1+}(\vec{r}, t) \Psi_{2+}(\vec{r}, t) d^3\vec{r} \chi_+(\frac{1}{2}\hbar) \chi_+(\frac{1}{2}\hbar) + \int_{\vec{r}} \Psi_{1+}(\vec{r}, t) \Psi_{2+}(\vec{r}, t) d^3\vec{r} \chi_+(-\frac{1}{2}\hbar) \chi_+(-\frac{1}{2}\hbar) \\ &= \langle \Psi_{1+} | \Psi_{2+} \rangle \langle \uparrow | \uparrow \rangle \end{aligned}$$

where by definition

$$\langle \uparrow | \uparrow \rangle = \chi_+(\frac{1}{2}\hbar) \chi_+(\frac{1}{2}\hbar) + \chi_+(-\frac{1}{2}\hbar) \chi_+(-\frac{1}{2}\hbar)$$

Examining more closely,  $\langle \uparrow | \uparrow \rangle = 1$  since by definition  $\chi_+(\frac{1}{2}\hbar) = 1$  and  $\chi_+(-\frac{1}{2}\hbar) = 0$ . So we have

$$\langle \Psi_{1+} \uparrow | \Psi_{2+} \uparrow \rangle = \langle \Psi_{1+} | \Psi_{2+} \rangle$$

Just like  $\langle \uparrow | \uparrow \rangle = 1$ , we have  $\langle \downarrow | \downarrow \rangle = 1$  and  $\langle \uparrow | \downarrow \rangle = 0$ , so  $\uparrow$  and  $\downarrow$  are orthonormal. As another example, then:

$$\langle \Psi_{1+} \uparrow | \Psi_{2-} \downarrow \rangle = \langle \Psi_{1+} | \Psi_{2-} \rangle \langle \uparrow | \downarrow \rangle = 0$$

### 4.6.3 Wave function for multiple particles with spin

The extension of the ideas of the previous sections towards multiple particles is straightforward. For two particles, such as the two electrons of the hydrogen molecule, the full wave function follows from the “every possible combination” idea as

$$\Psi(\vec{r}_1, S_{z1}, \vec{r}_2, S_{z2}; t) \tag{4.20}$$

The value of  $|\Psi(\vec{r}_1, S_{z1}, \vec{r}_2, S_{z2}; t)|^2 d^3\vec{r}_1 d^3\vec{r}_2$  gives the probability of simultaneously finding particle 1 within a vicinity  $d^3\vec{r}_1$  of  $\vec{r}_1$  with spin angular momentum in the  $z$ -direction  $S_{z1}$ , and particle 2 within a vicinity  $d^3\vec{r}_2$  of  $\vec{r}_2$  with spin angular momentum in the  $z$ -direction  $S_{z2}$ .

Restricting the attention again to spin  $\frac{1}{2}$  particles like electrons, protons and neutrons, there are now four possible spin states at any given point,

$$\uparrow\uparrow \quad \uparrow\downarrow \quad \downarrow\uparrow \quad \downarrow\downarrow$$

where the first arrow indicates the first particle and the second the second. So, the wave function can now be written using purely spatial functions and purely spin functions as

$$\Psi_{++}(\vec{r}_1, \vec{r}_2; t) \uparrow\uparrow + \Psi_{+-}(\vec{r}_1, \vec{r}_2; t) \uparrow\downarrow + \Psi_{-+}(\vec{r}_1, \vec{r}_2; t) \downarrow\uparrow + \Psi_{--}(\vec{r}_1, \vec{r}_2; t) \downarrow\downarrow \tag{4.21}$$

#### 4.6.4 Example: the hydrogen molecule

As an example, this section considers the ground state of the hydrogen molecule. It was found in section 4.2 that the spatial wave function must be of the approximate form

$$a [\psi_L(\vec{r}_1)\psi_R(\vec{r}_2) + \psi_R(\vec{r}_1)\psi_L(\vec{r}_2)]$$

where  $\psi_L$  was the ground state of the left hydrogen atom, and  $\psi_R$  the one of the right one;  $a$  was just a normalization constant. This solution excluded all consideration of spin.

Including spin, the full wave function must be of the general form

$$\Psi_{++}(\vec{r}_1, \vec{r}_2; t) \uparrow\uparrow + \Psi_{+-}(\vec{r}_1, \vec{r}_2; t) \uparrow\downarrow + \Psi_{-+}(\vec{r}_1, \vec{r}_2; t) \downarrow\uparrow + \Psi_{--}(\vec{r}_1, \vec{r}_2; t) \downarrow\downarrow$$

whether it is the ground state or not. As you might expect, in the ground state, each of the four spatial functions  $\Psi_{\pm\pm}$  must be proportional to the lowest-energy spatial solution above. Anything else would have more than the lowest possible energy {23}.

So the approximate ground state including spin must take the form

$$a [\psi_L(\vec{r}_1)\psi_R(\vec{r}_2) + \psi_R(\vec{r}_1)\psi_L(\vec{r}_2)] [c_{++} \uparrow\uparrow + c_{+-} \uparrow\downarrow + c_{-+} \downarrow\uparrow + c_{--} \downarrow\downarrow] \quad (4.22)$$

where  $c_{++}$ ,  $c_{+-}$ ,  $c_{-+}$ , and  $c_{--}$  are constants.

#### 4.6.5 Triplet and singlet states

In the case of two particles with spin  $1/2$ , it is often more convenient to use slightly different basic states to describe the spin states than the four arrow combinations  $\uparrow\uparrow$ ,  $\uparrow\downarrow$ ,  $\downarrow\uparrow$ , and  $\downarrow\downarrow$ . The more convenient basic states can be written in  $|s m\rangle$  ket notation, and they are:

$$\underbrace{|1 1\rangle = \uparrow\uparrow \quad |1 0\rangle = \frac{1}{\sqrt{2}} (\uparrow\downarrow + \downarrow\uparrow) \quad |1 -1\rangle = \downarrow\downarrow}_{\text{the triplet states}} \quad \underbrace{|0 0\rangle = \frac{1}{\sqrt{2}} (\uparrow\downarrow - \downarrow\uparrow)}_{\text{the singlet state}} \quad (4.23)$$

A state  $|s m\rangle$  has *net* spin  $s$ , giving a net square angular momentum  $s(s+1)\hbar^2$ , and has *net* angular momentum in the  $z$ -direction  $m\hbar$ . For example, if the two particles are in the state  $|1 1\rangle$ , the net square angular momentum is  $2\hbar^2$ , and their net momentum in the  $z$ -direction is  $\hbar$ .

The  $\uparrow\downarrow$  and  $\downarrow\uparrow$  states can be written as

$$\uparrow\downarrow = \frac{1}{\sqrt{2}} (|1 0\rangle + |0 0\rangle) \quad \downarrow\uparrow = \frac{1}{\sqrt{2}} (|1 0\rangle - |0 0\rangle)$$

This shows that while they have zero angular momentum in the  $z$ -direction; they *do not* have a value for the net spin: they have a 50/50 probability of net spin 1 and net spin 0. A consequence is that  $\uparrow\downarrow$  and  $\downarrow\uparrow$  cannot be written in  $|sm\rangle$  ket notation; there is no value for  $s$ .

Incidentally, note that  $z$ -components of angular momentum simply add up, as the Newtonian analogy suggests. For example, for  $\uparrow\downarrow$ , the  $\frac{1}{2}\hbar$  spin angular momentum of the first electron adds to the  $-\frac{1}{2}\hbar$  of the second electron to produce zero. But Newtonian analysis does not allow square angular momenta to be added together, and neither does quantum mechanics. In fact, it is quite a messy exercise to actually prove that the triplet and singlet states have the net spin values claimed above, see chapter 7.1.

## 4.7 Identical Particles

A number of the counter-intuitive features of quantum mechanics have already been discussed: The fundamental impossibility of improving the accuracy of both position and momentum beyond a given limit. Collapse of the wave function. A hidden random number generator. Quantized energies and angular momenta. Nonexisting angular momentum vectors. Intrinsic angular momentum. Electrons being neither on Mars or on Venus until they pop up at either place. Superluminal interactions. But nature has one more trick on its sleeve, and it is a big one.

Nature entangles all identical particles with each other. Specifically, it requires that the wave function remains unchanged if any two identical bosons are interchanged. If particles  $i$  and  $j$  are identical bosons, then:

$$\Psi(\vec{r}_1, S_{z1}, \dots, \vec{r}_i, S_{zi}, \dots, \vec{r}_j, S_{zj}, \dots) = \Psi(\vec{r}_1, S_{z1}, \dots, \vec{r}_j, S_{zj}, \dots, \vec{r}_i, S_{zi}, \dots) \quad (4.24)$$

On the other hand, nature requires that the wave function changes sign if any two identical fermions are interchanged

If particles  $i$  and  $j$  are identical fermions, (say, both electrons), then:

$$\Psi(\vec{r}_1, S_{z1}, \dots, \vec{r}_i, S_{zi}, \dots, \vec{r}_j, S_{zj}, \dots) = -\Psi(\vec{r}_1, S_{z1}, \dots, \vec{r}_j, S_{zj}, \dots, \vec{r}_i, S_{zi}, \dots) \quad (4.25)$$

In other words, the wave function must be symmetric with respect to exchange of identical bosons, and antisymmetric with respect to interchange of identical fermions. This greatly restricts what wave functions can be.

For example, consider what this means for the hydrogen molecule. The approximate ground state of lowest energy was in the previous section found to be

$$a [\psi_L(\vec{r}_1)\psi_R(\vec{r}_2) + \psi_R(\vec{r}_1)\psi_L(\vec{r}_2)] [c_{++} \uparrow\uparrow + c_{+-} \uparrow\downarrow + c_{-+} \downarrow\uparrow + c_{--} \downarrow\downarrow]$$

were  $\psi_L$  was the ground state of the left hydrogen atom,  $\psi_R$  the one of the right one, first arrows indicate the spin of electron 1 and second arrows the one of electron 2, and  $a$  and the  $c_{\pm\pm}$  are constants.

Now, since the two electrons are identical fermions, this wave function must be antisymmetric with respect to interchange of the two electrons. Interchanging the electrons turns the wave function into

$$a [\psi_L(\vec{r}_2)\psi_R(\vec{r}_1) + \psi_R(\vec{r}_2)\psi_L(\vec{r}_1)] [c_{++} \uparrow\uparrow + c_{+-} \downarrow\uparrow + c_{-+} \uparrow\downarrow + c_{--} \downarrow\downarrow]$$

or, with the terms reordered,

$$a [\psi_L(\vec{r}_1)\psi_R(\vec{r}_2) + \psi_R(\vec{r}_1)\psi_L(\vec{r}_2)] [c_{++} \uparrow\uparrow + c_{-+} \uparrow\downarrow + c_{+-} \downarrow\uparrow + c_{--} \downarrow\downarrow]$$

This can only be the negative of the noninterchanged version (4.7) if  $c_{++} = 0$ ,  $c_{+-} = -c_{-+}$ , and  $c_{--} = 0$ .

So, due to the antisymmetrization requirement, the full wave function of the ground state must be,

$$a [\psi_L(\vec{r}_1)\psi_R(\vec{r}_2) + \psi_R(\vec{r}_1)\psi_L(\vec{r}_2)] c_{-+} [\uparrow\downarrow - \downarrow\uparrow]$$

or after normalization,

$$ca [\psi_L(\vec{r}_1)\psi_R(\vec{r}_2) + \psi_R(\vec{r}_1)\psi_L(\vec{r}_2)] \frac{\uparrow\downarrow - \downarrow\uparrow}{\sqrt{2}}$$

where  $c$  has magnitude one. It is seen that the antisymmetrization requirement restricts the spin state to be the “singlet” one, as defined in the previous section. It is the singlet spin state that achieves the sign change when the two electrons are interchanged; the spatial part remains unchanged.

If the electrons would have been bosons, the spin state could have been any combination of the three triplet states. The symmetrization requirement for fermions is much more restrictive than the one for bosons.

## 4.8 Ways to Symmetrize the Wave Function

This section discusses ways that the symmetrization requirements for wave functions of systems of identical particles can be achieved in general. This is a key issue in the numerical solution of any nontrivial quantum system, so we will look at it in some detail.

It will be assumed that the approximate description of the wave function is done using a set of chosen one-particle basis functions, or “states”,  $\phi_1(\vec{r}, S_z)$ ,  $\phi_2(\vec{r}, S_z)$ , etcetera. An example

of this is the approximate ground state of the hydrogen molecule from the previous section, which can be written like

$$\frac{a}{\sqrt{2}} [\psi_L(\vec{r}_1) \uparrow \psi_R(\vec{r}_2) \downarrow -\psi_L(\vec{r}_1) \downarrow \psi_R(\vec{r}_2) \uparrow +\psi_R(\vec{r}_1) \uparrow \psi_L(\vec{r}_2) \downarrow -\psi_R(\vec{r}_1) \downarrow \psi_L(\vec{r}_2) \uparrow]$$

This consists of four one-particle states:

$$\phi_1(\vec{r}, S_z) = \psi_L(\vec{r}) \uparrow \quad \phi_2(\vec{r}, S_z) = \psi_L(\vec{r}) \downarrow \quad \phi_3(\vec{r}, S_z) = \psi_R(\vec{r}) \uparrow \quad \phi_4(\vec{r}, S_z) = \psi_R(\vec{r}) \downarrow$$

The first of the four states represents a single electron in the ground state around the left proton with spin up, the second a single electron in the same spatial state with spin down, etcetera. For better accuracy, more states could be included, say excited atomic states in addition to the ground states.

For the general case that  $N$  chosen states  $\phi_1(\vec{r}, S_z), \phi_2(\vec{r}, S_z), \dots, \phi_N(\vec{r}, S_z)$  are used to describe  $Z$  particles  $1, 2, \dots, Z$ , the most general possible wave function assumes the form:

$$\Psi = \sum_{n_1=1}^N \sum_{n_2=1}^N \dots \sum_{n_Z=1}^N a_{n_1 n_2 \dots n_Z} \phi_{n_1}(\vec{r}_1, S_{z1}) \phi_{n_2}(\vec{r}_2, S_{z2}) \dots \phi_{n_Z}(\vec{r}_Z, S_{zZ}) \quad (4.26)$$

where the  $a_{n_1 n_2 \dots n_Z}$  are numerical coefficients that are to be chosen to satisfy the physical constraints on the wave function, including the antisymmetrization requirement.

This summation is again the “every possible combination” idea of combining every possible state for particle 1 with every possible state for particle 2, etcetera. As a consequence, the total sum above contains  $N^Z$  terms: there are  $N$  possibilities for state  $n_1$  of particle 1, times  $N$  possibilities for state  $n_2$  of particle 2, ... In general, then, a corresponding total of  $N^Z$  coefficients  $a_{n_1 n_2 \dots n_Z}$  must be determined to find out the precise wave function.

But for identical particles, the number that must be determined is much less. To focus the thoughts, we will work out how many for the example that four states are used to describe two particles, like in the hydrogen molecule case above, and then see how it changes for other numbers of states and particles.

If there are four states,  $N = 4$ , and two particles,  $Z = 2$ , the above sum (4.26) for  $\Psi$  consists of  $4^2 = 16$  terms, which can be ordered into 10 groups:

$$\begin{aligned} I : & a_{11}\phi_1(\vec{r}_1, S_{z1})\phi_1(\vec{r}_2, S_{z2}) \\ II : & a_{22}\phi_2(\vec{r}_1, S_{z1})\phi_2(\vec{r}_2, S_{z2}) \\ III : & a_{33}\phi_3(\vec{r}_1, S_{z1})\phi_3(\vec{r}_2, S_{z2}) \\ IV : & a_{44}\phi_4(\vec{r}_1, S_{z1})\phi_4(\vec{r}_2, S_{z2}) \\ V : & a_{12}\phi_1(\vec{r}_1, S_{z1})\phi_2(\vec{r}_2, S_{z2}) + a_{21}\phi_2(\vec{r}_1, S_{z1})\phi_1(\vec{r}_2, S_{z2}) \\ VI : & a_{13}\phi_1(\vec{r}_1, S_{z1})\phi_3(\vec{r}_2, S_{z2}) + a_{31}\phi_3(\vec{r}_1, S_{z1})\phi_1(\vec{r}_2, S_{z2}) \\ VII : & a_{14}\phi_1(\vec{r}_1, S_{z1})\phi_4(\vec{r}_2, S_{z2}) + a_{41}\phi_4(\vec{r}_1, S_{z1})\phi_1(\vec{r}_2, S_{z2}) \\ VIII : & a_{23}\phi_2(\vec{r}_1, S_{z1})\phi_3(\vec{r}_2, S_{z2}) + a_{32}\phi_3(\vec{r}_1, S_{z1})\phi_2(\vec{r}_2, S_{z2}) \\ IX : & a_{24}\phi_2(\vec{r}_1, S_{z1})\phi_4(\vec{r}_2, S_{z2}) + a_{42}\phi_4(\vec{r}_1, S_{z1})\phi_2(\vec{r}_2, S_{z2}) \\ X : & a_{34}\phi_3(\vec{r}_1, S_{z1})\phi_4(\vec{r}_2, S_{z2}) + a_{43}\phi_4(\vec{r}_1, S_{z1})\phi_3(\vec{r}_2, S_{z2}) \end{aligned}$$

In each group, all terms involve the *same* pair of states, but in a different *order*. Different groups have a different pair of states.

More generally, if there are  $Z$  identical particles instead of 2, every term in a group will use the same set of  $Z$  states, but each term has them in a different order. Even then, if the  $Z$  states are all the same, the group still has only a single term. At the other extreme however, if the  $Z$  states in a group are all different, that group has as much as  $Z!$  terms, since  $Z!$  is the number of ways that  $Z$  different states can be arranged.

Consider now first the case that the particles involved are identical bosons. The symmetrization requirement is then that interchanging the particles must leave the wave function unchanged. In the example, interchanging particles means that  $(\vec{r}_1, S_{z1})$  changes into  $(\vec{r}_2, S_{z2})$  and vice-versa. This interchange does nothing to the terms in groups  $I$  through  $IV$ . But in group  $V$ , interchanging particles 1 and 2 turns the first term into the second, though still with numerical coefficient  $a_{12}$ , and vice versa. The only way this can leave  $\Psi$  unchanged is if  $a_{12} = a_{21}$ ; the two coefficients in the group must be equal.

Similarly the coefficients in each of the groups  $VI$  through  $X$  must be equal. Hence the number of unknown coefficients that still must be found to determine  $\Psi$  has been reduced from 16 to 10 by the symmetrization requirement.

The reduction is even larger for fermions, such as for the two electrons of the hydrogen molecule example. For, interchanging two fermions must change the sign of the wave function. But interchanging particles 1 and 2 turns the terms in groups  $I$  through  $IV$  back into themselves. The only way something can be the negative of itself is if it is zero. It follows that  $a_{11}$ ,  $a_{22}$ ,  $a_{33}$ , and  $a_{44}$  must all be zero.

Further, in each of the groups  $V$  through  $X$ , the two coefficients must be opposites, e.g.  $a_{21} = -a_{12}$ , to achieve a change of sign if the particles are interchanged. So only six unknown coefficients survive the antisymmetrization requirement. This is less than half of the sixteen we started out with.

There is a very neat way of writing the antisymmetrized wave function of systems of fermions, which is especially convenient for larger numbers of particles. It is done using determinants. The antisymmetric wave function of our example is:

$$\begin{aligned} \Psi = & a_{12} \left| \begin{array}{cc} \phi_1(\vec{r}_1, S_{z1}) & \phi_2(\vec{r}_1, S_{z1}) \\ \phi_1(\vec{r}_2, S_{z2}) & \phi_2(\vec{r}_2, S_{z2}) \end{array} \right| + a_{13} \left| \begin{array}{cc} \phi_1(\vec{r}_1, S_{z1}) & \phi_3(\vec{r}_1, S_{z1}) \\ \phi_1(\vec{r}_2, S_{z2}) & \phi_3(\vec{r}_2, S_{z2}) \end{array} \right| + \\ & a_{14} \left| \begin{array}{cc} \phi_1(\vec{r}_1, S_{z1}) & \phi_4(\vec{r}_1, S_{z1}) \\ \phi_1(\vec{r}_2, S_{z2}) & \phi_4(\vec{r}_2, S_{z2}) \end{array} \right| + a_{23} \left| \begin{array}{cc} \phi_2(\vec{r}_1, S_{z1}) & \phi_3(\vec{r}_1, S_{z1}) \\ \phi_2(\vec{r}_2, S_{z2}) & \phi_3(\vec{r}_2, S_{z2}) \end{array} \right| + \\ & a_{24} \left| \begin{array}{cc} \phi_2(\vec{r}_1, S_{z1}) & \phi_4(\vec{r}_1, S_{z1}) \\ \phi_2(\vec{r}_2, S_{z2}) & \phi_4(\vec{r}_2, S_{z2}) \end{array} \right| + a_{34} \left| \begin{array}{cc} \phi_3(\vec{r}_1, S_{z1}) & \phi_4(\vec{r}_1, S_{z1}) \\ \phi_3(\vec{r}_2, S_{z2}) & \phi_4(\vec{r}_2, S_{z2}) \end{array} \right| \end{aligned}$$

These determinants are called “Slater determinants”.

More generally, when there are  $Z$  fermions instead of only two, there is one Slater determinant of the form

$$\frac{1}{\sqrt{Z!}} \begin{vmatrix} \phi_{n_1}(\vec{r}_1, S_{z1}) & \phi_{n_2}(\vec{r}_1, S_{z1}) & \phi_{n_3}(\vec{r}_1, S_{z1}) & \cdots & \phi_{n_Z}(\vec{r}_1, S_{z1}) \\ \phi_{n_1}(\vec{r}_2, S_{z2}) & \phi_{n_2}(\vec{r}_2, S_{z2}) & \phi_{n_3}(\vec{r}_2, S_{z2}) & \cdots & \phi_{n_Z}(\vec{r}_2, S_{z2}) \\ \phi_{n_1}(\vec{r}_3, S_{z3}) & \phi_{n_2}(\vec{r}_3, S_{z3}) & \phi_{n_3}(\vec{r}_3, S_{z3}) & \cdots & \phi_{n_Z}(\vec{r}_3, S_{z3}) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \phi_{n_1}(\vec{r}_Z, S_{zZ}) & \phi_{n_2}(\vec{r}_Z, S_{zZ}) & \phi_{n_3}(\vec{r}_Z, S_{zZ}) & \cdots & \phi_{n_Z}(\vec{r}_Z, S_{zZ}) \end{vmatrix} \quad (4.27)$$

for each group of terms with  $Z$  different states  $\phi_{n_1}, \phi_{n_2}, \dots, \phi_{n_Z}$ . The normalization factor  $1/\sqrt{Z!}$  has been thrown in merely to ensure that if the states  $\phi_n$  are orthonormal, then so are the Slater determinants. Using Slater determinants ensures the required sign changes of fermion systems automatically, because determinants change sign if two rows are interchanged.

There is no way to describe a system of  $Z$  identical fermions with less than  $Z$  different states  $\phi_n$ ; a determinant must have all its columns different or it will be zero. This important observation is known as the “Pauli exclusion principle”.  $Z$  electrons occupying  $Z$  states exclude a  $Z+1$ th fermion from simply entering the same  $Z$  states; a new state must be added to the mix for each additional electron. So, the more identical fermions there are in a system, the more different states are required to describe it.

In the case that the minimum of  $Z$  states is used to describe  $Z$  identical fermions, the anti-symmetrization requirement reduces the  $Z^Z$  different coefficients  $a_{n_1 n_2 \dots n_Z}$  into a single one,  $a_{11\dots 1}$ , multiplying a single Slater determinant. This obviously is a tremendous reduction in degrees of freedom.

At the other extreme, when the number of states  $N$  is much larger than the number of particles  $Z$ , most terms have all indices different and the reduction is “only” from  $N^Z$  to about  $N^Z/Z!$  terms. The latter would also be true for identical bosons.

The states better be chosen to produce a good approximation to the wave function with a small number of terms. As an arbitrary example to focus the thoughts, if  $N = 100$  states are used to describe an arsenic atom, with  $Z = 33$  electrons, there would be a prohibitive  $10^{66}$  terms in the sum (4.26). Even after reduction to Slater determinants, there would still be a prohibitive  $3 \cdot 10^{26}$  or so coefficients left.

The basic “Hartree-Fock” approach goes to the extreme in reducing the number of states: it only uses a single Slater determinant, but rather than choosing the  $Z$  states  $\phi_n$  a priori, they are adjusted to give the best approximation that is possible with a single Slater determinant.

## 4.9 Matrix Formulation

When the number of unknowns in a quantum mechanical problem has been reduced to a finite number, the problem can be reduced to a linear algebra one. This allows the problem to be solved using standard analytical or numerical techniques. This section describes how the linear algebra problem can be obtained.

Typically, quantum mechanical problems can be reduced to a finite number of unknowns using a finite set of different “states”, as in the previous section. There are other ways to make the problems finite, it does not really make a difference here. But in general some simplification will still be needed afterwards. A multiple sum like equation (4.26) for distinguishable particles is awkward to work with, and when some coefficients drop out for identical particles, its gets worse. So as a first step, it is best to order the terms involved in some way; any ordering will do. Ordering allows each term to be indexed by a single index  $j$ , being the place of the term in the ordering.

In other words, using an ordering, the wave function for a total of  $Z$  particles can be written more simply as:

$$\Psi = \sum_j a_j \psi_j(\vec{r}_1, S_{z1}, \vec{r}_2, S_{z2}, \dots, \vec{r}_Z, S_{zZ}) \quad (4.28)$$

where the functions  $\psi_j$  are allowed to be anything; individual products of states for distinguishable particles as in (4.26), Slater determinants for identical fermions, or whatever. The only thing that will be assumed is that they are mutually orthonormal. (Which means that the underlying set of states  $\phi_n(\vec{r}, S_z)$  described in the previous section should be orthonormal.)

The energy eigenvalue problem  $H\psi = E\psi$  takes the form:

$$\sum_j H a_j \psi_j = \sum_j E a_j \psi_j$$

The trick is now to take the inner product of both sides of this equation with each function  $\psi_i$  in the set of functions in turn. This produces, using the fact that the functions are orthonormal,

$$\sum_j H_{ij} a_j = E a_i \quad \text{with} \quad H_{ij} = \langle \psi_i | H \psi_j \rangle \quad \text{for } i = 1, 2, \dots \quad (4.29)$$

which is just a finite-size matrix eigenvalue problem.

Since the functions  $\psi_j$  are known, chosen, functions, and the Hamiltonian  $H$  is also known, the matrix coefficients  $H_{ij}$  can be determined. The eigenvalues  $E$  and corresponding eigenvectors  $(a_1, a_2, \dots)$  can then be found using linear algebra procedures. Each eigenvector produces a corresponding eigenfunction  $\sum_j a_j \psi_j$  with an energy equal to the eigenvalue  $E$ .

## 4.10 Global Symmetrization [Background]

Going back to the hydrogen molecule example in section 4.7, it is all nice and well to say that the wave function must be antisymmetric with respect to exchange of the two electrons 1 and 2, so the spin state of the molecule must be the singlet one. But what about electron 3 in figure 4.4, which can with 50% chance be found on Mars and otherwise on Venus? Should not the wave function also be antisymmetric, for example, with respect to exchange of this electron 3 in space with electron 1 on the hydrogen molecule on Earth? And would this not locate electron 3 in space also in part on our hydrogen molecule, and electron 1 also partly in space?

The answer is: absolutely. Nature treats *all* electrons as one big connected bunch. The given solution for the hydrogen molecule is not correct; it should have included *every* electron in the universe, not just two of them. Every electron in the universe is just as much present on this single hydrogen molecule as the two I started out with assuming.

From the difficulty in describing the 33 electrons of the arsenic atom, imagine having to describe all electrons in the universe at the same time! If the universe is truly flat, this number would not even be finite. Fortunately, it turns out that the observed quantities can be correctly predicted pretending there are only two electrons involved. Antisymmetrization with far away electrons does not change the properties of the local solution. But we should really remember to avoid committing ourselves to *which* two electrons we are talking about.



# Chapter 5

## Examples of Multiple-Particle Systems

### 5.1 Heavier Atoms

This section solves the electron configuration of the atoms of elements heavier than hydrogen. A crude approximation will be made to deal with the mutual interactions of the electrons. Still, many properties of the elements can be understood using this crude model, such as their geometry and chemical properties, and how the Pauli exclusion principle raises the energy of the electrons of the heavier atoms,

The atoms of different elements are distinguished by their atomic number  $Z$ , which is the number of protons in the nucleus. For the neutral atoms considered in this section,  $Z$  is also the number of electrons circling the nucleus.

#### 5.1.1 The Hamiltonian eigenvalue problem

The procedure to find the ground state of the heavier atoms is similar to the one for the hydrogen atom of chapter 3.2. The total energy Hamiltonian for the electrons of an element with atomic number  $Z$  with is:

$$H = \sum_{j=1}^Z \left\{ -\frac{\hbar^2}{2m_e} \nabla_j^2 - \frac{e^2 Z}{4\pi\epsilon_0 r_j} + \frac{1}{2} \sum_{k \neq j}^Z \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_j - \vec{r}_k|} \right\} \quad (5.1)$$

In the sum, the first term represents the kinetic energy of electron  $j$  out of  $Z$ , the second the attractive potential due to the nuclear charge  $Ze$ , and the final term is the repulsion by all the other electrons. In the Hamiltonian as written, it is assumed that the energy of each repulsion is shared equally by the two electrons involved, accounting for the factor  $\frac{1}{2}$ .

The Hamiltonian eigenvalue problem for the energy states takes the form:

$$H\psi(\vec{r}_1, S_{z1}, \vec{r}_2, S_{z2}, \dots, \vec{r}_Z, S_{zZ}) = E\psi(\vec{r}_1, S_{z1}, \vec{r}_2, S_{z2}, \dots, \vec{r}_Z, S_{zZ})$$

### 5.1.2 Approximate solution using separation of variables

The Hamiltonian eigenvalue problem of the previous subsection cannot be solved exactly. The repulsive interactions between the electrons, given by the last term in the Hamiltonian are too complex.

More can be said under the really poor approximation that each electron “sees” a repulsion by the other  $Z - 1$  electrons that averages out as if the other electrons are located in the nucleus. The other  $Z - 1$  electrons then reduce the net charge of the nucleus from  $Ze$  to  $e$ . An other way of saying this is that each of the  $Z - 1$  other electrons “shields” one proton in the nucleus, allowing only a single proton charge to filter through.

In this crude approximation, the electrons do not notice each other at all; they only see a single charge *hydrogen* nucleus. Obviously then, the wave function solutions for each electron should be the  $\psi_{nlm}$  eigenfunctions of the hydrogen atom, which were found in chapter 3.2.

More precisely, the Hamiltonian is approximated by

$$H = \sum_{j=1}^Z \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \frac{e^2}{4\pi\epsilon_0 r_j} \right\} \quad (5.2)$$

The approximate Hamiltonian eigenvalue problem can now be solved using a method of separation of variables in which it is assumed that the wave function equals:

$$\psi = \phi_1(\vec{r}_1, S_{z1})\phi_2(\vec{r}_2, S_{z2}) \dots \phi_Z(\vec{r}_Z, S_{zZ})$$

where the states  $\phi_1, \phi_2, \dots$  are still to be determined. After substitution of this assumption into  $H\psi = E\psi$ , the problems for the individual electrons can be separated out using similar ideas as used for the harmonic oscillator in chapter 2.7.2. It is then found that each of the functions  $\phi_1, \phi_2, \dots$  satisfies the same problem as the electron in the hydrogen atom, chapter 3.2.1, hence must have the same solutions.

In particular, for electron 1, a complete set of solutions for  $\phi_1(\vec{r}_1, S_{z1})$  is, from chapter 3.2.2, but now also including spin:

$$\psi_{100}(\vec{r}_1) \uparrow, \psi_{100}(\vec{r}_1) \downarrow, \psi_{200}(\vec{r}_1) \uparrow, \psi_{200}(\vec{r}_1) \downarrow, \psi_{211}(\vec{r}_1) \uparrow, \psi_{211}(\vec{r}_1) \downarrow, \dots$$

A typical solution in this set will be indicated by  $\psi_{n_1 l_1 m_1}(\vec{r}_1) \uparrow$ , where  $n_1, l_1$ , and  $m_1$  are the quantum numbers of the solution, and  $\uparrow$  can either be spin up or spin down.

The problems for the other electrons are the same, so they have equivalent solutions. The combined energy eigenfunctions for the entire atom are therefore all of the form

$$\psi_{n_1 l_1 m_1}(\vec{r}_1) \uparrow \psi_{n_2 l_2 m_2}(\vec{r}_2) \uparrow \dots \psi_{n_Z l_Z m_Z}(\vec{r}_Z) \uparrow \quad (5.3)$$

Any distinct possible choice of the  $3Z$  quantum numbers and  $Z$  spin values produces a different eigenfunction for the complete atom.

This solves the Hamiltonian eigenvalue problem under the shielding approximation. However, the electrons are identical fermions, so in general we will still have to combine different eigenfunctions together to satisfy the antisymmetrization requirements for electron exchange, as discussed in chapter 4.8.

### 5.1.3 Hydrogen and helium

In this subsection, we begin the discussion of the approximate ground states of the elements. Although the approximations made are crude, the results do give a lot of qualitative insight into the nature of the elements.

Atomic number  $Z = 1$  corresponds to hydrogen, which was already discussed in chapter 3.2. The lowest energy state, or ground state, is  $\psi_{100}$ , also called the “1s” state, and the single electron can be in the spin-up or spin-down versions of that state, or in any combination of the two. The most general ground state wave function is therefore:

$$\Psi(\vec{r}_1, S_{z1}) = c_1 \psi_{100}(\vec{r}_1) \uparrow + c_2 \psi_{100}(\vec{r}_1) \downarrow \quad (5.4)$$

The “ionization energy” that would be needed to remove the electron from the atom is the absolute value of the energy eigenvalue  $E_1$ , or 13.6 eV, as derived in chapter 3.2.

For helium, with  $Z = 2$ , in the ground state both electrons are in the lowest possible energy state  $\psi_{100}$ . But since electrons are identical fermions, the antisymmetrization requirement now rears its head. It requires that the two states  $\psi_{100}(\vec{r}) \uparrow$  and  $\psi_{100}(\vec{r}) \downarrow$  appear together in the form of a Slater determinant (chapter 4.8):

$$\Psi(\vec{r}_1, S_{z1}, \vec{r}_2, S_{z2}; t) = \frac{c}{\sqrt{2}} \begin{vmatrix} \psi_{100}(\vec{r}_1) \uparrow & \psi_{100}(\vec{r}_1) \downarrow \\ \psi_{100}(\vec{r}_2) \uparrow & \psi_{100}(\vec{r}_2) \downarrow \end{vmatrix} \quad (5.5)$$

or, writing out the Slater determinant:

$$c \psi_{100}(\vec{r}_1) \psi_{100}(\vec{r}_2) \frac{\uparrow \downarrow - \uparrow \downarrow}{\sqrt{2}}$$

The spatial part is symmetric with respect to exchange of the two electrons. The spin state is antisymmetric; it is the singlet configuration with zero net spin of chapter 4.6.5.



Figure 5.1: Approximate solutions for hydrogen (left) and helium (right).

Figure 5.1 shows the probability density for the first two elements, indicating where electrons are most likely to be found.

It is good to remember that the  $\psi_{100} \uparrow$  and  $\psi_{100} \downarrow$  states are commonly indicated as the “K shell” after the first initial of the airline of the Netherlands.

The analysis predicts that the ionization energy to remove *one* electron from helium would be 13.6 eV, the same as for the hydrogen atom. This is a very bad approximation indeed; the truth is almost double, 24.6 eV.

The problem is the made assumption that the repulsion by the other electron “shields” one of the two protons in the helium nucleus, so that only a single-proton hydrogen nucleus is seen. When electron wave functions overlap significantly as they do here, their mutual repulsion is a lot less than you would naively expect. As a result, the second proton is only partly shielded, and the electron is held much more tightly than the analysis predicts.

However, despite the inaccuracy of the approximation chosen, it is probably best to stay consistent, and not fool around at random. It must just be accepted that the theoretical energy levels will be too small in magnitude {24}.

The large ionization energy of helium is one reason that it is chemically inert. Helium is called a “noble” gas, presumably because nobody expects nobility to do anything.

#### 5.1.4 Lithium to neon

The next element is lithium, with three electrons. This is the first element for which the antisymmetrization requirement forces the theoretical energy to go above the hydrogen ground state level  $E_1$ . The reason is that there is no way to create an antisymmetric wave function for three electrons using only the two lowest energy states  $\psi_{100} \uparrow$  and  $\psi_{100} \downarrow$ . A Slater determinant for three electrons must have three different states. One or more of the eight  $\psi_{2lm} \downarrow$  states with energy  $E_2$  will have to be thrown into the mix.

This effect of the antisymmetrization requirement, that a new state must become “occupied” every time an electron is added is known as the Pauli exclusion principle. It causes the energy values to become larger and larger as the supply of low energy states runs out.

The transition to the higher energy level  $E_2$  is reflected in the fact that in the “periodic table” of the elements, table 5.1, lithium starts a new row.

	I	II	III	IV	V	VI	VII	0
K	H 1 13.6 2.20							He 2 24.6 —
L	Li 3 5.4 0.98	Be 4 9.3 1.57	B 5 8.3 2.04	C 6 11.3 2.55	N 7 14.5 3.04	O 8 13.6 3.44	F 9 17.4 3.98	Ne 10 21.6 —
M	Na 11 5.1 0.93	Mg 12 7.6 1.31	Al 13 6.0 1.61	Si 14 8.1 1.90	P 15 10.5 2.19	S 16 10.4 2.58	Cl 17 13.0 3.16	Ar 18 15.8 —
N	K 19 4.3 0.82	Ca 20 6.1 1.00	Ga 31 6.0 1.81	Ge 32 7.9 2.01	As 33 9.8 2.18	Se 34 9.7 2.55	Br 35 11.8 2.96	Kr 36 14.0 —

transition metals:

Sc 21 6.5 1.36	Ti 22 6.8 1.54	V 23 6.7 1.63	Cr 24 6.8 1.66	Mn 25 7.4 1.55	Fe 26 7.9 1.83	Co 27 7.9 1.88	Ni 28 7.6 1.91	Cu 29 7.7 1.9	Zn 30 9.4 1.65
-------------------	-------------------	------------------	-------------------	-------------------	-------------------	-------------------	-------------------	------------------	-------------------

Table 5.1: Abbreviated periodic table of the elements, showing element symbol, atomic number, ionization energy, and electronegativity.

For the third electron of the lithium atom, the available states with theoretical energy  $E_2$  are the  $\psi_{200}\uparrow$  “2s” states and the  $\psi_{211}\uparrow$ ,  $\psi_{210}\uparrow$ , and  $\psi_{21-1}\uparrow$  “2p” states, a total of eight possible states. These states are commonly called the “L shell.”

Within the crude nuclear shielding approximation made, all eight states have the same energy. However, on closer examination, the spherically symmetric 2s states really have less energy than the 2p ones. Very close to the nucleus, shielding is not a factor and the full attractive nuclear force is felt. So a state in which the electron is more likely to be close to the nucleus has less energy. That are the 2s states; in the 2p states, which have nonzero orbital angular momentum, the electron tends to stay away from the immediate vicinity of the nucleus {25}.

Within the assumptions made, there is no preference with regard to the spin direction of the 2s state, allowing two Slater determinants to be formed.

$$\frac{c_1}{\sqrt{6}} \begin{vmatrix} \psi_{100}(\vec{r}_1)\uparrow & \psi_{100}(\vec{r}_1)\downarrow & \psi_{200}(\vec{r}_1)\uparrow \\ \psi_{100}(\vec{r}_2)\uparrow & \psi_{100}(\vec{r}_2)\downarrow & \psi_{200}(\vec{r}_2)\uparrow \\ \psi_{100}(\vec{r}_3)\uparrow & \psi_{100}(\vec{r}_3)\downarrow & \psi_{200}(\vec{r}_3)\uparrow \end{vmatrix} + \frac{c_2}{\sqrt{6}} \begin{vmatrix} \psi_{100}(\vec{r}_1)\uparrow & \psi_{100}(\vec{r}_1)\downarrow & \psi_{200}(\vec{r}_1)\downarrow \\ \psi_{100}(\vec{r}_2)\uparrow & \psi_{100}(\vec{r}_2)\downarrow & \psi_{200}(\vec{r}_2)\downarrow \\ \psi_{100}(\vec{r}_3)\uparrow & \psi_{100}(\vec{r}_3)\downarrow & \psi_{200}(\vec{r}_3)\downarrow \end{vmatrix} \quad (5.6)$$

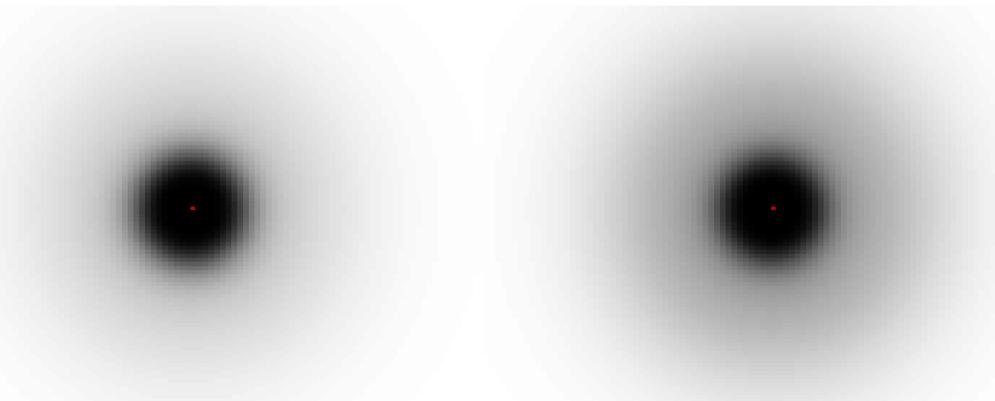


Figure 5.2: Approximate solutions for lithium (left) and beryllium (right).

It is common to say that the “third electron goes into a  $\psi_{200}$ ” state. Of course that is not quite precise; the Slater determinants above have the first two electrons in  $\psi_{200}$  states too. But the third electron adds the third state to the mix, so in that sense it more or less “owns” the state. For the same reason, the Pauli exclusion principle is commonly phrased as “no two electrons may occupy the same state”, even though the Slater determinants imply that all electrons share all states equally.

Since the third electron is bound with the much lower energy  $|E_2|$  instead of  $|E_1|$ , it is rather easily given up. Despite the fact that the lithium ion has a nucleus that is 50% stronger than the one of helium, it only takes a ionization energy of 5.4 eV to remove an electron from lithium, versus 24.6 eV for helium. The theory would predict a ionization energy  $|E_2| = 3.4$  eV for lithium, which is close, so it appears that the two 1s electrons shield their protons quite well from the 2s one. This is in fact what one would expect, since the 1s electrons are quite close to the nucleus compared to the large radial extent of the 2s state.

Lithium will readily give up its loosely bound third electron in chemical reactions. Conversely, helium would have even less hold on a third electron than lithium, because it has only two protons in its nucleus. Helium simply does not have what it takes to seduce an electron away from another atom. This is the second part of the reason that helium is chemically inert: it neither will give up its electrons nor take on additional ones.

Thus the Pauli exclusion principle causes different elements to behave chemically in very different ways. Even elements that are just one unit apart in atomic number such as helium (inert) and lithium (very active).

For beryllium, with four electrons, the same four states as for lithium combine in a single  $4 \times 4$  Slater determinant;

$$\frac{c}{\sqrt{24}} \begin{vmatrix} \psi_{100}(\vec{r}_1) \uparrow & \psi_{100}(\vec{r}_1) \downarrow & \psi_{200}(\vec{r}_1) \uparrow & \psi_{200}(\vec{r}_1) \downarrow \\ \psi_{100}(\vec{r}_2) \uparrow & \psi_{100}(\vec{r}_2) \downarrow & \psi_{200}(\vec{r}_2) \uparrow & \psi_{200}(\vec{r}_2) \downarrow \\ \psi_{100}(\vec{r}_3) \uparrow & \psi_{100}(\vec{r}_3) \downarrow & \psi_{200}(\vec{r}_3) \uparrow & \psi_{200}(\vec{r}_3) \downarrow \\ \psi_{100}(\vec{r}_4) \uparrow & \psi_{100}(\vec{r}_4) \downarrow & \psi_{200}(\vec{r}_4) \uparrow & \psi_{200}(\vec{r}_4) \downarrow \end{vmatrix} \quad (5.7)$$

The ionization energy jumps up to 9.3 eV, due to the increased nuclear strength and the fact that the fellow 2s electron does not shield its proton as well as the two 1s electrons do theirs.

For boron, one of the  $\psi_{21m}$  “2p” states will need to be occupied. Within the approximations made, there is no preference for any particular state. As an example, figure 5.3 shows the approximate solution in which the  $\psi_{210}$ , or “ $2p_z$ ” state is occupied. It may be recalled from figure 3.5 that this state remains close to the  $z$ -axis (which is horizontal in the figure.) As a result, the wave function becomes directional. The ionization energy decreases a bit to 8.3

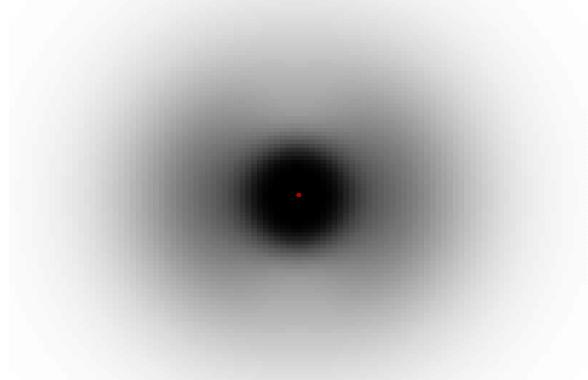


Figure 5.3: Example approximate solution for boron.

eV, indicating that indeed the 2p states have higher energy than the 2s ones.

For carbon, a second  $\psi_{21m}$  state needs to be occupied. Within the made approximations, the second 2p electron could also go into the  $2p_z$  state. However, in actuality, repulsion by the electron already in the  $2p_z$  state makes it preferable for the new electron to stay away from the  $z$ -axis, which it can do by going into the  $2p_x$  state. This state is around the vertical  $x$ -axis instead of the horizontal  $z$ -axis. As noted in chapter 3.2,  $2p_x$  is a  $\psi_{21m}$  combination state.

For nitrogen, the third 2p electron can go into the  $2p_y$  state, which is around the  $y$ -axis. There are now three 2p electrons, each in a different spatial state.

However, for oxygen the game is up. There are no more free spatial states in the L shell. The new electron will have to go, say, into the  $p_y$  state, pairing up with the electron already there in an opposite-spin singlet state. The repulsion by the fellow electron in the same state reflects in a decrease in ionization energy compared to nitrogen.

For fluorine, the next electron goes into the  $2p_x$  state, leaving only the  $2p_z$  state unpaired.

For neon, all 2p electrons are paired, and the L shell is full. This makes neon an inert noble gas like helium: it cannot accommodate any more electrons at the  $E_2$  energy level, and, with the strongest nucleus among the L-shell elements, it holds tightly onto the electrons it has.

On the other hand, the previous element, fluorine, has a nucleus that is almost as strong,

and it can accommodate an additional electron in its unpaired  $2p_z$  state. So fluorine is very willing to steal an electron if it can get away with it. The capability to draw electrons from other elements is called “electronegativity,” and fluorine is the most electronegative of them all.

Neighboring elements oxygen and nitrogen are less electronegative, but oxygen can accommodate two additional electrons rather than one, and nitrogen will even accommodate three.

### 5.1.5 Sodium to argon

Starting with sodium (sodium), the  $E_3$ , or “M shell” will begin to be filled. Sodium has a single  $3s$  electron in the outermost shell, which makes it much like lithium, with a single  $2s$  electron in its outermost shell. Since the outermost electrons are the critical ones in chemical behavior, sodium is chemically much like lithium. Both are metals with a “valence” of one; they are willing to sacrifice one electron.

Similarly, the elements following sodium in the third row of the periodic table 5.1 mirror the corresponding elements in the previous row. Near the end of the row, the elements are again eager to accept additional electrons in the still vacant  $3p$  states.

Finally argon, with no  $3s$  and  $3p$  vacancies left, is again inert. This is actually somewhat of a surprise, because the  $E_3$  M-shell also includes  $10 \psi_{32m} \uparrow$  states. These states of increased angular momentum are called the “ $3d$ ” states. According to the approximations made, the  $3s$ ,  $3p$ , and  $3d$  states would all have the same energy. So it might seem that argon could accept additional electrons into the  $3d$  states.

But it was already noted that the p states in reality have more energy than the s states, and the d states have even more. The reason is the same: the d states stay even further away from the nucleus than the p states. Because of the higher energy of the d states, argon is really not willing to accept additional electrons.

### 5.1.6 Kalium to krypton

The logical continuation of the story so far would be that the kalium atom would be the first one to put an electron into a  $3d$  state. However, by now the shielding approximation starts to fail not just quantitatively, but qualitatively. The  $3d$  states actually have so much more energy than the  $3s$  states that they even exceed the energy of the  $4s$  states. Kalium puts its last electron into a  $4s$  state, not a  $3d$  one. This makes its outer shell much like the ones of lithium and sodium, so it starts a new row in the periodic table.

The next element, calcium, fills the  $4s$  shell, putting an end to that game. Since the six  $4p$

states have more energy, the next ten elements now start filling the skipped 3d states with electrons, leaving the N-shell with 2 electrons in it. (Actually, this is not quite precise; the 3d and 4s energies are closely together, and for copper and chromium one of the two 4s electrons turns out to switch to a 3d state.) In any case, it takes until gallium until the six 4p states start filling, which is fully accomplished at krypton. Krypton is again a noble gas, though it can form a weak bond with chlorine.

Continuing to still heavier elements, the energy levels get even more confused. We will stop while we are still ahead.

## 5.2 Chemical Bonds

The electron states, or “atomic orbitals”, of the elements discussed in the previous section form the basis for the “valence bond” description of chemical bonds. This section summarizes some of the basic ideas involved.

### 5.2.1 Covalent sigma bonds

As pointed out in the previous section, helium is chemically inert: its outermost, and only, shell can hold two electrons, and it is full. But hydrogen has only one electron, leaving a vacant position for another 1s electron. As discussed earlier in chapter 4.2, two hydrogen atoms are willing to *share* their electrons. This gives each atom in some sense two electrons in its shell, filling it up. The shared state has lower energy than the two separate atoms, so the H<sub>2</sub> molecule stays together. A sketch of the shared 1s electrons was given in figure 4.2.

Fluorine has one vacant spot for an electron in its outer shell just like hydrogen; its outer shell can contain 8 electrons and fluorine has only seven. One of its 2p states, assume it is the horizontal axial state 2p<sub>z</sub>, has only one electron in it instead of two. Two fluorine atoms can share their unpaired electrons much like hydrogen atoms do and form an F<sub>2</sub> molecule. This gives each of the two atoms a filled shell. The fluorine molecular bond is sketched in figure 5.4 (all other electrons have been omitted.) This bond between p electrons looks quite different from the H<sub>2</sub> bond between s electrons in figure 4.2, but it is again a covalent one, in which the electrons are shared. In addition, both bonds are called “sigma” bonds: if we look at either bond *from the side*, it looks rotationally symmetric, just like an s state. (Sigma is the Greek equivalent of the letter s; it is written as  $\sigma$ .)

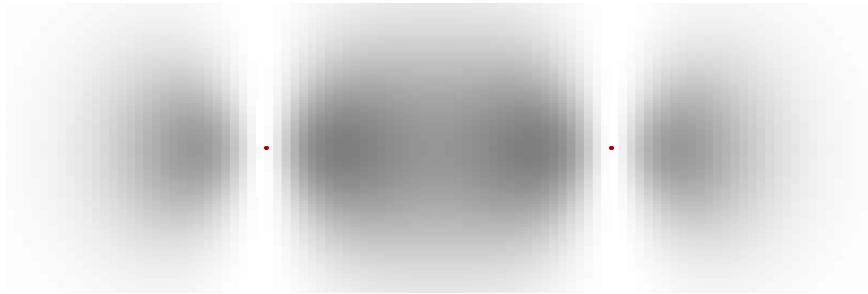


Figure 5.4: Covalent sigma bond consisting of two  $2p_z$  states.

### 5.2.2 Covalent pi bonds

The  $N_2$  nitrogen molecule is another case of covalent bonding. Nitrogen atoms have a total of three unpaired electrons, one each in the  $2p_x$ ,  $2p_y$ , and  $2p_z$  states. Two nitrogen atoms can share their unpaired  $2p_z$  electrons in a sigma bond the same way that fluorine does, longitudinally.

However, the  $2p_x$  and  $2p_y$  states are normal to the line through the nuclei; these states must be matched up sideways. Figure 5.5 illustrates this for the bond between the two vertical  $2p_x$  states. This covalent bond, and the corresponding one between the  $2p_y$  states, looks like a p

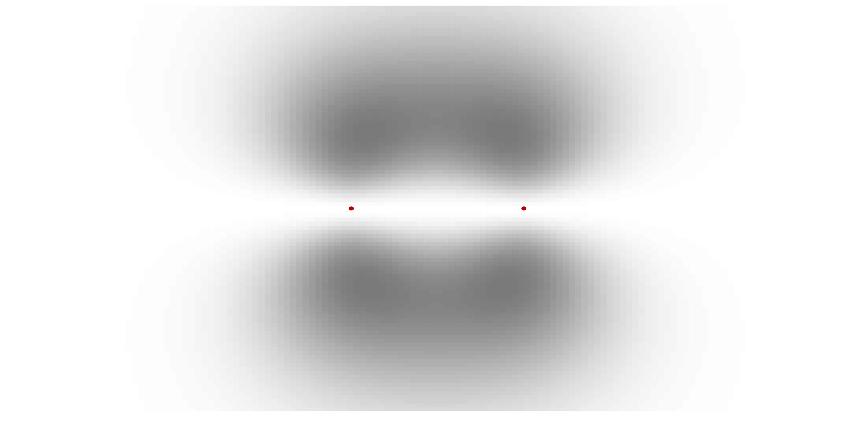


Figure 5.5: Covalent pi bond consisting of two  $2p_x$  states.

state when seen from the side, and it is called a “pi” or  $\pi$  bond.

So, the  $N_2$  nitrogen molecule is held together by two pi bonds in addition to a sigma bond, making a triple bond. It is a relatively inert molecule.

### 5.2.3 Polar covalent bonds and hydrogen bonds

Oxygen, located in between fluorine and nitrogen in the periodic table, has two unpaired electrons. It can share these electrons with another oxygen atom to form  $O_2$ , the molecular oxygen we breath. However, it can instead bind with two hydrogen atoms to form  $H_2O$ , the water we drink.

In the water molecule, the lone  $2p_z$  electron of oxygen is paired with the  $1s$  electron of one hydrogen atom, as shown in figure 5.6. Similarly, the lone  $2p_y$  electron is paired with the  $1s$

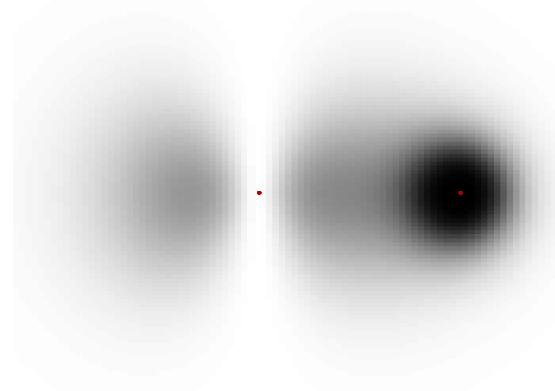


Figure 5.6: Covalent sigma bond consisting of a  $2p_z$  and a  $1s$  state.

electron of the other hydrogen atom. Both bonds are sigma bonds: they are located on the connecting line between the nuclei. But in this case each bond consists of a  $1s$  and a  $2p$  state, rather than states of the same type.

Since the  $x$  and  $y$  axis are orthogonal, the two hydrogen atoms in water should be at a 90 degree angle from each other. (Without valence bond theory, the most logical guess would surely have been that they would be at opposite sides of the oxygen atom.) The predicted 90 degree angle is in fair approximation to the experimental value of 105 degrees.

The reason that the actual angle is a bit more may be understood from the fact that the oxygen atom has a higher affinity for the shared electrons, or electronegativity, than the hydrogen atoms. It will pull the electrons partly away from the hydrogen atoms, giving itself some negative charge, and the hydrogen atoms a corresponding positive one. The positively charged hydrogen atoms repel each other, increasing their angle a bit. If we go down one place in the periodic table below oxygen, to the larger sulfur atom,  $H_2S$  has its hydrogen atoms under about 93 degrees, quite close to 90 degrees.

Bonds like the one in water, where the negative electron charge shifts towards the more electronegative atom, are called “polar” covalent bonds. It has significant consequences for water, since the positively charged hydrogen atoms can electrostatically attract the negatively charged oxygen atoms on *other* molecules. This has the effect of creating bonds between

different molecules called “hydrogen bonds.” While much weaker than covalent bonds, they are strong enough to affect the physical properties of water. For example, they are the reason that water is normally a liquid instead of a gas, and that ice floats on water.

### 5.2.4 Promotion and hybridization

While valence bond theory managed to explain a number of chemical bonds so far, two more important ingredients need to be added. Otherwise it will not at all be able to explain organic chemistry, the chemistry of carbon critical to life.

Carbon has two unpaired 2p electrons just like oxygen does; the difference between the atoms is that oxygen has in addition two paired 2p electrons. With two unpaired electrons, it might seem that carbon should form two bonds like oxygen.

But that is not what happens; normally carbon forms four bonds instead of two. In chemical bonds, one of carbon’s paired 2s electrons moves to the empty 2p state, leaving carbon with four unpaired electrons. It is said that the 2s electron is “promoted” to the 2p state. This requires energy, but the energy gained by having four bonds more than makes up for it.

Promotion explains why a molecule such as CH<sub>4</sub> forms. Including the 4 shared hydrogen electrons, the carbon atom has 8 electrons in its outer shell, so its shell is full. It has made as many bonds as it can support.

However, promotion is still not enough to explain the molecule. If the CH<sub>4</sub> molecule was merely a matter of promoting one of the 2s electrons into the vacant 2p<sub>y</sub> state, the molecule should have three hydrogen atoms under 90 degrees, sharing the 2p<sub>x</sub>, 2p<sub>y</sub> and 2p<sub>z</sub> electrons respectively, and one hydrogen atom elsewhere, sharing the remaining 2s electron. In reality, the CH<sub>4</sub> molecule is shaped like a regular tetrahedron, with angles of 109.5 degrees between all four hydrogens.

The explanation is that, rather than using the 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub>, and 2s states directly, the carbon atom forms new combinations of the four called “hybrid” states. (This is not unlike how the torus-shaped  $\psi_{211}$  and  $\psi_{21-1}$  states were recombined in chapter 3.2 to produce the equivalent 2p<sub>x</sub> and 2p<sub>y</sub> pointer states.)

In case of CH<sub>4</sub>, the carbon converts the 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub> states into four new states. These are called sp<sup>3</sup> states, since they are formed from one s and three p states. They are

given by:

$$|\text{sp}_a^3\rangle = \frac{1}{2}(|2s\rangle + |2p_x\rangle + |2p_y\rangle + |2p_z\rangle)$$

$$|\text{sp}_b^3\rangle = \frac{1}{2}(|2s\rangle + |2p_x\rangle - |2p_y\rangle - |2p_z\rangle)$$

$$|\text{sp}_c^3\rangle = \frac{1}{2}(|2s\rangle - |2p_x\rangle + |2p_y\rangle - |2p_z\rangle)$$

$$|\text{sp}_d^3\rangle = \frac{1}{2}(|2s\rangle - |2p_x\rangle - |2p_y\rangle + |2p_z\rangle)$$

where the kets denote the wave functions of the indicated states.

All four  $\text{sp}^3$  hybrids have the same shape, shown in figure 5.7. The asymmetrical shape can

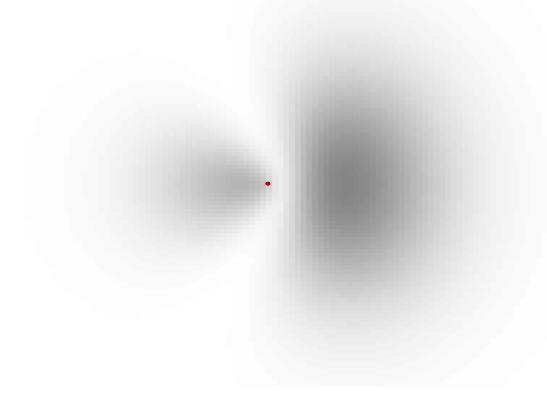


Figure 5.7: Shape of an  $\text{sp}^3$  hybrid state.

increase the overlap between the wave functions in the bond. The four  $\text{sp}^3$  hybrids are under equal 109.5 degrees angles from each other, producing the tetrahedral structure of the  $\text{CH}_4$  molecule. And of diamond, for that matter. With the atoms bound together in all spatial directions, diamond is an extremely hard material.

But carbon is a very versatile atom. In graphite, and carbon nanotubes, carbon atoms arrange themselves in layers instead of three dimensional structures. Carbon achieves this trick by leaving the 2p-state in the direction normal to the plane, call it  $p_x$ , out of the hybridization. The two 2p states in the plane plus the 2s state can then be combined into three  $\text{sp}^2$  states:

$$|\text{sp}_a^2\rangle = \frac{1}{\sqrt{3}}|2s\rangle + \frac{2}{\sqrt{6}}|2p_z\rangle$$

$$|\text{sp}_b^2\rangle = \frac{1}{\sqrt{3}}|2s\rangle - \frac{1}{\sqrt{6}}|2p_z\rangle + \frac{1}{\sqrt{2}}|2p_y\rangle$$

$$|\text{sp}_c^2\rangle = \frac{1}{\sqrt{3}}|2s\rangle - \frac{1}{\sqrt{6}}|2p_z\rangle - \frac{1}{\sqrt{2}}|2p_y\rangle$$

Each is shaped as shown in figure 5.8. These planar hybrids are under 120 degree angles from

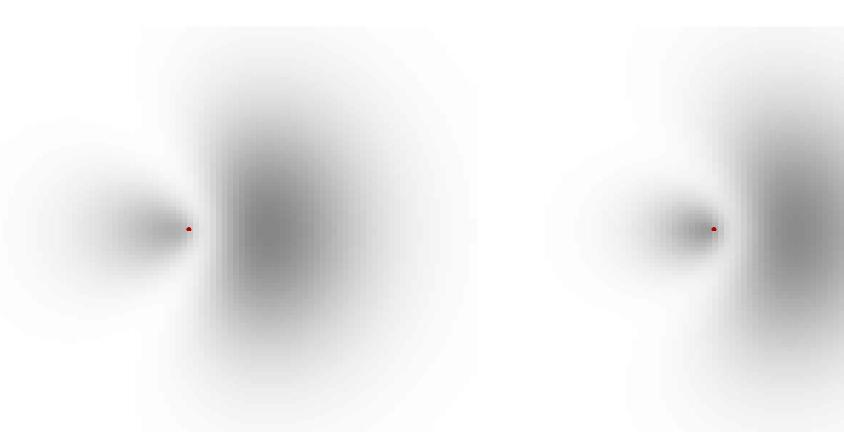


Figure 5.8: Shapes of the  $sp^2$  (left) and  $sp$  (right) hybrids.

each other, giving graphite its hexagonal structure. The left-out p electrons normal to the plane can form pi bonds with each other. A planar molecule formed using  $sp^2$  hybridization is ethylene ( $C_2H_4$ ); it has all six nuclei in the same plane. The pi bond normal to the plane prevents out-of-plane rotation of the nuclei around the line connecting the carbons, keeping the plane rigid.

Finally, carbon can combine the 2s state with a single 2p state to form two  $sp$  hybrids under 180 degrees from each other:

$$|sp_a\rangle = \frac{1}{\sqrt{2}}(|2s\rangle + |2p_z\rangle)$$

$$|sp_b\rangle = \frac{1}{\sqrt{2}}(|2s\rangle - |2p_z\rangle)$$

An example  $sp$  hybridization is acetylene ( $C_2H_2$ ), which has all its four nuclei on a single line.

### 5.2.5 Ionic bonds

Ionic bonds are the extreme polar bonds; they occur if there is a big difference between the electronegativities of the atoms involved.

An example is kitchen salt,  $NaCl$ . The sodium atom has only one electron in its outer shell, a loosely bound 3s one. The chlorine has seven electrons in its outer shell and needs only one more 3p one to fill it. When the two react, the chlorine does not just share the lone electron of the sodium atom, it simply takes it away. It makes the chlorine a negatively charged ion. Similarly, it leaves the sodium as a positively charged ion.

The charged ions are bound together by electrostatic forces. Since these forces act in all directions, each ion does not just attract the opposite ion it exchanged the electron with, but

all surrounding opposite ions. And since in salt each sodium ion is surrounded by six chlorine ions and vice versa, the number of bonds that exists is large.

Since so many bonds must be broken to take a ionic substance apart, their properties are quite different from covalently bounded substances. For example, salt is a solid with a high melting point, while the covalently bounded  $\text{Cl}_2$  chlorine molecule is normally a gas, since the bonds between different molecules are weak.

### 5.2.6 Limitations of valence bond theory

Valence bond theory does a terrific job of describing chemical bonds, producing a lot of essentially correct, and very nontrivial predictions, but it does have limitations.

One place it fails is for the  $\text{O}_2$  oxygen molecule. In the molecule, the atoms share their unpaired  $2p_x$  and  $2p_z$  electrons. With all electrons symmetrically paired in the spatial states, the electrons should all be in singlet spin states having no net spin. However, it turns out that oxygen is strongly paramagnetic, indicating that there is in fact net spin. The problem in valence bond theory that causes this error is that it ignores the already paired-up electrons in the  $2p_y$  states. In the molecule, the filled  $2p_y$  states of the atoms are next to each other and they do interact. In particular, one of the total of four  $2p_y$  electrons jumps over to the  $2p_x$  states, where it only experiences repulsion by two other electrons instead of by three. The spatial state of the electron that jumps over is no longer equal to that of its twin, allowing them to have equal instead of opposite spin.

Valence bond theory also has problems with single-electron bonds such as the hydrogen molecular ion, or with benzene, in which the carbon atoms are held together with what is essentially 1.5 bonds, or rather, bonds shared as in a two state system. Excited states produce major difficulties. Various fixes and improved theories exist.

## 5.3 Confined Electrons

Heisenberg's uncertainty relationship implies that the more we try to confine a set of particles spatially, the more linear momentum they have to have. Such increased momentum means increased kinetic energy.

Confined fermions, such as the valence electrons in solids, add another twist. They cannot all just go into whatever is the state of lowest energy: the Pauli exclusion principle, (or antisymmetrization requirement), forces them to spread out to higher energy states. The resulting large kinetic energy of the electrons creates an internal pressure, called "degeneracy pressure", that allows solids to withstand high external pressures without collapsing. This

section analyzes this using a highly idealized model called the “free electron gas.”

### 5.3.1 The Hamiltonian eigenvalue problem

The first step to solve the problem of confined electrons is to write down the Hamiltonian. To keep things simple, we will follow the simple but surprisingly effective model of Sommerfeld. In this model it assumed that the electrons do not experience any forces. Of course, electrons should repel each other, but the crude assumption is that the net force comes from all directions and averages away. Similarly, valence electrons moving through a crystal structure should experience forces from the atoms they pass, but this too will be ignored. We have what is called a free electron gas, in which the potential is a constant. This potential will be taken to be zero. (A nonzero value would merely shift the energy levels by that amount without changing the physics.)

Under those assumptions, the total energy Hamiltonian is just the kinetic energy operator  $\hat{T}$  of chapter 2.3, and the Hamiltonian eigenvalue problem for each electron is

$$-\frac{\hbar^2}{2m_e} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \psi = E\psi \quad (5.8)$$

It will further be assumed that the electrons are confined to a rectangular solid block of dimensions  $\ell_x \times \ell_y \times \ell_z$ :

$$0 \leq x \leq \ell_x \quad 0 \leq y \leq \ell_y \quad 0 \leq z \leq \ell_z \quad (5.9)$$

The boundary condition on the surface of the block is that  $\Psi = 0$  there. Physically, if electrons attempt to escape from the solid their potential energy increases rapidly because the atom nuclei pull them back. This means that the wave function beyond the surface must be vanishingly small, and becomes zero on the surface in case of perfect confinement.

### 5.3.2 Solution by separation of variables

The Hamiltonian eigenvalue problem derived in the previous section can be solved much like that of the harmonic oscillator in chapter 2.7.2, and it is really simpler. The problem is in fact equivalent to the particle in the pipe of chapter 2.6.

Assuming that each eigenfunction takes the form  $\psi = X(x)Y(y)Z(z)$  like for the harmonic oscillator, the eigenvalue problem falls apart into partial problems in each of the three coordinate directions. In particular, the partial problem in the  $x$  direction is:

$$-\frac{\hbar^2}{2m_e} \frac{\partial^2 X}{\partial x^2} = E_x X$$

where  $E_x$  is the measurable value of the kinetic energy in the  $x$ -direction.

The normalized solutions of this equation are all of the form

$$\sqrt{\frac{2}{\ell_x}} \sin(k_x x)$$

in which  $k_x$  is a constant which is called the “wave number in the  $x$ -direction.” The higher the value of this wave number, the more rapidly the sine oscillates up and down in the  $x$ -direction. To avoid counting equivalent eigenfunctions twice,  $k_x$  must be taken positive.

The sinusoidal solution above may be checked by simple substitution in the partial problem. Doing so produces the following important relationship between the wave number and the partial energy eigenvalue:

$$E_x = \frac{\hbar^2}{2m_e} k_x^2$$

So, the wave number  $k_x$  is a direct measure for the energy  $E_x$  of the state.

To satisfy the boundary condition that  $\psi = 0$  at  $x = \ell_x$ ,  $\sin(k_x \ell_x)$  must be zero, which is only true for discrete values of the wave number  $k_x$ :

$$k_x = n_x \frac{\pi}{\ell_x} \quad \text{with } n_x \text{ a natural number}$$

Note that the wave numbers are equally spaced;

$$k_{x1} = \frac{\pi}{\ell_x}, \quad k_{x2} = 2\frac{\pi}{\ell_x}, \quad k_{x3} = 3\frac{\pi}{\ell_x}, \quad k_{x4} = 4\frac{\pi}{\ell_x}, \dots$$

Each value is an constant amount  $\pi/\ell_x$  greater than the previous one. Since the wave number is a measure of the energy, these values for the wave number also fix the energy eigenvalues:

$$E_{x1} = \frac{\hbar\pi^2}{2m_e\ell_x^2}, \quad E_{x2} = 4\frac{\hbar\pi^2}{2m_e\ell_x^2}, \quad E_{x3} = 9\frac{\hbar\pi^2}{2m_e\ell_x^2}, \quad E_{x4} = 16\frac{\hbar\pi^2}{2m_e\ell_x^2}, \dots$$

The problems in the  $y$ - and  $z$ -directions are equivalent to the one in the  $x$ -direction, and they have similar solutions. The final three-dimensional combined energy eigenfunctions depend therefore on the values of a so-called “wave number vector”  $\vec{k} = (k_x, k_y, k_z)$  and they are, properly normalized:

$$\psi_{\vec{k}} = \sqrt{\frac{8}{\ell_x \ell_y \ell_z}} \sin(k_x x) \sin(k_y y) \sin(k_z z) \quad (5.10)$$

The corresponding energy eigenvalues only depend on the square magnitude  $k$  of the wave number vector:

$$E_k = \frac{\hbar^2}{2m_e} (k_x^2 + k_y^2 + k_z^2) \equiv \frac{\hbar^2}{2m_e} k^2 \quad (5.11)$$

The possible wave number vector values are

$$k_x = n_x \frac{\pi}{\ell_x} \quad k_y = n_y \frac{\pi}{\ell_y} \quad k_z = n_z \frac{\pi}{\ell_z} \quad \text{with } n_x, n_y, \text{ and } n_z \text{ natural numbers} \quad (5.12)$$

### 5.3.3 Discussion of the solution

This section examines the physical interpretation of the results obtained in the previous subsection.

Each solution turned out to be in terms of a wave number vector  $\vec{k}$ , so to understand it, we must first examine the possible values of this vector. Since the possible values of the components  $(k_x, k_y, k_z)$  are equally spaced in each individual direction, (5.12), the possible wave number vectors form an infinite grid of points as illustrated in figure 5.9.

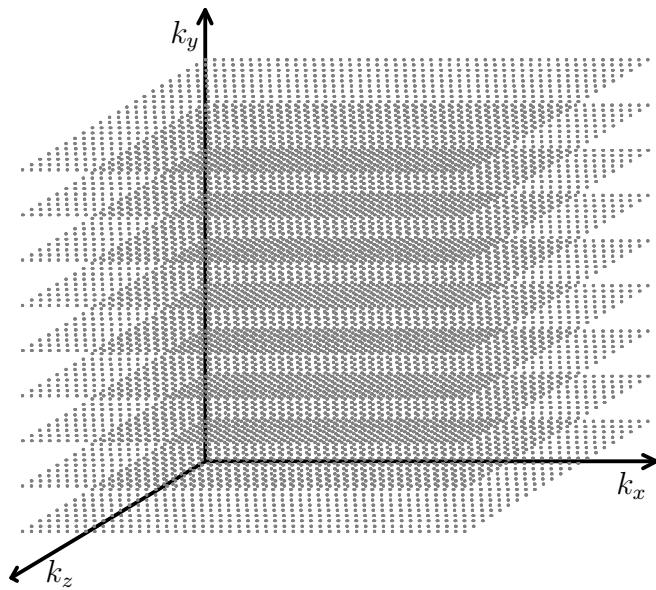


Figure 5.9: Allowed wave number vectors.

Each *point* in this wave number space represents one set of values  $(k_x, k_y, k_z)$ , corresponding to *one* eigenfunction

$$\psi_{\vec{k}} = \sqrt{\frac{8}{\ell_x \ell_y \ell_z}} \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

with an energy:

$$E_k = \frac{\hbar^2}{2m_e} (k_x^2 + k_y^2 + k_z^2) \equiv \frac{\hbar^2}{2m_e} k^2$$

This energy is simply the square distance  $k^2$  of the point from the origin in wave number space, times a simple numerical factor  $\hbar^2/2m_e$ . So the wave number space figure 5.9 also graphically illustrates the possible energy levels by means of the distances of the points to the origin. In particular the lowest energy state available to the electrons occurs for the wave number vector point closest to the origin of wave number space.

That point corresponds to the lowest energy state in the energy spectrum sketched in figure 5.10. Similarly the points farther from the origin in wave number space have correspondingly

higher energy values in the spectrum. (It should be pointed out that actually, the energy levels are not quite as equally spaced as it seems from the shown spectrum figure 5.10.)

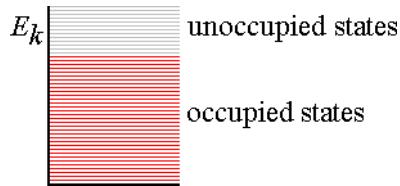


Figure 5.10: Schematic energy spectrum of the free electron gas.

The most interesting eigenfunction is again the ground state of lowest energy, corresponding to absolute zero temperature. If the electrons would have been nice docile bosons, in the ground state they would all be willing to pile into the bottom state of lowest energy in the spectrum. But, just like for the electrons of the atoms in section 5.1, the Pauli exclusion principle allows no more than two electrons for each spatial energy state, one with spin up and one with spin down. So, only two electrons can go into the bottom energy state. The more electrons there are, the more different states must be occupied, and hence, the further the occupied states in the spectrum extend upwards towards higher energy levels. This can raise the energy greatly, since the number of electrons in a macroscopic solid is huge, much more than could possibly be shown in a figure like figure 5.10.

Seen in wave number space figure 5.9, the number of wave number points occupied must be one half the number of electrons. Within that constraint, the lowest energy occurs when the states squeeze as closely to the origin as possible. As a result, the occupied states will cluster around the origin in an eighth of a sphere, as shown in figure 5.11.

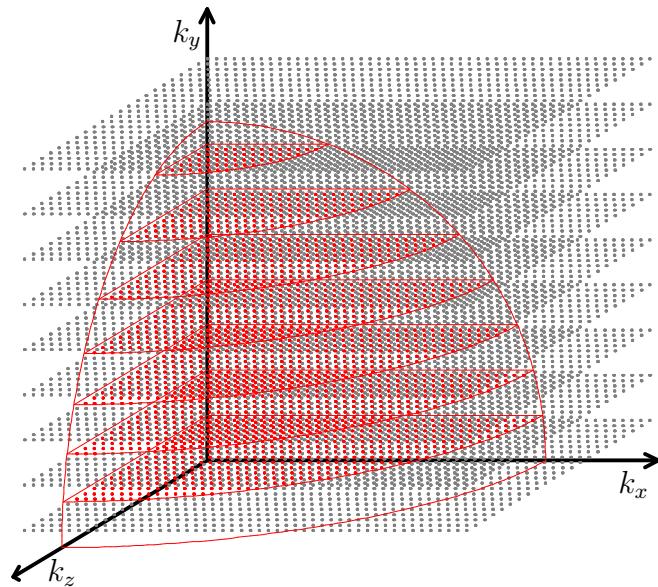


Figure 5.11: Occupied wave number states and Fermi surface in the ground state

The spherical outside surface of the occupied energy states is called the “Fermi surface”. The corresponding energy, the highest occupied energy level, is called the “Fermi energy.” Fermi surfaces are of critical importance in understanding the properties of metals.

### 5.3.4 A numerical example

As an example of the energies involved, consider a  $1 \text{ cm}^3$  block of copper. The block will contain  $8.5 \cdot 10^{22}$  valence electrons, and with up to two electrons allowed per energy state at least  $4.25 \cdot 10^{22}$  different energy states must be occupied.

As shown in figure 5.11, in the ground state of lowest energy, these states form an octant of a sphere in wave number space. But since there are so many electrons, the sphere extends far from the origin, enclosing a lot more state points than could possibly be shown. And remember that the distance from the origin gives the energy of the states. With the states extending so far from origin, the average kinetic energy is as much as a factor  $10^{15}$  larger than what it would have been if the electrons were all in the state of lowest energy right next to the origin. In fact, the average kinetic energy becomes so large that it dwarfs normal heat motion. Copper stays effectively in this ground state until it melts, shrugging off temperature changes.

Macroscopically, the large kinetic energy of the electrons leads to a “degeneracy pressure” on the outside surfaces of the region containing the electrons. This pressure is quite large, of order  $10^{10} \text{ Pa}$ ; it is balanced by the nuclei pulling on the electrons trying to escape, keeping them in the solid. Note that it is *not* mutual repulsion of the electrons that causes the degeneracy pressure; all forces on the electrons were ignored. It is the uncertainty relationship that requires spatially confined electrons to have momentum, and the exclusion principle that explodes the resulting amount of kinetic energy, creating fast electrons that are as hard to contain as students on the last day of classes.

Compared to a  $10^{10} \text{ Pa}$  degeneracy pressure, the normal atmospheric pressure of about  $10^5 \text{ Pa}$  hardly adds any additional compression. Pauli’s exclusion principle makes liquids and solids quite incompressible under normal pressures.

### 5.3.5 The density of states and confinement [Advanced]

The free electron gas is a simple model, but it illustrates a lot of what is different in quantum mechanics compared to classical mechanics. This section provides more insight in what the solution really tells us.

First, of course, it tells us that the possible energy states are discrete, and only two electrons can go into a single state. The Fermi energy and the degeneracy pressure result.

Which brings up the first question: given an energy  $E$ , like the Fermi energy, how many states are there with energy no more than  $E$ ? Assuming the state points are densely spaced in  $k$ -space, this is easy to answer. Consider again figure 5.11. Each point represents a little block, of “volume”, (in  $k$ -space),

$$\Delta k_x \times \Delta k_y \times \Delta k_z = \frac{\pi}{\ell_x} \times \frac{\pi}{\ell_y} \times \frac{\pi}{\ell_z}$$

compare (5.12). Now consider the octant of the sphere bounded by the energy levels  $E$ ; that has a “volume”

$$\frac{1}{8} \frac{4}{3} \pi \left( \frac{2mE}{\hbar^2} \right)^{3/2}$$

since its square radius equals  $2mE/\hbar^2$ . To figure out the number  $N$  of the little blocks that are contained within the octant of the sphere, just take the ratio of the two “volumes”:

$$N = \frac{1}{8} \frac{4}{3} \pi \left( \frac{2mE}{\hbar^2} \right)^{3/2} / \frac{\pi}{\ell_x} \times \frac{\pi}{\ell_y} \times \frac{\pi}{\ell_z} = C \ell_x \ell_y \ell_z E^{3/2}$$

where  $C$  is just shorthand for a collection of constants that are not of interest for our story. Since each little block represents one state, the number of energy states with energy less than  $E$  is also  $N$ .

Note that  $\ell_x \ell_y \ell_z$  is the physical volume of the box in which the electrons are contained, (rather than the mathematical “volumes” in  $k$  space that we manipulated above.) So the formula gets even simpler if you define  $S$  to be the number of states *per unit volume* of the box:

$$S = CE^{3/2}.$$

We have found the number of states with energy *less* than a given value  $E$ .

But physicists are also interested in knowing how many there are with energy approximately *equal* to  $E$ . To express the latter more precisely, we will define the “Density Of States” (DOS) as the number of states with energies in a narrow range about  $E$ , per unit volume and per unit energy range. That makes DOS just the derivative of the states per unit volume  $S$ :

$$\text{DOS} = 1.5CE^{1/2} \tag{5.13}$$

This function is plotted in figure 5.12. One thing it shows is that at higher energy levels, there are more states available.

That would finish the analysis, except that there is a problem. Remember, we found the states  $S$  below a given energy level  $E$  by computing how many little state volumes are contained within the octant of the sphere. That is all very fine when the energy states are densely spaced together in  $k$ -space, but its starts to unravel when they get farther apart. An energy state can either be less than a given energy  $E$  or not: even if half its volume is inside the sphere octant, the state itself will still be outside, not halfway in.

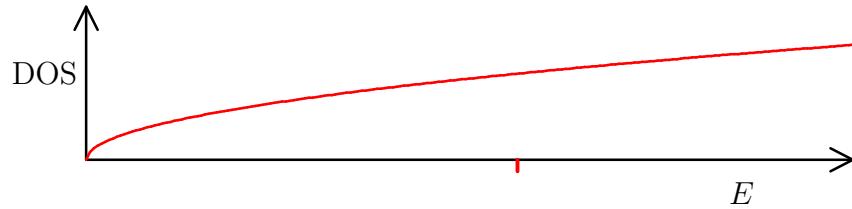


Figure 5.12: Density of states for the free electron gas.

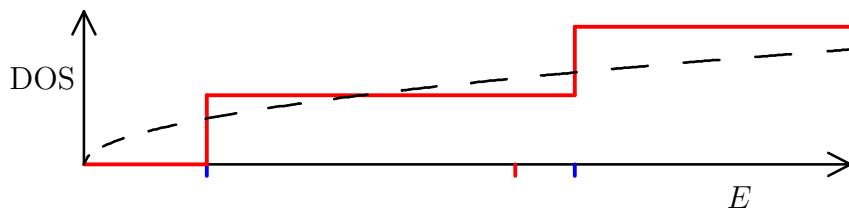
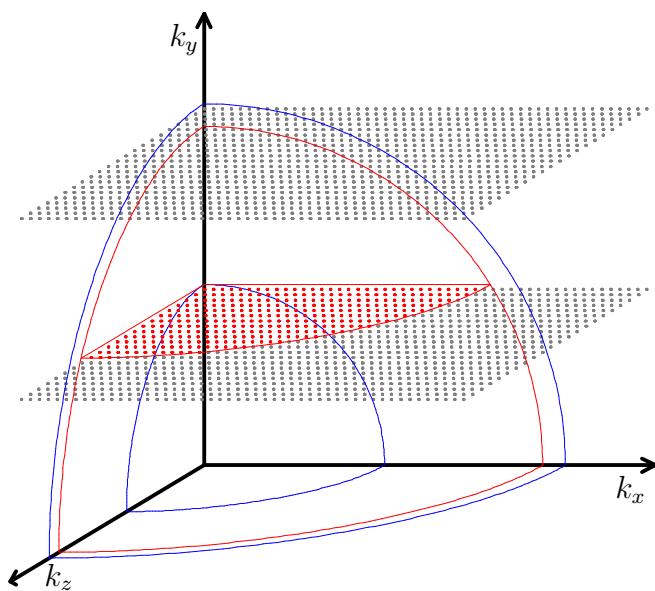


Figure 5.13: Energy states, top, and density of states, bottom, when there is confinement in the  $y$ -direction, as in a quantum well.

That makes a difference when we, for example, squeeze down on the  $y$ -dimension of the box to confine the electrons significantly in the  $y$ -direction in order to create a “quantum well”. Since the spacing of the energy states  $\Delta k_y$  equals  $\pi/\ell_y$ , making  $\ell_y$  small spreads the states well apart in the  $k_y$ -direction, as shown in figure 5.13. Compare this to the nonconfined case figure 5.11.

A look at figure 5.13 shows that now there are no energy states at all, hence no density of states, until the energy, indicated by the size of the red sphere, hits the level of the smaller blue sphere which signifies the start of the first plane of states. When the energy gets a bit above that threshold level, the energy sphere initially gobbles up quite a few states relative to the much reduced box size, and the density of states jumps up. But after that jump, the density of states does not grow like the nonconfined case in figure 5.12 did: while the nonconfined case keeps adding more and more circles of states, here there is only one circle until we eventually hit the level of the second blue sphere. The density of states remains constant before that happens, reflecting the fact that both the area of the circle and the partial energies  $E_x + E_z$  increase proportional to the square of the radius of the circle.

When the energy does hit the level of the larger blue sphere, states from the second plane of states are added, and the DOS jumps up once more. By jumps in the DOS like that, the growth of the nonconfined DOS of figure 5.12 will be approximated when the energy gets big enough.

We can limit the size of the electron-containing box in both the  $y$  and  $z$  directions to create a “quantum wire” where there is full freedom of motion only in the  $x$ -direction. This case is shown in figure 5.14. Now the states separate into individual lines of states. There are no energy states, hence no DOS, until the energy exceeds the level of the smaller blue sphere which just reaches the line of states closest to the origin. Just above that level, a lot of states are encountered relative to the small box volume, and the DOS jumps way up. When the energy increases further, however, the DOS comes down again: compared to the less confined cases, no new lines of states are added until the energy hits the level of the larger blue sphere, at which time the DOS jumps way up once again. Mathematically, the DOS of each line is proportional to the inverse square root of the excess energy above the one needed to reach the line.

Finally, if we make the box small in all three directions, we create a “quantum dot” or “artificial atom”. Now each energy state is a separate point, figure 5.15. The DOS is now zero unless the energy sphere exactly hits one of the individual points, in which case the DOS is infinite. So, the DOS is a set of vertical spikes. Mathematically, the contribution of each state to the DOS is proportional to a delta function located at that energy.

(It may be pointed out that strictly speaking, every DOS is in reality a set of delta functions. It is only if we average the delta functions over a small energy range, chosen based on how dense the points are in  $k$ -space, that we get the smooth mathematical functions of the previous three examples as approximations.)

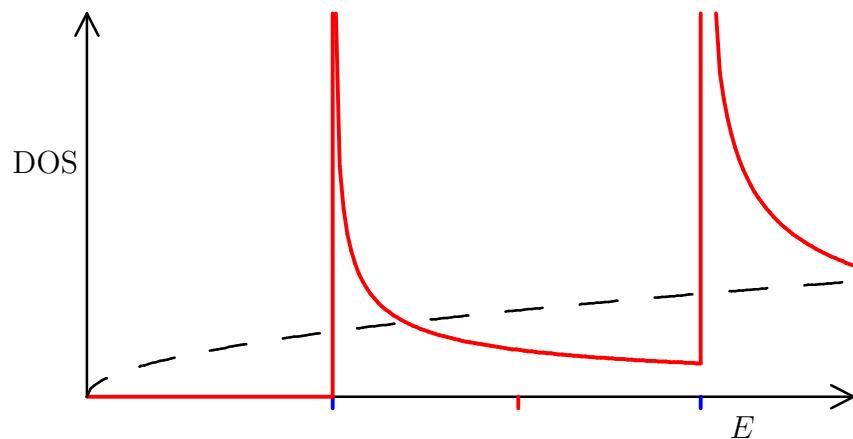
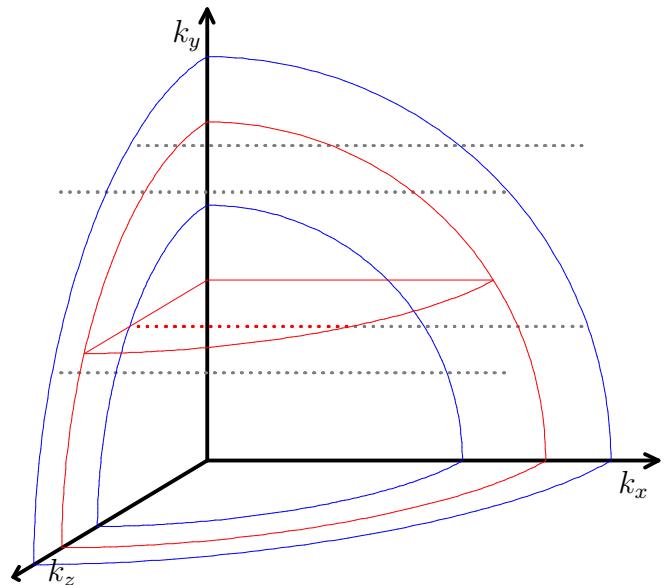


Figure 5.14: Energy states, top, and density of states, bottom, when there is confinement in both the  $y$ - and  $z$ -directions, as in a quantum wire.

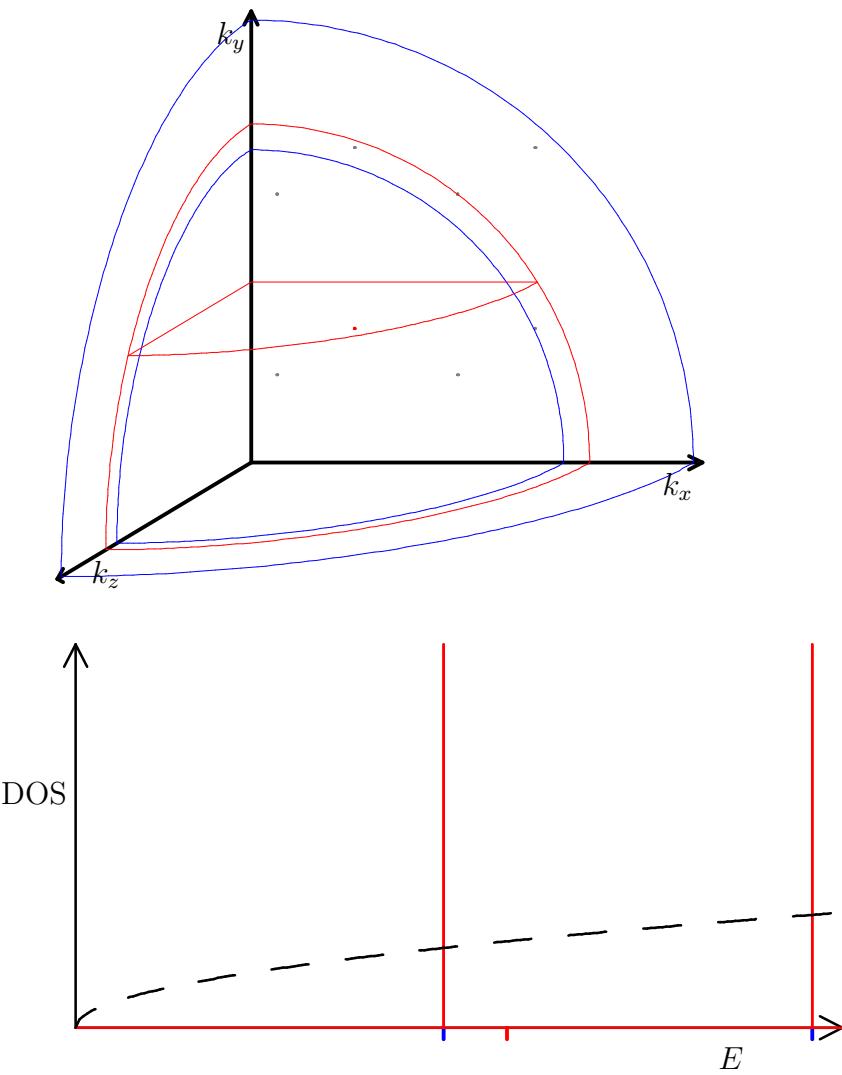


Figure 5.15: Energy states, top, and density of states, bottom, when there is confinement in all three directions, as in a quantum dot or artificial atom.

## 5.4 Band Structure

Metals whose valence electrons can be described by the free electron gas of the previous section readily conduct electricity: it requires only a small amount of energy to excite electrons to slightly higher energy levels in which they can achieve a net motion of electric charge, (say from one side of the solid to the other.) Indeed, a nonsuperconducting metal might have a resistance as low as  $10^{-10}$  ohm-cm near absolute zero temperature and the conduction electrons readily move unimpeded past  $10^8$  interatomic spacings [4, pp. 143,175]. But how to account for the fact that a good insulator might have a resistance that is larger by a gigantic factor  $10^{32}$ ?

“Bloch theory” explains this dramatic difference by including some of the forces on the electrons when they move through the solid’s crystal structure. It turns out that these forces have the tendency to cause the energy levels to group together in “bands”, as sketched in the spectra of figure 5.16.

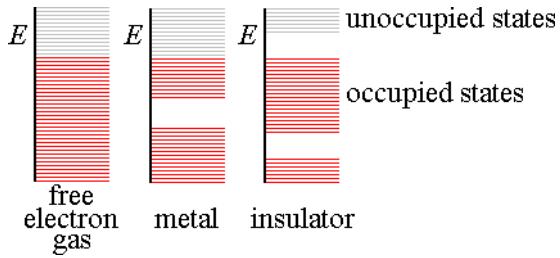


Figure 5.16: Sketch of free electron and banded energy spectra.

Now for a metal, this banding has no great consequences. But insulators completely fill up a band, called the “valence band” and the next higher energy band, called the “conduction band,” starts at an energy that is a significant amount higher. This jump in energy is called the “band gap”. To create a combination of slightly excited energy states that describe net electron motion is no longer possible for an insulator, since there are no free energy states left in the valence band.

Of course, if the electrons are somehow given enough additional energy to cross the band gap, conduction is again possible. A small number of electrons may get such energy through random heat motion, especially if the band gap is relatively small. Also, stray atoms of the wrong element may be present. Stray atoms with too few valence electrons can create vacancies in the valence band. On the other hand, stray atoms with valence electrons too many can put these electrons into the conduction band. In either case, the strays will allow some conduction.

Such changes in electrical properties can also be done deliberately for various purposes, such as in semi-conductor applications. Energy can be provided in the form of light, heat, or voltage, stray atoms can deliberately be added by “doping” the material with another one,

and materials with holes in their valence bands can physically be joined to materials with electrons in their conduction band, to create various very interesting effects at the contact surface.

### 5.4.1 Derivation [Advanced]

In this subsection, the tendency for the formation of energy bands will be derived. The problem to be solved is the energy levels available to valence electrons in a solid that is shaped like a rectangular block of dimensions  $\ell_x \times \ell_y \times \ell_z$ . The atoms of the solid are assumed to be arranged in a crystal-lattice structure that has Cartesian periodicity. As a result, the electrons will experience a crystal lattice potential with a periodicity on the small scale of the atoms. We will still ignore true particle-particle interactions, time variations of the lattice potential, lattice defects, etcetera.

To further simplify the analysis, it will be assumed that the lattice potential is small. Such an analysis illustrates some of the ideas of a mathematical approach called “small perturbation theory”. Those afraid of a bit of mathematics be warned.

#### The free electron gas in terms of exponentials

Since it will be assumed that the lattice potential is small, the starting point of the analysis is the free electron gas solution derived in section 5.3 for the case of no lattice potential. The free electron gas energy eigenfunctions were:

$$\psi_{\vec{k}0} = \sqrt{\frac{8}{\ell_x \ell_y \ell_z}} \sin(k_x x) \sin(k_y y) \sin(k_z z) \quad (5.14)$$

From now on subscript 0 will be added to the free electron gas solution to indicate that it is the solution only if the lattice potential is zero.

Sines are relatively awkward to work with mathematically. It is convenient to take them apart into exponentials using Euler’s identity (1.5), to produce the equivalent solution:

$$\psi_{\vec{k}0} = \sqrt{\frac{8}{\ell_x \ell_y \ell_z}} \frac{e^{ik_x x} - e^{-ik_x x}}{2i} \frac{e^{ik_y y} - e^{-ik_y y}}{2i} \frac{e^{ik_z z} - e^{-ik_z z}}{2i}$$

Multiplying out shows that every eigenfunction consists of eight complex exponentials, each of the form of the form  $e^{i(\pm k_x x \pm k_y y \pm k_z z)}$ . It may further be verified that each of these exponentials *by itself* is still a free electron gas energy eigenfunction. A bar will be used to distinguish these exponential eigenfunctions from the sinusoidal ones:

$$\bar{\psi}_{\vec{k}0} \equiv e^{i\vec{k}\cdot\vec{r}} \quad (5.15)$$

They have the same energy as the sinusoidal solutions, namely

$$E_{k0} = \frac{\hbar^2}{2m_e} k^2 \quad (5.16)$$

Since both positive and negative wave number values appear in the exponentials, now the possible  $\vec{k}$  values fill not just the positive octant as in figure 5.11, but the entire wave number space. For plotting simplicity, only the  $k_z = 0$  plane is shown in figure 5.17. (While technically

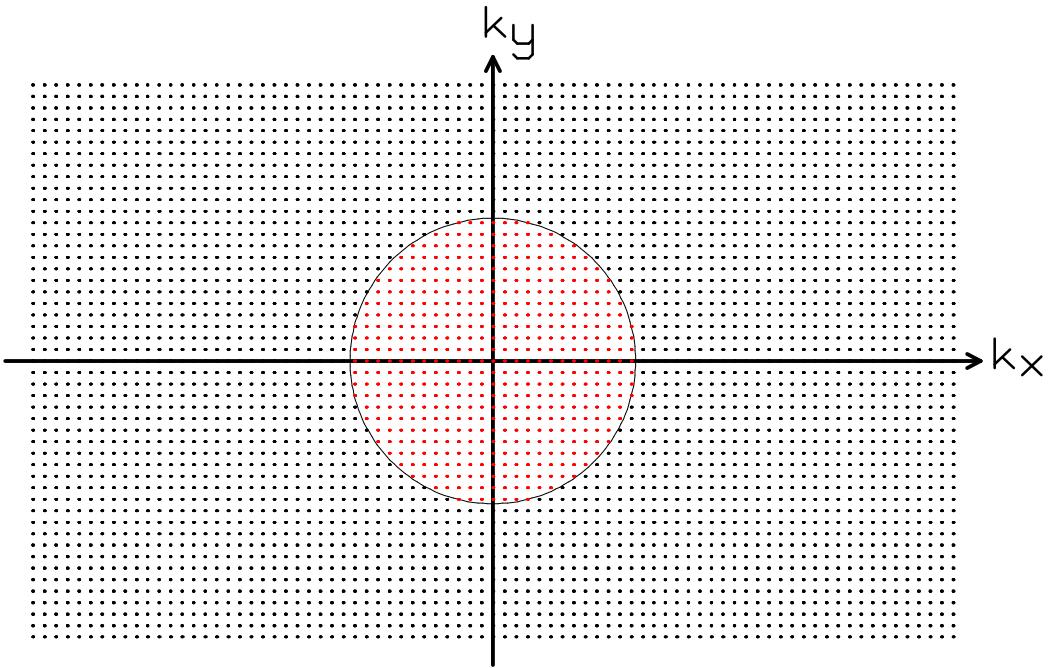


Figure 5.17: Cross section of the full wave number space.

the  $k_z = 0$  plane is not of interest for the assumed boundary conditions, it is still representative of arbitrary  $\vec{k}$ .) Each point in this wave number space stands for a different exponential solution (5.15), with an energy (5.16) which is proportional to the square distance of the point from the origin. Note that the spacings in the  $k_x$ - and  $k_y$ -directions are equal in figure 5.17; this indicates that the block containing the electrons has the same size in the  $x$  and  $y$ -directions. The analysis below works whether or not this is true.

While working with exponentials simplifies the math, it is important to note that only the sinusoidal solutions satisfy the boundary condition that  $\Psi = 0$  on the surface of the block. The exponential solutions do not, they are instead periodic in each direction, with periods  $2\ell_x$ ,  $2\ell_y$ , and  $2\ell_z$ . For now this difference in boundary conditions will be ignored. Also, we will not bother to normalize the exponential eigenfunctions.

### The small perturbation approach

The approach to analyze the effect of a lattice potential will be to start with the free electron gas eigenfunctions  $\bar{\psi}_{\vec{k}0}$  of the previous subsubsection, corresponding to zero lattice potential, and then to figure out how they change into slightly different eigenfunctions  $\bar{\psi}_{\vec{k}}$  if a *small* lattice potential  $V$  is added.

Mathematically, the requirement that the potential is small can be expressed by writing it in the form

$$V(x, y, z) = \varepsilon V_1(x, y, z) \quad (5.17)$$

where  $\varepsilon$  is a scale factor that is required to be small. The scaled potential  $V_1$  will be assumed to be an appropriate one to describe forces exerted by atoms arranged in a rectangular periodic lattice. It will also be required to be symmetric about the lattice faces to simplify dealing with the surface boundary conditions.

The energy eigenfunctions  $\bar{\psi}_{\vec{k}}$  are now of course going to depend on what the scale factor  $\varepsilon$  is. Any arbitrary eigenfunction  $\bar{\psi}_{\vec{k}}$  and its eigenvalue  $E_k$  can be expanded in a power series in  $\varepsilon$ :

$$\bar{\psi}_{\vec{k}}(x, y, z; \varepsilon) = \bar{\psi}_{\vec{k}0}(x, y, z) + \varepsilon \bar{\psi}_{\vec{k}1}(x, y, z) + \varepsilon^2 \bar{\psi}_{\vec{k}2}(x, y, z) + \dots \quad (5.18)$$

$$E_k = E_{k0} + \varepsilon E_{k1} + \varepsilon^2 E_{k2} + \dots \quad (5.19)$$

In the absence of a lattice potential, or in other words when  $\varepsilon = 0$ , the above two power series produce the exponential free electron gas eigenfunction  $\bar{\psi}_{\vec{k}0}(x, y, z)$  and corresponding eigenvalue  $E_{k0}$  of the previous subsubsection.

If we figure out the next few terms,  $\bar{\psi}_{\vec{k}1}, \bar{\psi}_{\vec{k}2}, \dots$  and  $E_{k1}, E_{k2}, \dots$ , then we can see how the solution changes for small lattice potential ( $\varepsilon$  small but not zero.) Note that for small enough  $\varepsilon$ , the higher order powers of  $\varepsilon$  in the power series can be neglected. As a consequence  $\varepsilon E_{k1}$  should tell us how each energy eigenvalue changes due to the small lattice potential  $\varepsilon V_1$ . (Actually, this is incorrect since it will turn out that  $E_{k1} = 0$ ; it will be  $\varepsilon^2 E_{k2}$  that will tell us the change in energy.) We can then examine why the energy levels would band together.

To figure out the higher order terms, we will have to use the Hamiltonian eigenvalue problem

$$[\hat{T} + \varepsilon V_1] \bar{\psi}_{\vec{k}} = E_k \bar{\psi}_{\vec{k}}$$

where  $\hat{T}$  is the kinetic energy operator. Substitution of the two power series into this problem and multiplying out produces

$$\begin{aligned} & [\hat{T} - E_{k0}] \bar{\psi}_{\vec{k}0} \\ & + \varepsilon \{ [\hat{T} - E_{k0}] \bar{\psi}_{\vec{k}1} + [V_1 - E_{k1}] \bar{\psi}_{\vec{k}0} \} \\ & + \varepsilon^2 \{ [\hat{T} - E_{k0}] \bar{\psi}_{\vec{k}2} + [V_1 - E_{k1}] \bar{\psi}_{\vec{k}1} - E_{k2} \bar{\psi}_{\vec{k}0} \} \\ & + \dots = 0 \end{aligned} \quad (5.20)$$

For this power series to be zero as required, the coefficient of *each* power of  $\varepsilon$  must be zero. This gives a sequence of problems to be solved, one for each power of  $\varepsilon$ . They will be solved in turn in the next three subsubsections.

### Zeroth order solution

The requirement that the net coefficient of  $\varepsilon^0$  in the power series (5.20) equals zero is:

$$[\hat{T} - E_{k0}] \bar{\psi}_{\vec{k}0} = 0 \quad (5.21)$$

The solution should be the free electron gas one,

$$\bar{\psi}_{\vec{k}0} = e^{i\vec{k}\cdot\vec{r}} = e^{i(k_x x + k_y y + k_z z)} \quad E_{k0} = \frac{\hbar^2}{2m_e} k^2 \quad (5.22)$$

This can be verified by direct substitution, noting that the kinetic energy operator equals

$$\hat{T} = -\frac{\hbar^2}{2m_e} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right]$$

From now on,  $\vec{k}$  will be treated as a *given* wave number vector; it indicates the particular free electron gas eigenfunction that we are trying to correct for  $\varepsilon \neq 0$  by adding higher order terms.

### First order solution

The requirement that the net coefficient of  $\varepsilon^1$  in the power series (5.20) equals zero gives:

$$[\hat{T} - E_{k0}] \bar{\psi}_{\vec{k}1} + [V_1 - E_{k1}] \bar{\psi}_{\vec{k}0} = 0 \quad (5.23)$$

This equation is to be solved to find  $\bar{\psi}_{\vec{k}1}$ , the leading order deviation from the free electron gas eigenfunction, and  $E_{k1}$ , the leading order deviation from the free electron gas energy level.

The first standard trick to solve such problems is to write the perturbation wave function in terms of the unperturbed wave functions. In this case, this means that we write  $\bar{\psi}_{\vec{k}1}$  as a combination of the exponential free electron gas eigenfunctions:

$$\bar{\psi}_{\vec{k}1} = \sum_{\text{all } \vec{l}} c_{1\vec{l}} e^{i\vec{l}\cdot\vec{r}} \quad (5.24)$$

Note that we use a new wave number symbol  $\vec{l}$  since  $\vec{k}$  is already reserved to indicate the particular free electron gas eigenfunction that we are trying to correct for the lattice potential.

Writing  $\bar{\psi}_{\vec{k}1}$  in terms of the exponentials automatically ensures that it satisfies the periodic boundary conditions.

To fully determine what  $\bar{\psi}_{\vec{k}1}$  is, the coefficients  $c_{1\vec{l}}$  must still be found. This must be done by substituting the above sum for  $\bar{\psi}_{\vec{k}1}$  into the first order Hamiltonian (5.23). It turns out to be convenient to rerotate the summation index  $\vec{l}$  once more, to  $\vec{\lambda}$ , in doing so, and then the Hamiltonian becomes:

$$\sum_{\text{all } \vec{\lambda}} [E_{\lambda 0} - E_{k0}] c_{1\vec{\lambda}} e^{i\vec{\lambda}\cdot\vec{r}} + [V_1 - E_{k1}] e^{i\vec{k}\cdot\vec{r}} = 0 \quad (5.25)$$

where  $E_{\lambda 0} = \hbar^2 \lambda^2 / 2m_e$ .

The second standard trick is now to take the inner product of this Hamiltonian problem with each unperturbed eigenfunction. In this particular case, that really means that for each unperturbed eigenfunction  $e^{i\vec{l}\cdot\vec{r}}$ , we multiply the Hamiltonian problem (5.25) by  $e^{-i\vec{l}\cdot\vec{r}}$ , integrate that over the periodic range  $-\ell_x \leq x \leq \ell_x$ ,  $-\ell_y \leq y \leq \ell_y$ ,  $-\ell_z \leq z \leq \ell_z$ , and divide by the volume of integration. This produces:

$$[E_{l0} - E_{k0}] c_{1\vec{l}} + V_{\vec{l}\vec{k}} - E_{k1} \delta_{\vec{l}\vec{k}} = 0 \quad (5.26)$$

since, first, by orthogonality, the integration gets rid of all terms in the sum over  $\vec{\lambda}$  except the single one for which  $\vec{\lambda} = \vec{l}$ , and for the same reason  $\delta_{\vec{l}\vec{k}}$ , representing the integral of the final term, is one if  $\vec{l} = \vec{k}$  and zero otherwise. Finally  $V_{\vec{l}\vec{k}}$  is simply *defined* as the integral arising from the lattice potential term in (5.25):

$$V_{\vec{l}\vec{k}} \equiv \frac{1}{8\ell_x\ell_y\ell_z} \int_{x=-\ell_x}^{\ell_x} \int_{y=-\ell_y}^{\ell_y} \int_{z=-\ell_z}^{\ell_z} e^{-i\vec{l}\cdot\vec{r}} V_1 e^{i\vec{k}\cdot\vec{r}} dx dy dz \quad (5.27)$$

Since  $V_1$  is assumed to be given, the value of integral  $V_{\vec{l}\vec{k}}$  can in principle be found for any  $\vec{l}$  and  $\vec{k}$ .

So (5.26) is an algebraic equation for the coefficient  $c_{1\vec{l}}$ . There is one such equation for every  $\vec{l}$ , so we have one equation for each coefficient  $c_{1\vec{l}}$  in the description (5.24) of  $\bar{\psi}_{1\vec{k}}$ . Solve and we have found  $\bar{\psi}_{1\vec{k}}$ .

It should be noted however that  $V_1$  must be extended towards negative coordinate values to do the integrals  $V_{\vec{l}\vec{k}}$ . It turns out that  $V_1$  must be extended symmetrically:  $V_1(x, y, z) = V_1(|x|, |y|, |z|)$ . The reason is the way the obtained *periodic* solutions  $\bar{\psi}_{\vec{k}}(x, y, z; \varepsilon)$  will be turned back into solutions satisfying the original boundary conditions on the outside surface of the solid block. The boundary condition  $\Psi = 0$  at  $x = 0$  is satisfied by forming the antisymmetric combination

$$\bar{\psi}_{\vec{k}}(x, y, z; \varepsilon) - \bar{\psi}_{\vec{k}}(-x, y, z; \varepsilon)$$

but this only works if  $\bar{\psi}_{\vec{k}}(-x, y, z; \varepsilon)$  is also a solution, which requires that  $V_1$  is symmetric around  $x = 0$ . Antisymmetry around  $x = 0$  combined with periodicity of period  $2\ell_x$  then

makes the boundary condition at  $x = \ell_x$  automatic. Further similar combinations ensure the boundary conditions on the  $y$ - and  $z$ -boundaries. The need to extend the potential symmetrically toward negative coordinate values is the reason for the requirement mentioned in subsubsection 5.4.1 that the lattice potential is symmetric around the lattice faces. We do not want the symmetric extension to destroy the periodicity of the lattice potential.

The further solution process depends critically on what the lattice potential integrals  $V_{\vec{l}\vec{k}}$  are. To determine the integral for any arbitrary  $\vec{l}$  and  $\vec{k}$ , the lattice potential  $V_1$  itself can also be written in terms of the unperturbed exponentials:

$$V_1 = \sum_{\vec{v}} V_{\vec{v}} e^{i\vec{v}\cdot\vec{r}} \quad (5.28)$$

with  $\vec{v}$  the summation index. However, most of the coefficients  $V_{\vec{v}}$  will have to be zero if the potential describes an atom-scale lattice. In particular, if there are  $N_x$  lattice cells in the  $x$ -direction, then the exponential  $e^{iv_x x}$  must return to the same value after a small lattice cell length of only  $\ell_x/N_x$ . That requires, according to the Euler identity (1.5), that

$$v_x = n'_x \frac{2\pi N_x}{\ell_x} \quad \text{with } n'_x \text{ integer} \quad (5.29)$$

The resulting  $2\pi N_x/\ell_x$  wave number vector spacing is a factor  $2N_x$  larger than the basic spacing of the wave number grid. And since the number  $N_x$  of atom-scale lattice cells is very large in a macroscopic solid, this means that the  $\vec{v}$ -values where  $V_1$  has a nonzero coefficient are spaced widely apart. The same is of course true for the spacings in the  $y$ - and  $z$ -directions.

The wide spacings of the nonzero coefficients  $V_{\vec{v}}$  turn out to greatly simplify the analysis. They cause most of the lattice potential integrals  $V_{\vec{l}\vec{k}}$  to be zero too. It can be seen that for a given  $\vec{k}$ , shown as a fat red dot in wave number space figure 5.18, the  $V_{\vec{l}\vec{k}}$  are only nonzero at the wave number vectors  $\vec{l}$  shown as blue stars. These wave number vectors will be referred to as the “ $\vec{k}$ -grid”. Like the coefficients of  $V_1$  itself, the spacing of the  $\vec{k}$ -grid is in integer multiples of  $2N_x$ ,  $2N_y$ , and  $2N_z$  too.

The values of  $V_{\vec{l}\vec{k}}$  on the  $\vec{k}$ -grid are found to be:

$$V_{\vec{l}\vec{k}} = V_{\vec{l}-\vec{k}} = V_{\vec{k}\vec{l}}^* \quad (5.30)$$

The last inequality applies since  $V_1$  is real. Since the constant part of the potential  $V_0$  can already be accommodated by the free electron gas solution, it can be assumed that  $V_{\vec{k}\vec{k}} = 0$ .

Returning after all this to the solution of the equation for the coefficients  $c_{1\vec{l}}$  of  $\bar{\psi}_{\vec{k}1}$ ,

$$[E_{l0} - E_{k0}]c_{1\vec{l}} + V_{\vec{l}\vec{k}} - E_{k1}\delta_{\vec{l}\vec{k}} = 0 \quad (5.31)$$

there are three different cases to distinguish.

First, if  $\vec{l}$  is *not* on the  $\vec{k}$ -grid, then  $V_{\vec{l}\vec{k}}$  is zero, and  $\delta_{\vec{l}\vec{k}}$  is too, so these coefficients  $c_{1\vec{l}}$  must be zero. (Actually, this is not strictly required when  $\vec{l}$  is on the “ $k$ -sphere”, shown in cross

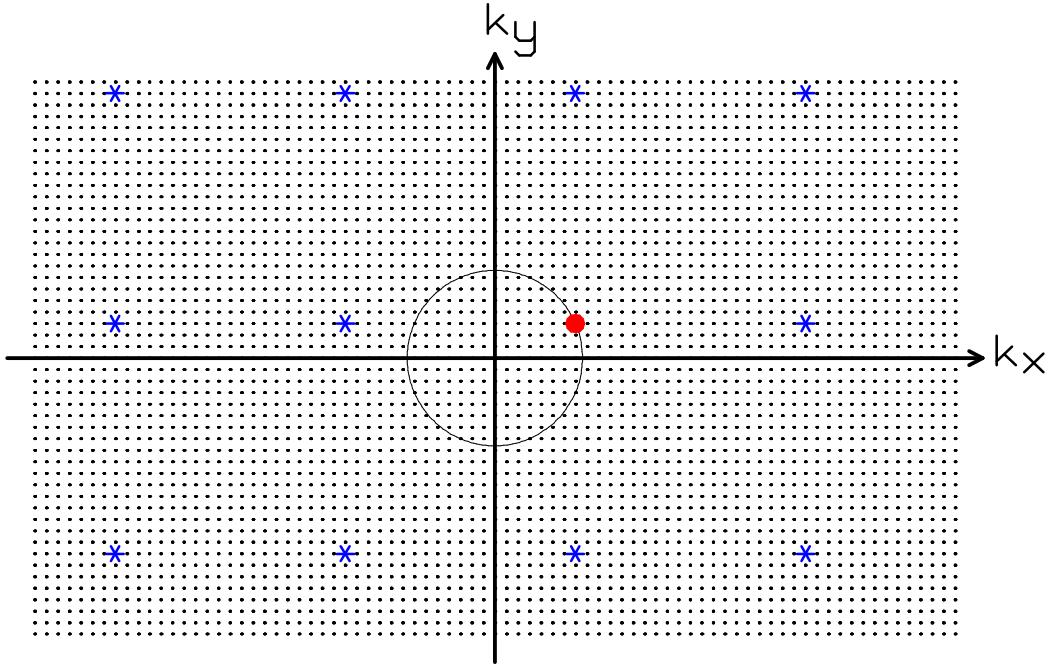


Figure 5.18: The  $\vec{k}$ -grid and  $k$ -sphere in wave number space.

section as the circle in figure 5.18 above. For these points,  $E_{l0} = E_{k0}$ , so the coefficients  $c_{1\vec{l}}$  could be anything, and we simply choose them to be zero.) The bottom line is that there are no nonzero coefficients  $c_{1\vec{l}}$  except on the  $\vec{k}$ -grid.

Second, if  $\vec{l} = \vec{k}$ , then  $E_{l0} = E_{k0}$ ,  $V_{\vec{k}\vec{k}} = 0$ , and  $\delta_{\vec{k}\vec{k}} = 1$  so we must have that the first order perturbation energy  $E_{k1} = 0$ . This is disappointing because it tells us nothing about how much the energy is different from the free electron gas value  $E_{k0}$  for small but nonzero lattice potential. We will need to find  $E_{k2}$  to see how the potential changes the energy.

Last, if  $\vec{l}$  is on the  $\vec{k}$ -grid but not equal to  $\vec{k}$ , then  $\delta_{\vec{l}\vec{k}} = 0$  but  $V_{\vec{l}\vec{k}}$  is in general nonzero. A problem now arises if  $\vec{l}$  is on the  $k$ -sphere where  $E_{l0} = E_{k0}$ , because then the equation cannot be satisfied. Our solution method only works if the  $\vec{k}$ -grid has no other points on the  $k$ -sphere besides  $\vec{k}$  itself. Fortunately, since the points on the  $\vec{k}$ -grid are so very widely spaced, this excludes only a relatively small number of eigenfunctions. (For those eigenfunctions, it must be assumed that  $\bar{\psi}_{\vec{k}0}$  is a combination of all exponentials on the  $k$ -sphere, instead of just a single one, and things get much more messy.)

Under the condition that no  $\vec{k}$ -grid points are on the  $k$ -sphere, the solution for the coefficients is:

$$c_{1\vec{l}} = -\frac{V_{\vec{l}\vec{k}}}{E_{l0} - E_{k0}} \quad \text{for } \vec{l} \text{ on the } \vec{k}\text{-grid} \quad (5.32)$$

This solves the first order problem.

Note that we excluded the denominator in (5.32) from being zero, since by assumption  $l$  may

not be on the  $\vec{k}$ -sphere, but not from being potentially very small. This will become important when we examine the final results. (Unlike it may seem from the above, the excluded cases with  $E_{l0} = E_{k0}$  for some grid points do *not* produce infinite solutions, but they do in general have  $E_{k1}$  nonzero, so an energy change that is roughly a factor  $1/\varepsilon$  larger than usual.)

## Second order solution

The requirement that the net coefficient of  $\varepsilon^2$  in the power series (5.20) equals zero gives the second order Hamiltonian problem:

$$[\hat{T} - E_{k0}] \bar{\psi}_{\vec{k}2} + V_1 \bar{\psi}_{\vec{k}1} - E_{k2} \bar{\psi}_{\vec{k}0} = 0 \quad (5.33)$$

This can be solved much like the first order one, by writing the second order wave function perturbation  $\bar{\psi}_{\vec{k}2}$  also in terms of the unperturbed eigenfunctions,

$$\bar{\psi}_{\vec{k}2} = \sum_{\text{all } \vec{n}} c_{2\vec{n}} e^{i\vec{n}\cdot\vec{r}} \quad (5.34)$$

substituting in the Hamiltonian, rennotating, and taking an inner product with each eigenfunction  $e^{i\vec{n}\cdot\vec{r}}$ . The result is:

$$[E_{n0} - E_{k0}] c_{2\vec{n}} + \sum_{\text{all } \vec{l}} V_{\vec{n}\vec{l}} c_{1\vec{l}} - E_{k2} \delta_{\vec{n}\vec{k}} = 0 \quad (5.35)$$

For wave number vectors  $\vec{n}$  not on the  $\vec{k}$ -grid in figure 5.18, this equation is again satisfied by setting the corresponding  $c_{2\vec{n}}$  equal to zero. Note that in the second term,  $c_{1\vec{l}}$  is only nonzero on the  $\vec{k}$ -grid, and  $V_{\vec{n}\vec{l}}$  is only nonzero if  $\vec{n}$  and  $\vec{l}$  are on the same grid, so for a nonzero value,  $\vec{n}$  has to be on the  $\vec{k}$ -grid with  $\vec{l}$ .

Next, for  $\vec{n} = \vec{k}$ , we obtain the desired expression for the energy  $E_{k2}$ :

$$E_{k2} = \sum_{\vec{l}} V_{\vec{k}\vec{l}} c_{1\vec{l}}$$

If we substitute in the expressions for  $V_{\vec{k}\vec{l}}$ , and  $c_{1\vec{l}}$  obtained in the previous subsubsection, we get:

$$E_{k2} = - \sum_{\vec{l}} \frac{|V_{\vec{l}-\vec{k}}|^2}{E_{l0} - E_{k0}} \quad (5.36)$$

where the sum runs over the wave numbers on the  $k$ -grid, excluding  $\vec{k}$  itself.

We could now in principle proceed with finding the coefficients  $c_{2\vec{n}}$  on the  $\vec{k}$ -grid, but we have what we really wanted, an expression for the change in energy  $\varepsilon^2 E_{k2}$  from the free electron gas level.

### Discussion of the energy changes

The previous subsubsections determined how the energy changes from the free electron gas values due to a small lattice potential. It was found that an energy level  $E_{k0}$  without lattice potential changes due to the lattice potential by an amount:

$$\varepsilon^2 E_{k2} = -\varepsilon^2 \sum_{\vec{l}} \frac{|V_{\vec{l}-\vec{k}}|^2}{E_{l0} - E_{k0}} \quad (5.37)$$

Here  $\varepsilon$  was a suitable measure of the size of the lattice potential; the  $V_{\vec{l}-\vec{k}}$  were coefficients that determine the precise details of the chosen lattice potential;  $\vec{k}$  was the wave number vector of the considered free electron gas solution, shown as a red dot in figure 5.18,  $\vec{l}$  was a summation index over the blue  $\vec{k}$ -grid points of that figure, and  $E_{l0}$  and  $E_{k0}$  were proportional to the square distances from the origin to points  $\vec{l}$ , respectively  $\vec{k}$ .  $E_{k0}$  is also the initial energy level.

The expression above for the energy change is not valid when  $E_{l0} = E_{k0}$ , in which case it would incorrectly give infinite change in energy. However, it does apply when  $E_{l0} \approx E_{k0}$ , in which case it predicts unusually large changes in energy. The condition  $E_{l0} \approx E_{k0}$  means that a blue star  $\vec{l}$  on the  $\vec{k}$ -grid in figure 5.18 is almost the same distance from the origin as the point  $\vec{k}$  itself.

One case for which this happens is when the integer wave number index  $n_x$  numbering the wave number points in the  $x$ -direction is almost a multiple of the number  $N_x$  of crystal-structure lattice cells in the  $x$ -direction. As an example, figure 5.19 shows two neighboring states  $\vec{k}$  straddling the vertical plane  $n_x = N_x$ , shown as a vertical line, and their grid  $\vec{l}$ -values that cause near-infinite energy changes.

For the left of the two states,  $E_{l0}$  is just a bit larger than  $E_{k0}$ , so the energy change (5.37) due to the lattice potential is large and negative. I will represent all energy decreases graphically by moving the points towards the origin, in order that the distance from the origin continues to indicate the energy of the state. That means that I will move the left state strongly towards the origin. Consider now the other state just to the right;  $E_{l0}$  for that state is just a bit less than  $E_{k0}$ , so the energy change of this state will be large and positive; graphically, I will move this point strongly away from the origin. The result is that the energy levels are torn apart along the plane  $n_x = N_x$ .

The same happens at other planes on which  $n_x$  is a nonzero multiple of  $N_x$ , (shown as vertical lines in the wave number space cross section 5.19) or  $n_y$  a nonzero multiple of  $N_y$ , (shown as horizontal lines) or  $n_z$  a nonzero multiple of  $N_z$  (not visible in the cross section). There will be some other planes as well, depending on circumstances.

Figure 5.20 shows an example of energy levels that are torn apart by an arbitrarily chosen lattice potential. (The energy levels as shown are relative to the one of the center state.) If the lattice potential is strong enough, it can cause the energy levels of, for example, the

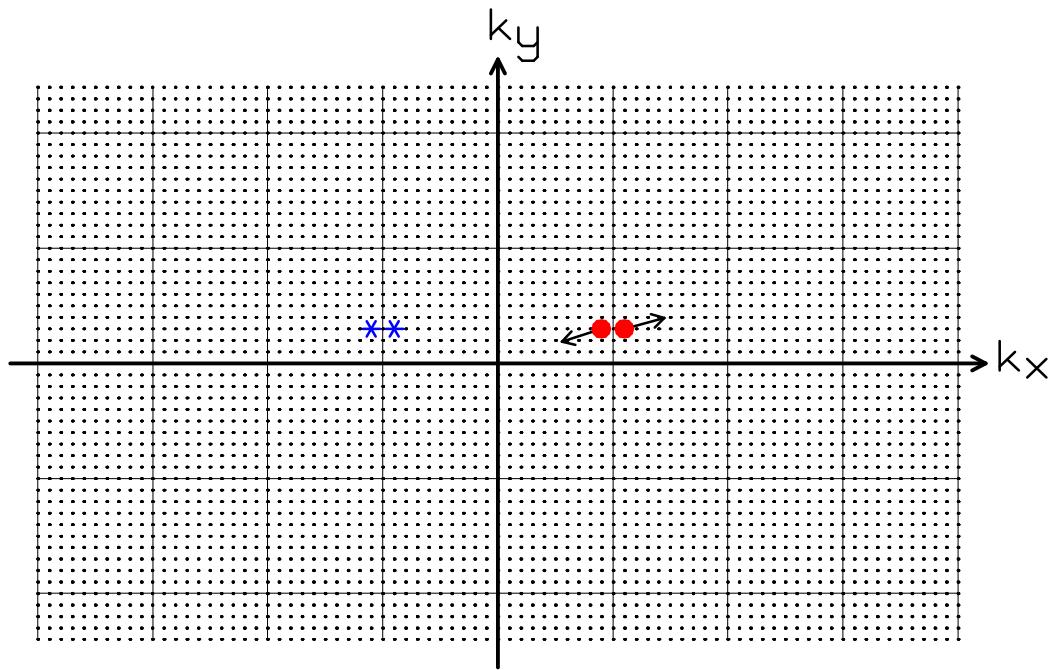


Figure 5.19: Tearing apart of the wave number space energies.

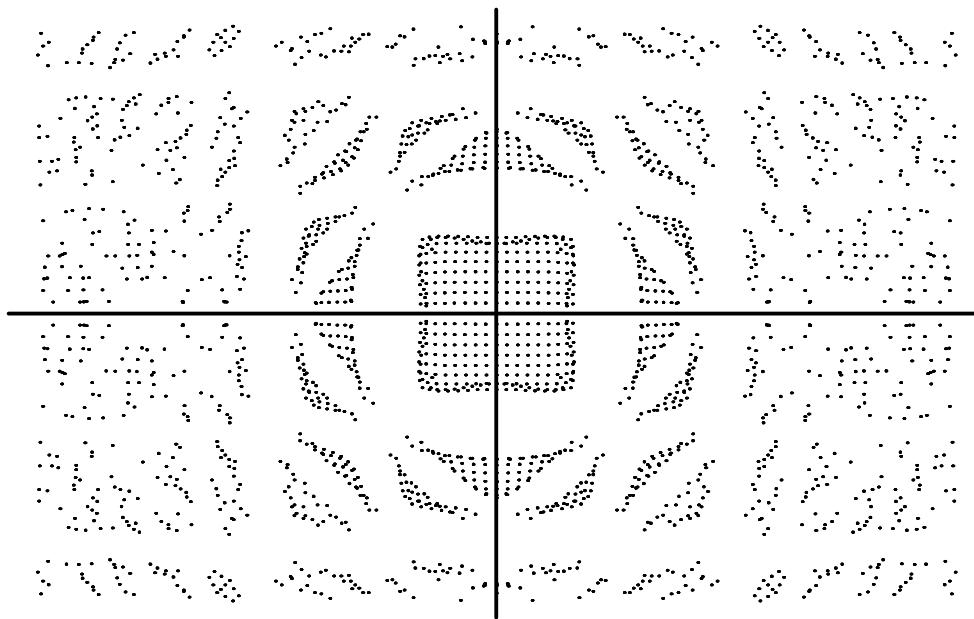


Figure 5.20: Energy, as radial distance from the origin, for varying wave number vector directions.

center patch to be everywhere lower than those of the outlying areas. The electrons will then

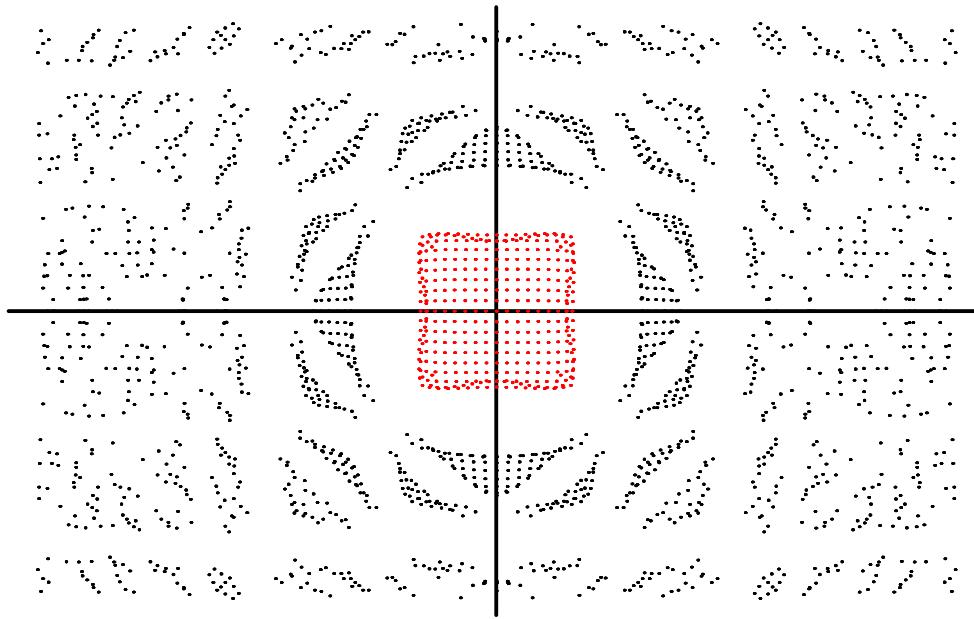


Figure 5.21: Occupied levels in the ground state for two valence electrons per lattice cell.

occupy the center patch states first, as shown in figure 5.21. There are  $N_x N_y N_z$  spatial states satisfying the correct boundary conditions in the center patch, so two valence electrons per lattice cell would just fill it. We then have an insulator whose electrons are stuck in a filled valence band. They would need to jump an energy gap to reach the outlying regions.

Note that we did not put any real requirements on the crystal structure lattice potential beyond that it had to have Cartesian periodicity. We did require symmetry around the lattice faces, but this requirement can be avoided using different boundary conditions. The fact that the energy levels get torn apart regardless of the details of the lattice potential illustrates that the forming of energy bands is a quite general phenomenon.

## 5.5 Quantum Statistical Mechanics

As various observations in previous sections indicate, it is not possible to solve the equations of quantum mechanics exactly and completely unless it is a very small number of particles under very simple conditions. Even then, “exactly” probably means “numerically exactly”, not analytically. Fortunately, there is good news: statistical mechanics can make meaningful predictions about the behavior of large numbers of particles without trying to write down the solution for every single particle.

A complete coverage is beyond the scope of this document, but some key results should be mentioned. As the energy spectra figure 5.16 and other examples in previous sections noted,

at absolute zero temperature a system of identical fermions such as electrons completely fills the lowest available energy states. There will be one electron per state in the lowest states, (assuming that spin is included in the state count, otherwise two electrons per state.) The higher energy states remain unoccupied. In other words, there is one electron per state below a dividing energy level and zero electrons per state above that energy level. The dividing energy level between occupied and empty states is the Fermi energy.

For temperatures  $T$  greater than absolute zero, heat energy allows at least some electrons to move to higher energy levels. The law of statistical mechanics that tells us how many, on average, is the so-called “Fermi-Dirac distribution”; it predicts the *average* number of fermions per state to be

$$\text{Fermi-Dirac distribution: } n = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1} \quad (5.38)$$

where  $\epsilon$  is the energy level of the state,  $k_B$  is the Boltzmann constant, and  $\mu$  is some function of the temperature  $T$  that is called the “chemical potential.” Derivations of this distribution may be found in [3] or [6].

Let’s examine the algebra of the formula. First of all,  $n$  cannot be more than one, because the exponential is greater than zero. This is as it should be: according to the Pauli exclusion principle there can be at most one electron in each state, so the average per state  $n$  must be one or less. Next, at absolute zero the chemical potential  $\mu$  equals the Fermi energy. As a result, at absolute zero temperature, energy levels  $\epsilon$  above the Fermi energy have the argument of the exponential infinite, (a positive number divided by a zero approached from positive values), hence the exponential infinite, hence  $n = 0$ ; there are zero particles in those states. On the other hand, for energy states below the Fermi level, the argument of the exponential is minus infinity, hence the exponential is zero, hence  $n = 1$ ; those states have one electron in every state. That is just what it should be.

At a temperature slightly higher than zero, not much changes in this math, except for states close to the Fermi energy. In particular, states just below the Fermi energy will on average lose some electrons to states just above the Fermi energy. The electrons in states just below the Fermi level are close enough to the empty states to jump to them. The affected energy levels extend over a range of roughly  $k_B T$  around the Fermi energy. In the copper example of section 5.3.4, even at normal temperatures the affected range is still very small compared to the Fermi energy itself. However, the affected range can be appreciable in other cases.

Identical bosons satisfy quite different statistics than fermions. For bosons, the number of particles outside the ground state satisfies the “Bose-Einstein distribution:”

$$\text{Bose-Einstein distribution: } n = \frac{1}{e^{(\epsilon-\mu)/k_B T} - 1} \quad (5.39)$$

Note that bosons do not satisfy the exclusion principle; there can be multiple bosons per state. Also note that the chemical potential  $\mu$  in Bose-Einstein distributions cannot exceed the lowest energy level, because the average number  $n$  of particles in an energy state cannot be negative. In fact, when the chemical potential does reach the lowest energy level, (something

that has been observed to occur at extremely low temperatures), the Bose-Einstein distribution indicates that the number of particles in the lowest energy state becomes large; too large to still be correctly described by the distribution, in fact. If this happens, it is called Bose-Einstein condensation. A significant number of bosons then pile together into the same state of absolutely lowest energy, and behave as if they are essentially all the same particle. This is presumably what happens to liquid helium when it becomes a superfluid. A particle “cannot get in its own way” while moving around, and superfluid helium moves freely about without the internal friction that other fluids have.

For high-enough energy levels, both the Fermi-Dirac and Bose-Einstein distributions simplify to the classical “Maxwell-Boltzmann distribution:”

$$\text{Maxwell-Boltzmann distribution: } n = e^{-(\epsilon - \mu)/k_B T} \quad (5.40)$$

which was derived well before the advent of quantum mechanics.



# Chapter 6

## Time Evolution

### 6.1 The Schrödinger Equation

In Newtonian mechanics, Newton's second law states that the linear momentum changes in time proportional to the applied force;  $dm\vec{v}/dt = m\vec{a} = \vec{F}$ . The equivalent in quantum mechanics is the Schrödinger equation, which describes how the wave function evolves. This section discusses this equation, and a few of its immediate consequences.

The Schrödinger equation says that the time derivative of the wave function is obtained by applying the Hamiltonian on it. More precisely:

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad (6.1)$$

The solution to the Schrödinger equation can immediately be given for most cases of interest. The only condition that needs to be satisfied is that the Hamiltonian depends only on the state the system is in, and not explicitly on time. This condition is satisfied in all cases discussed so far, including the harmonic oscillator, the hydrogen and heavier atoms, the molecules, and the lattice potential, so the following solution applies to them all.

*To satisfy the Schrödinger equation, write the wave function  $\Psi$  in terms of the energy eigenfunctions  $\psi_n$  of the Hamiltonian,*

$$\Psi = c_1(t)\psi_1 + c_2(t)\psi_2 + \dots = \sum_n c_n(t)\psi_n \quad (6.2)$$

*Then the coefficients  $c_n$  must then evolve in time as complex exponentials:*

$$c_n(t) = c_n(0)e^{-iE_n t/\hbar} \quad \text{for every value of } n \quad (6.3)$$

The initial values  $c_n(0)$  of the coefficients are not determined from the Schrödinger equation, but from whatever initial condition for the wave function is given.

As always, the eigenfunctions may be indexed by multiple indices, rather than by a single index  $n$ . As an example, the full wave function for the electron of an hydrogen atom is, in terms of the energy eigenfunctions  $\psi_{nlm}$  derived in chapter 3.2, and including electron spin:

$$\Psi = \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^l c_{nlm+}(0) e^{-iE_nt/\hbar} \psi_{nlm}(r, \theta, \phi) \uparrow + c_{nlm-}(0) e^{-iE_nt/\hbar} \psi_{nlm}(r, \theta, \phi) \downarrow$$

(This ignores any external disturbances and small errors due to spin and relativity.)

The above solution in terms of eigenfunctions covers most cases of interest, but as noted, it is not valid if the Hamiltonian depends explicitly on time. That possibility arises when there are external influences on the system; in such cases the energy does not just depend on what state the system itself is in, but also on what the external influences are like at the time.

### 6.1.1 Energy conservation

Assuming that there are no external influences, the Schrödinger equation implies that the energy of a system is conserved. To see why, remember that the coefficients  $c_n$  of the energy eigenfunctions give the probability for the corresponding energy. While according to the Schrödinger equation these coefficients vary with time, their square magnitudes do not:

$$|c_n(t)|^2 \equiv c_n^*(t)c_n(t) = c_n^*(0)e^{iE_nt/\hbar}c_n(0)e^{-iE_nt/\hbar} = |c_n(0)|^2$$

So according to the orthodox interpretation, the probability of measuring a given energy level does not vary with time either. For example, the wave function for a hydrogen atom at the excited energy level  $E_2$  might be of the form:

$$\Psi = e^{-iE_2 t/\hbar} \psi_{210} \uparrow$$

(This corresponds to an assumed initial condition in which all  $c_{nlm\pm}$  are zero except  $c_{210+} = 1$ .) The square magnitude of the exponential is one, so the energy of this excited atom will stay  $E_2$  with 100% certainty for all time. The energy is conserved.

This also illustrates that left to itself, an excited atom will maintain its energy indefinitely. It will *not* emit a photon and drop back to the unexcited energy  $E_1$ . The reason that excited atoms spontaneously emit radiation is that they are perturbed. Like the harmonic oscillator was not at rest even in its ground state, the electromagnetic field has a ground state of nonzero energy. So, even if no radiation is explicitly directed at the atom, it will be perturbed by some, making the Hamiltonian of the atom dependent of time and the probabilities will no longer be constant. Eventually, at a time that is observed to be random for reasons discussed in chapter 7.6.2, the perturbations cause the excited atom to drop back to the lower energy state. While

dropping back, it emits a photon with an energy that exactly matches the difference between the excited and lower energy eigenvalues.

Returning to the unperturbed atom, it should also be noted that even if the energy is uncertain, still the probabilities of measuring the various energy levels do not change with time. As an arbitrary example, the following wave function describes a case of an undisturbed hydrogen atom where the energy has a 50%/50% chance of being measured as  $E_1$  (-13.6 eV) or as  $E_2$  (-3.4 eV):

$$\Psi = \frac{1}{\sqrt{2}}e^{-iE_1t/\hbar}\psi_{100}\downarrow + \frac{1}{\sqrt{2}}e^{-iE_2t/\hbar}\psi_{210}\uparrow$$

The 50/50 probability applies regardless how long the wait is before the measurement is done.

### 6.1.2 Stationary states

The previous subsection examined the time variation of energy, but the Schrödinger equation also determines how the other physical properties, such as positions and momenta, of a given system vary with time.

The simplest case is that in which the energy is certain, in other words, states in which the wave function is a *single* energy eigenfunction:

$$\Psi = c_n(0)e^{-iE_nt/\hbar}\psi_n$$

It turns out, {26}, that none of the physical properties of such a state changes with time. The physical properties may be uncertain, but the probabilities for their possible values will remain the same. For that reason, states of definite energy are called “stationary states.”

Hence it is not really surprising that none of the energy eigenfunctions derived so far had any resemblance to the classical Newtonian picture of a particle moving around. Each energy eigenfunction by itself is a stationary state. There will be no change in the probability of finding the particle at any given location regardless of the time you look, so how could it possibly resemble a classical particle that is at different positions at different times?

Similarly, while classically the linear momentum of a particle that experiences forces will change with time, in energy eigenstates the chances of measuring a given momentum do not change with time.

To get time variations of physical quantities, states of different energy must be combined. In other words, there must be uncertainty in energy.

### 6.1.3 Time variations of symmetric two-state systems

The simplest case of physical systems that can have a nontrivial dependence on time are systems described by two different states. Some examples of such systems were given in chapter 4.3. One was the hydrogen molecular ion, consisting of two protons and one electron. In that case, there was a state  $\psi_1$  in which the electron was in the ground state around one proton, and a state  $\psi_2$  in which it was around the other proton. Another example was the ammonia molecule, where the nitrogen atom was at one side of its ring of hydrogens in state  $\psi_1$ , and at the other side in state  $\psi_2$ . This section examines the time variation of such systems.

It will be assumed that the states  $\psi_1$  and  $\psi_2$  are physically equivalent, like the mentioned examples. In that case, according to chapter 4.3 the ground state of lowest energy, call it  $E_L$ , is an equal combination of the two states  $\psi_1$  and  $\psi_2$ . The state of highest energy  $E_H$  is also a equal combination, but with the opposite sign. The solution of the Schrödinger equation is in terms of these two combinations of states, {27}:

$$\Psi = c_L e^{-iE_L t/\hbar} \frac{\psi_1 + \psi_2}{\sqrt{2}} + c_H e^{-iE_H t/\hbar} \frac{\psi_1 - \psi_2}{\sqrt{2}}$$

Consider now the case of the hydrogen molecular ion, and assume that the electron is around the first proton, so in state  $\psi_1$ , at time  $t = 0$ . The wave function must then be:

$$\Psi = c_L e^{-iE_L t/\hbar} \left[ \frac{\psi_1 + \psi_2}{\sqrt{2}} + e^{-i(E_H - E_L)t/\hbar} \frac{\psi_1 - \psi_2}{\sqrt{2}} \right]$$

At time zero, this produces indeed state  $\psi_1$ , but when the exponential in the last term becomes  $-1$ , the system converts into state  $\psi_2$ . The electron has jumped over to the other proton.

The time this takes is

$$\frac{\pi\hbar}{E_H - E_L}$$

since  $e^{-i\pi} = -1$ , (1.5). After another time interval of the same length the electron will be back in state  $\psi_1$  around the first proton, and so on.

Note that this time interval for the two protons to exchange the electron is inversely proportional to the energy difference  $E_H - E_L$ . In chapter 4.3 this energy difference appeared in another context: it is twice the molecular binding energy produced by the “exchange terms” when the electron is shared. It is interesting now to see that this binding energy also determines the time it takes for the electron to be exchanged if it is not shared. The more readily the protons exchange the nonshared electron, the more the binding energy of the shared state will be.

The mathematics for the time evolution of the nitrogen atom in ammonia is similar. If measurements locate the nitrogen atom at one side of the hydrogen ring, then after a certain

time, it will pop over to the other side. However, the more interesting thing about the ammonia molecule is the difference in energy levels itself: transitions from  $E_H$  to  $E_L$  produce microwave radiation, allowing a maser to be constructed.

### 6.1.4 Time variation of expectation values

The time evolution of more complex systems can be described in terms of the energy eigenfunctions of the system, just like for the two state systems of the previous subsection. However, finding the eigenfunctions may not be easy.

Fortunately, it is possible to find the evolution of the expectation value of physical quantities without solving the energy eigenvalue problem. The expectation value, defined in chapter 3.3, gives the average of the possible values of the physical quantity.

The Schrödinger equation requires that the expectation value  $\langle a \rangle$  of any physical quantity  $a$  with associated operator  $A$  evolves in time as:

$$\frac{d\langle a \rangle}{dt} = \left\langle \frac{i}{\hbar} [H, A] \right\rangle + \left\langle \frac{\partial A}{\partial t} \right\rangle \quad (6.4)$$

The derivation is in note {28}. The commutator  $[H, A]$  of  $A$  with the Hamiltonian was defined in chapter 3.4 as  $HA - AH$ . The final term in (6.4) is usually zero, since most operators do not explicitly depend on time.

The above evolution equation for expectation values does not require the energy eigenfunctions, but it does require the commutator. Its main application is to relate quantum mechanics to Newtonian mechanics, as in the next section. (Some minor applications that we will leave to the notes for the interested are the “virial theorem” {29} relating kinetic and potential energy and the Mandelshtam-Tamm version of the “energy-time uncertainty principle”  $\Delta E \Delta t \geq \frac{1}{2}\hbar$  {30}.)

Note that if  $A$  commutes with the Hamiltonian, i.e.  $[H, A] = 0$ , then the expectation value of the corresponding quantity  $a$  will not vary with time. Such a quantity has eigenfunctions that are also energy eigenfunctions, so it has the same time-preserved statistics as energy. Equation (6.4) demonstrates this for the expectation value, but the standard deviation, etcetera, would not change with time either.

### 6.1.5 Newtonian motion

The purpose of this section is to show that even though Newton’s equations do not apply to very small systems, they are correct for macroscopic systems.

The trick is to note that for a macroscopic particle, the position and momentum are very precisely defined. Many unavoidable physical effects, such as incident light, colliding air atoms, earlier history, etcetera, will narrow down position and momentum of a macroscopic particle to great accuracy. Heisenberg's uncertainty relationship says that they must have uncertainties big enough that  $\sigma_x \sigma_{p_x} \geq \frac{1}{2}\hbar$ , but  $\hbar$  is far too small for that to be noticeable on a macroscopic scale. Normal light changes the momentum of a rocket ship in space only immeasurably little, but it is quite capable of locating it to excellent accuracy.

With little uncertainty in position and momentum, both can be approximated accurately by their expectation values. It follows that we should be able to get the evolution of macroscopic systems from the evolution equation (6.4) of the previous subsection for expectation values. We will just need to work out the commutator that appears in it.

Consider one-dimensional motion of a particle in a potential  $V(x)$  (the three-dimensional case goes exactly the same way). The Hamiltonian  $H$  is:

$$H = \frac{\hat{p}_x^2}{2m} + V(x)$$

where  $\hat{p}_x$  is the linear momentum operator and  $m$  the mass of the particle.

Now according to evolution equation (6.4), the expectation position  $\langle x \rangle$  changes at a rate:

$$\frac{d\langle x \rangle}{dt} = \left\langle \frac{i}{\hbar} [H, \hat{x}] \right\rangle = \left\langle \frac{i}{\hbar} \left[ \frac{\hat{p}_x^2}{2m} + V(x), \hat{x} \right] \right\rangle \quad (6.5)$$

Recalling the properties of the commutator from chapter 3.4,  $[V(x), \hat{x}] = 0$ , since multiplication commutes, and

$$[\hat{p}_x^2, \hat{x}] = \hat{p}_x [\hat{p}_x, \hat{x}] + [\hat{p}_x, \hat{x}] \hat{p}_x = -\hat{p}_x [\hat{x}, \hat{p}_x] - [\hat{x}, \hat{p}_x] \hat{p}_x = -2i\hbar \hat{p}_x$$

So the rate of change of expectation position becomes:

$$\frac{d\langle x \rangle}{dt} = \left\langle \frac{p_x}{m} \right\rangle \quad (6.6)$$

This is exactly the Newtonian expression for the change in position with time, because Newtonian mechanics defines  $p_x/m$  to be the velocity. However, it is in terms of expectation values.

To figure out how the expectation value of momentum varies, the commutator  $[H, \hat{p}_x]$  is needed. Now  $\hat{p}_x$  commutes, of course, with itself, but just like it does not commute with  $\hat{x}$ , it does not commute with the potential energy  $V(x)$ :

$$[V, \hat{p}_x] \Psi = \frac{\hbar}{i} \left( V \frac{\partial \Psi}{\partial x} - \frac{\partial V \Psi}{\partial x} \right) = -\frac{\hbar}{i} \frac{\partial V}{\partial x} \Psi$$

so  $[V, \hat{p}_x]$  must be  $-\hbar\partial V/\text{i}\partial x$ .

As a result, the rate of change of the expectation value of linear momentum becomes:

$$\frac{d\langle p_x \rangle}{dt} = \left\langle -\frac{\partial V}{\partial x} \right\rangle \quad (6.7)$$

This is Newton's second law in terms of expectation values: Newtonian mechanics defines the negative derivative of the potential to be the force, so the right hand side is the expectation value of the force. The left hand side is equivalent to mass times acceleration.

The fact that the expectation values satisfy the classical equations is known as "Ehrenfest's theorem."

(For a quantum system, however, it should be cautioned that even the expectation values do not truly satisfy Newtonian equations. Newtonian equations use the force at the expectation value of position, instead of the expectation value of the force. If the force varies nonlinearly over the range of possible positions, it makes a difference.)

## 6.2 Unsteady perturbations of two-state systems

This section takes a general look at what happens to a system that can be in two different energy eigenstates and we poke at it with a perturbation, say an electromagnetic field. A typical application is the emission and absorption of radiation by atoms, and a few of the basic ideas of this messy problem will be explained. (The next chapter does give a complete solution for the much cleaner two-state problem of nuclear magnetic resonance.)

We will use the energy eigenstates of the *unperturbed* system to describe the system both with and without the perturbation. So, let  $\psi_L$  be the unperturbed lowest energy state and  $\psi_H$  be the unperturbed highest energy, or "excited", state. In principle,  $\psi_L$  and  $\psi_H$  can be any two energy eigenstates of a system, but to be concrete, think of  $\psi_L$  as the  $\psi_{100}$  ground state of an hydrogen atom, and of  $\psi_H$  as an excited state like  $\psi_{210}$ , with energy  $E_2 > E_1$ .

### 6.2.1 Schrödinger equation for a two-state system

By assumption, the wave function can be approximated as a combination of the two unperturbed eigenstates:

$$\Psi = a\psi_L + b\psi_H \quad |a|^2 + |b|^2 = 1 \quad (6.8)$$

where  $|a|^2$  is the probability of the energy being measured as the lower value  $E_L$ , and  $|b|^2$  the one of the higher energy  $E_H$ . The sum of the two probabilities must be one; the two-state system must be found in either state, {31}.

Now first we need some fix for the hot potato of quantum mechanics, the part that “measurement” plays. We will assume that initially the system is in some given state with values  $a = a_0$  and  $b = b_0$ , maybe in the ground state  $|a_0| = 1$  and  $b_0 = 0$ . Then we turn on our perturbation for a limited time and assume that we have the system all to ourselves; all other perturbations that nature might do will be ignored during this time. After that, we turn our perturbation off again and let the rest of nature rush back in to “measure” the system. Obviously, this picture only makes physical sense if our perturbation is brief compared to the time it takes for the higher energy state to spontaneously transition back to the ground state. If the system transitions back to the ground state while we are still messing with it, then whatever equations we write down for the perturbation process are not going to be physically valid.

Assuming none of this is a problem, then if after the perturbation the system emits a photon with an energy equal to the energy difference between the high and low states, we can conclude that the system has been “measured” to have been in the elevated energy state after our perturbation (but is now back in the ground state.) The higher the probability  $|b|^2$  of the higher energy state after our perturbation, the more samples in a given number of systems will be “measured” to be in the elevated state, so the more photons we will get.

That is the general idea, now let’s work out the details. According to the Schrödinger equation, the time evolution is given as  $i\hbar\dot{\Psi} = H\Psi$ , or here

$$i\hbar(\dot{a}\psi_L + \dot{b}\psi_H) = H(a\psi_L + b\psi_H)$$

Separate equations for  $\dot{a}$  and  $\dot{b}$  can be obtained by taking dot products with  $\langle\psi_L|$ , respectively  $\langle\psi_h|$  and using orthonormality in the left hand side:

$$i\hbar\dot{a} = H_{LL}a + H_{LH}b \quad i\hbar\dot{b} = H_{HL}a + H_{HH}b \quad (6.9)$$

where we have defined the following “Hamiltonian coefficients”

$$H_{LL} = \langle\psi_L|H\psi_L\rangle, \quad H_{LH} = \langle\psi_L|H\psi_H\rangle, \quad H_{HL} = \langle\psi_H|H\psi_L\rangle, \quad H_{HH} = \langle\psi_H|H\psi_H\rangle. \quad (6.10)$$

Note that  $H_{LL}$  and  $H_{HH}$  are real, (1.15) and that  $H_{LH}$  and  $H_{HL}$  are complex conjugates,  $H_{HL} = H_{LH}^*$ .

A general analytical solution to the system (6.9) cannot be given, but we can get rid of half the terms in the right hand sides using the following trick: define new coefficients  $\bar{a}$  and  $\bar{b}$  by

$$a = \bar{a}e^{-i\int H_{LL} dt/\hbar} \quad b = \bar{b}e^{-i\int H_{HH} dt/\hbar} \quad (6.11)$$

Note that the new coefficients  $\bar{a}$  and  $\bar{b}$  are physically just as good as  $a$  and  $b$ : the probabilities are given by the square magnitudes of the coefficients, and the exponentials above have magnitude one, so the square magnitudes of  $\bar{a}$  and  $\bar{b}$  are exactly the same as those of  $a$  and  $b$ . Also, the initial conditions  $a_0$  and  $b_0$  are unchanged, since the exponentials are one at time zero (assuming we choose the integration constants suitably).

The equations for  $\bar{a}$  and  $\bar{b}$  are a lot simpler; substituting the definitions into (6.9) and simplifying:

$$i\hbar\dot{\bar{a}} = \bar{H}_{LH}\bar{b} \quad i\hbar\dot{\bar{b}} = \bar{H}_{HL}\bar{a} \quad (6.12)$$

where

$$\bar{H}_{LH} = \bar{H}_{HL}^* = H_{LH}e^{-i\int(H_{HH}-H_{LL})dt/\hbar} \quad (6.13)$$

### 6.2.2 Stimulated and spontaneous emission

The simplified evolution equations (6.12) that were derived in the previous section have a remarkable property: for every solution  $\bar{a}, \bar{b}$  there is a second solution  $\bar{a}_2 = \bar{b}^*, \bar{b}_2 = -\bar{a}^*$  that has the probabilities of the low and high energy states exactly reversed. It means that

*a perturbation that lifts a system out of the ground state will equally take that system out of the excited state.*

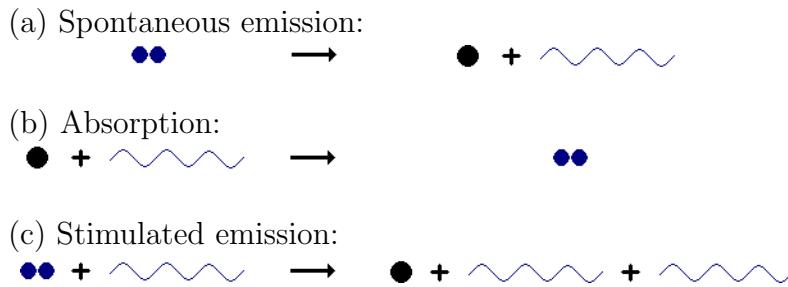


Figure 6.1: Emission and absorption of radiation by an atom.

Consider again the example of the atom. If the atom is in the excited state, it can spontaneously emit a photon, a quantum of electromagnetic energy, transitioning back to the ground state, as sketched in figure 6.1(a). That is spontaneous emission; the photon will have an energy equal to the difference between the two atom energies, and an electromagnetic frequency  $\omega_0$  found by dividing its energy by  $\hbar$ . The inverse of this process is where we perturb the ground state atom with an electromagnetic wave of frequency  $\omega_0$  and the atom absorbs one photon of energy from that wave, entering the excited state. That is absorption, as sketched in figure 6.1(b). But according to the reversed solution above, there must then also be a corresponding process where the same perturbing photon takes the system out of the *excited* state back to the *ground* state, figure 6.1(c). Because of energy conservation, this process, called “stimulated emission”, will produce a *second* photon.

It is the operating principle of the laser: if we have a collection of atoms all in the excited state, we can create a runaway process where a single photon stimulates an atom to produce a second photon, and then those two photons go on to produce two more, and so on. The result will be monochromatic, coherent light, since all its photons originate from the same source.

Note that we must initially have a “population inversion,” we must have more excited atoms than ground state ones, because absorption competes with stimulated emission for photons. Indeed, if we have a 50/50 mixture of ground state and excited atoms, then the processes of figures 6.1(b) and 6.1(c) exactly cancel each other’s effects.

Going back to spontaneous emission; as has been mentioned in section 6.1.1, there is really no such thing. The Schrödinger equation shows that an excited atom will maintain its energy indefinitely if not perturbed. Spontaneous emission, figure 6.1(a), is really stimulated emission figure 6.1(c), in which the triggering photon jumps into and out of existence due to the quantum fluctuations of the electromagnetic field.

### 6.2.3 Absorption of radiation

Let’s work out some of the details for the atom example to see more clearly how exactly an electromagnetic field interacts with the atom. The perturbing electromagnetic field will be assumed to be a monochromatic wave propagating along the  $y$ -axis. Such a wave takes the form

$$\vec{E} = \hat{k}E_0 \cos(\omega(t - y/c) - \phi) \quad \vec{B} = \hat{i}\frac{1}{c}E_0 \cos(\omega(t - y/c) - \phi).$$

where  $\vec{E}$  is the electric field strength,  $\vec{B}$  the magnetic field strength, the constant  $E_0$  is the amplitude of the electric field,  $\omega$  the natural frequency of the wave,  $c$  the speed of light, and  $\phi$  is some phase angle.

But really, we don’t need all that. At nonrelativistic velocities, the charged electron primarily reacts to the electric field, so we will ignore the magnetic field. Moreover, the atom, supposed to be at the origin, is so small compared to the typical wave length of an electromagnetic wave, (assuming it is light and not an X-ray,) that we can put  $y$  to zero and end up with a simple spatially uniform field:

$$\vec{E} = \hat{k}E_0 \cos(\omega t - \phi) \tag{6.14}$$

The Lyman-transition wave lengths are of the order of a thousand Å, and the atom about one Å, so this seems reasonable enough. Assuming that the internal time scales of the atom are small compared to  $\omega$ , we can find the corresponding Hamiltonian as the potential of a steady uniform electric field:

$$H_1 = eE_0 z \cos(\omega t - \phi) \tag{6.15}$$

(It is like the  $mgh$  potential energy of gravity, with the charge playing the part of the mass  $m$ , the electric field strength that of the gravity strength  $g$ , and  $z$  that of the height  $h$ .)

To this we must add the unperturbed Hamiltonian of the hydrogen atom; that one was written down in chapter 3.2.1, but its form is not important for the effect of the perturbation, and we will just refer to it as  $H_0$ . So the total Hamiltonian is

$$H = H_0 + H_1$$

with  $H_1$  as above.

Now we need the Hamiltonian matrix coefficients (6.10). Let's start with  $H_{LL}$ :

$$H_{LL} = \langle \psi_L | H_0 | \psi_L \rangle + \langle \psi_L | H_1 | \psi_L \rangle = E_L + eE_0 \cos(\omega t - \phi) \langle \psi_L | z | \psi_L \rangle$$

It can be seen from the symmetry properties of the eigenfunctions of the hydrogen atom as given in 3.2.4 that the final inner product is zero, and we just have that  $H_{LL}$  is the lower atom energy  $E_L$ . Similarly,  $H_{HH}$  is the higher atom energy  $E_H$ .

For  $H_{LH}$ , the inner product with  $H_0$  is zero, since  $\psi_L$  and  $\psi_H$  are orthogonal eigenfunctions of  $H_0$ , and the inner product with  $H_1$  gives:

$$H_{LH} = eE_0 \langle \psi_L | z | \psi_H \rangle \cos(\omega t - \phi)$$

Since  $H_{LH}$  represents the perturbation in our equations, clearly the key to how well the atom transition responds to a given electric field strength  $E_0$  is the inner product  $\langle \psi_L | ez | \psi_H \rangle$ . In the terms of electromagnetics, loosely speaking that is how well the wave functions produce an “electric dipole” effect, with the effective charge at the positive- $z$  side different from the one at the negative- $z$  side. For that reason, the approximation we made that the electric field is uniform is called the “electric dipole approximation.”

It is important, because assume that we would be looking at the hydrogen 2s to 1s transition, i.e.  $\psi_H = \psi_{200}$  and  $\psi_L = \psi_{100}$ . Both of these states are spherically symmetric, making the inner product  $\langle \psi_L | ez | \psi_H \rangle$  zero by symmetry. So, with no perturbation effect left, our prediction must then unavoidably be that the  $\psi_{200}$  state does not decay to the ground state! Transitions that cannot occur in the dipole approximation are called “forbidden transitions” If we include variations in the electric field (through Taylor series expansion), such forbidden transitions sometimes become possible, but not for spherically symmetric states. Indeed, the  $\psi_{200}$  excited state survives forever, on quantum scales, lasting about a tenth of a second rather than about a nanosecond for the non-spherically symmetric states. Its dominant decay is by the emission of two photons, rather than a single one. You now see why I selected  $\psi_{210}$  as the excited state in my example, rather than the more logical  $\psi_{200}$ .

Returning to the example, to get the Hamiltonian of the simplified system, according to (6.13) we need to multiply  $H_{LH}$  with

$$e^{-i \int (H_{HH} - H_{LL}) dt / \hbar} = e^{-i \int (E_H - E_L) dt / \hbar} = e^{-i\omega_0 t}$$

where we used the fact that the difference between the unperturbed energy levels is  $\hbar\omega_0$ , with  $\omega_0$  the frequency of the photon released when the system transitions from the high energy state to the low one. So the Hamiltonian coefficient of the simplified system is

$$\overline{H}_{LH} = eE_0 \langle \psi_L | z | \psi_H \rangle \cos(\omega t - \phi) e^{-i\omega_0 t}$$

And if we write  $H_{HH} - H_{LL}$  in terms of a frequency, we may as well do the same with the time-independent part of  $\bar{H}_{LH}$  too, and define a frequency  $\omega_1$  by

$$eE_0\langle\psi_L|z|\psi_H\rangle \equiv \hbar\omega_1. \quad (6.16)$$

Note however that unlike  $\omega_0$ ,  $\omega_1$  has no immediate physical meaning as a frequency; it is just a concise way of writing the effective strength level of the perturbation.

So our simplified system (6.12) for the coefficients  $\bar{a}$  and  $\bar{b}$  of the states  $\psi_L$  and  $\psi_H$  becomes:

$$\dot{\bar{a}} = -i\omega_1 \cos(\omega t - \phi) e^{-i\omega_0 t} \bar{b} \quad \dot{\bar{b}} = -i\omega_1 \cos(\omega t - \phi) e^{i\omega_0 t} \bar{a} \quad (6.17)$$

It is maybe a relatively simple-looking system of equations, but it is still not solvable by elementary means.

So we will approximate, and assume that the level of perturbation, hence  $\omega_1$ , is small. We will also assume that we start in the ground state,  $b_0 = 0$ , and even more simply, at  $a_0 = 1$ . If  $a_0$  is one and the changes in  $\bar{a}$ , given by the first of the two equations above, are small, then  $\bar{a}$  will *stay* about one. So in the second equation above, we can just ignore the factor  $\bar{a}$ . That makes this equation readily solvable, since according to Euler's equation (1.5), the cosine falls apart into two simple exponentials:

$$\cos(\omega t - \phi) = \frac{e^{i(\omega t - \phi)} + e^{-i(\omega t - \phi)}}{2}$$

Since there is no real difference between the two exponentials, we only need to solve for one of them if we allow  $\omega$  and  $\phi$  to have any value, positive or negative.

That makes it simple. The solution to

$$\dot{\bar{b}} = -\frac{1}{2}i\omega_1 e^{i\phi} e^{-i(\omega - \omega_0)t} \quad \bar{b}(0) = 0$$

is just

$$\bar{b} = \frac{\omega_1}{\omega - \omega_0} e^{i\phi} \frac{e^{-i(\omega - \omega_0)t} - 1}{2}$$

We are interest in the probability  $|\bar{b}|^2$  of being in the excited state, which is then

$$|\bar{b}|^2 = \left( \frac{\omega_1}{\omega - \omega_0} \right)^2 \sin^2((\omega - \omega_0)t/2) \quad (6.18)$$

Since by assumption the perturbation level  $\omega_1$  is small, you are only going to get a decent “transition probability”  $|\bar{b}|^2$  if  $\omega - \omega_0$  in the result above is correspondingly small. So, only perturbations with frequencies close to that of the emitted photon are going to do much good. The range of frequencies around  $\omega_0$  for which you get some decent response has a typical size  $\omega_1$ . The physical meaning of  $\omega_1$  is therefor as a frequency *range* rather than as a frequency by itself. (Since a small range of frequencies can be absorbed, the observed line in the absorption

spectrum is not going to be a mathematically thin line, but will have a small width. Such an effect is known as “spectral line broadening” {32}.)

It is also seen that we do not have to worry about the other exponential that the perturbation cosine fell apart in. Only the positive value of  $\omega$  can be close to  $\omega_0$ .

In the special case that the perturbation frequency  $\omega$  is exactly the photon frequency  $\omega_0$ , the expression above turns into:

$$|\bar{b}|^2 = \frac{1}{4}\omega_1^2 t^2 \quad (6.19)$$

so in this case the transition probability just keeps growing until  $a$  can no longer be assumed to be one as our approximation did. In fact, the transition probability cannot just keep growing as our result implies, it must stay less than one.

## 6.3 Conservation Laws and Symmetries [Background]

The purpose of this section is to explain where conservation laws such as conservation of linear and angular momentum come from, as well as give the reason why the corresponding operators take the form of differentiations. It should provide a better insight into how the mathematics of quantum mechanics relates to the basic physical properties of nature that we observe all the time.

Let’s pretend for now that we have never heard of angular momentum, nor that it would be preserved, nor what its operator would be. However, there is at least one operation we do know without being told about: rotating a system over an angle.

Consider the effect of this operation on a *complete system* in further empty space. Since empty space by itself has no preferred directions, it does not make a difference under what angle you initially position the system. Identical systems placed in different initial angular orientations will evolve the same, just seen from a different angle.

This “invariance” with respect to angular orientation has consequences when phrased in terms of operators and the Schrödinger equation. In particular, let a system of particles 1, 2, . . . , be described in spherical coordinates by a wave function:

$$\Psi(r_1, \theta_1, \phi_1, S_{z1}, r_2, \theta_2, \phi_2, S_{z2}, \dots)$$

and let  $R_\varphi$  be the operator that rotates this entire system over a given angle  $\varphi$  around the  $z$ -axis:

$$R_\varphi \Psi(r_1, \theta_1, \phi_1, S_{z1}, r_2, \theta_2, \phi_2, S_{z2}, \dots) = \Psi(r_1, \theta_1, \phi_1 + \varphi, S_{z1}, r_2, \theta_2, \phi_2 + \varphi, S_{z2}, \dots)$$

(For the formula as shown, the rotation of the system  $\varphi$  is in the direction of decreasing  $\phi$ . Or if you want, it corresponds to an observer or axis system rotated in the direction of increasing *phi*; in empty space, who is going to see the difference?)

Now the key point is that if space has no preferred direction, the operator  $R_\varphi$  must commute with the Hamiltonian:

$$HR_\varphi = R_\varphi H$$

After all, it should not make any difference at what angle compared to empty space the Hamiltonian is applied: if we first rotate the system and then apply the Hamiltonian, or first apply the Hamiltonian and then rotate the system, the result should be the same. For that reason, an operator such as  $R_\varphi$ , which commutes with the Hamiltonian of the considered system, is called a physical *symmetry* of the system.

The fact that  $R_\varphi$  and  $H$  commute has a mathematical consequence {14}: it means that  $R_\varphi$  must have a complete set of eigenfunctions that are also energy eigenfunctions, and for which the Schrödinger equation gives the evolution. In particular, if the system is initially an eigenfunction of the operator  $R_\varphi$  with a certain eigenvalue, it must *stay* an eigenfunction with this eigenvalue for all time, {33}. The eigenvalue remains the same during the evolution.

But wait. If this eigenvalue does not change with time, does that not mean that it is a conserved number? Is it not just like the money in your wallet if you do not take it out to spend any? Whether or not this eigenvalue will turn out to be important, it must be truly conserved. It is a physical quantity that does not change, just like the mass of our system does not change. So it appears we have here another conservation law, in addition to conservation of mass.

Let's examine the conserved eigenvalue of  $R_\varphi$  a bit closer to see what *physical* quantity it might correspond to. First of all, the magnitude of any eigenvalue of  $R_\varphi$  must be one: if it was not, the square integral of  $\Psi$  could increase by that factor during the rotation, but of course it must stay the same. Since the magnitude is one, the eigenvalue can be written in the form  $e^{ia}$  where  $a$  is some ordinary real number. We have narrowed down the eigenvalue a bit already.

But we can go further: the eigenvalue must more specifically be of the form  $e^{im\varphi}$ , where  $m$  is some real number independent of the amount of rotation. The reasons are that there must be no change in  $\Psi$  when the angle of rotation is zero, and a single rotation over  $\varphi$  must be the same as two rotations over an angle  $\frac{1}{2}\varphi$ . Those requirements imply that the eigenvalue is of the form  $e^{im\varphi}$ .

So  $e^{im\varphi}$  is a preserved quantity if the system starts out as the corresponding eigenfunction of  $R_\varphi$ . We can simplify that statement to say that  $m$  by itself is preserved; if  $m$  varied in time,  $e^{im\varphi}$  would too. Also, we might scale  $m$  by some constant, call it  $\hbar$ , so that we can conform to the dimensional units others, such as classical physicists, might turn out to be using for this preserved quantity.

We can just give a fancy name to this preserved quantity  $m\hbar$ . We can call it “net angular momentum around the  $z$ -axis” because that sounds less nerdy at parties than “scaled logarithm of the preserved eigenvalue of  $R_\varphi$ .” You might think of even better names, but whatever the

name, it is preserved: if the system starts out with a certain value of this angular momentum, it will retain that value for all time. (If it starts out with a combination of values, leaving uncertainty, it will keep that combination of values. The Schrödinger equation is linear, so we can add solutions.)

Next, we would like to define a nicer operator for this “angular momentum” than the rotation operators  $R_\varphi$ . The problem is that there are infinitely many of them, one for every angle  $\varphi$ , and they are all related, a rotation over an angle  $2\varphi$  being the same as two rotations over an angle  $\varphi$ . If we define a rotation operator over a very small angle, call it angle  $\varepsilon$ , then we can approximate all the other operators  $R_\varphi$  by just applying  $R_\varepsilon$  sufficiently many times. To make these approximations exact, we need to make  $\varepsilon$  infinitesimally small, but when  $\varepsilon$  becomes zero,  $R_\varepsilon$  would become just one. We have lost the operator we want by going to the extreme. The trick to avoid this is to subtract the limiting operator 1, and in addition, to avoid that the resulting operator then becomes zero, we must also divide by  $\varepsilon$ :

$$\lim_{\varepsilon \rightarrow 0} \frac{R_\varepsilon - 1}{\varepsilon}$$

is the operator we want.

Now consider what this operator really means for a single particle with no spin:

$$\lim_{\varepsilon \rightarrow 0} \frac{R_\varepsilon - 1}{\varepsilon} \Psi(r, \theta, \phi) = \lim_{\varepsilon \rightarrow 0} \frac{\Psi(r, \theta, \phi + \varepsilon) - \Psi(r, \theta, \phi)}{\varepsilon}$$

By definition, the final term is the partial derivative of  $\Psi$  with respect to  $\phi$ . So the operator we just defined is just the operator  $\partial/\partial\phi$ !

We can go one better still, because the eigenvalues of the operator just defined are

$$\lim_{\varepsilon \rightarrow 0} \frac{e^{im\varepsilon} - 1}{\varepsilon} = im$$

If we add a factor  $\hbar/i$  to the operator, the eigenvalues of the operator are going to be  $m\hbar$ , the quantity we defined to be the angular momentum. So we are led to define the angular momentum operator as:

$$\hat{L}_z \equiv \frac{\hbar}{i} \frac{\partial}{\partial\phi}$$

This agrees perfectly with what we got much earlier in chapter 3.1.2 from guessing that the relationship between angular and linear momentum is the same in quantum mechanics as in classical mechanics. Now we derived it from the fundamental rotational symmetry property of nature, instead of from guessing.

How about the angular momentum of a system of multiple, but still spinless, particles? It is easy to see that the operator

$$\frac{\hbar}{i} \lim_{\varepsilon \rightarrow 0} \frac{R_\varepsilon - 1}{\varepsilon}$$

now acts as a total derivative, equivalent to the sum of the partial derivatives of the individual particles. So the orbital angular momenta of the individual particles just add, as they do in classical physics.

How about spin? Well, we can take a hint from nature. If a particle in a given spin state has an inherent angular momentum in the  $z$ -direction  $m\hbar$ , then apparently the wave function of that particle changes by  $e^{im\varphi}$  when we rotate the particle over an angle  $\varphi$ . A surprising consequence is that if the system is rotated over an angle  $2\pi$ , half integer spin states do not return to the same value; they change sign. Since only the magnitude of the wave function is physically observable, this change of sign does not affect the physical symmetry.

With angular momentum defined, the rotation operator  $R_\varphi$  can be explicitly identified if you are curious. It is

$$R_\varphi = \exp(\varphi i \hat{L}_z / \hbar)$$

where the exponential of an operator is found by writing the exponential as a Taylor series.  $R_\varphi$  is called the “generator of rotations around the  $z$ -axis.” To check that it does indeed take the form above, expand the exponential in a Taylor series and multiply by a state with angular momentum  $L_z = m\hbar$ . The effect is seen to be to multiply the state by the Taylor series of  $e^{im\varphi}$  as it should. So  $R_\varphi$  gets all eigenstates and eigenvalues correct, and must therefore be right since the eigenstates are complete. As an additional check,  $R_\varphi$  can also be verified explicitly for purely orbital momentum states; for example, it turns the wave function  $\Psi(r, \theta, \phi)$  for a single particle into

$$\exp\left(\varphi \frac{i}{\hbar} \hat{L}_z\right) \Psi(r, \theta, \phi) = \exp\left(\varphi \frac{\partial}{\partial \phi}\right) \Psi(r, \theta, \phi)$$

and expanding the exponential in a Taylor series produces the Taylor series for  $\Psi(r, \theta, \phi + \varphi)$ , the correct expression for the wave function in the rotated coordinate system.

There are other symmetries of nature, and they give rise to other conservation laws and their operators. For example, nature is symmetric with respect to translations: it does not make a difference where in empty space you place your system. This symmetry gives rise to linear momentum conservation in the same way that rotational symmetry led to angular momentum conservation. Symmetry with respect to time delay gives rise to energy conservation.

Initially, it was also believed that nature was symmetric with respect to mirroring it (looking at the physics with a mirror). That gave rise to a law of conservation of “parity”. Parity is called “even” when the wave function remains the same when you replace  $\vec{r}$  by  $-\vec{r}$ , (a way of doing the mirroring which is called inversion), and odd if it changes sign. The parity of a complete system was believed to be preserved in time. However, it turned out that the weak nuclear force does not stay the same under mirroring, so that parity is not conserved when weak interactions play a role. Nowadays, most physicists believe that in order to get an equivalent system, in addition to the mirroring, you also need to replace the particles by their antiparticles, having opposite charge, and reverse the direction of time.

## 6.4 The Position and Linear Momentum Eigenfunctions

In subsequent sections, we will be looking at the time evolution of various quantum systems, as predicted by the Schrödinger equation. However, before we can do this, we first need to look at the eigenfunctions of position and linear momentum. That is something that so far we have been studiously avoiding. The problem is that the position and linear momentum eigenfunctions have awkward issues with normalizing them.

These normalization problems have consequences for the coefficients of the eigenfunctions. In the normal orthodox interpretation, the absolute squares of the coefficients should be the probabilities of getting the corresponding values of position, respectively linear momentum. But for position and linear momentum, this statement must be modified a bit.

One good thing is that unlike the Hamiltonian, which is specific to a given system, the position operator

$$\hat{\vec{r}} = (\hat{x}, \hat{y}, \hat{z})$$

and the linear momentum operator

$$\hat{\vec{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z) = \frac{\hbar}{i} \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

are the same for all systems. So, we only need to find their eigenfunctions once.

### 6.4.1 The position eigenfunction

The eigenfunction that corresponds to the particle being at a precise  $x$ -position  $\xi$ ,  $y$ -position  $\eta$ , and  $z$ -position  $\theta$  will be denoted by  $R_{\xi\eta\theta}(x, y, z)$ . The eigenvalue problem is:

$$xR_{\xi\eta\theta}(x, y, z) = \xi R_{\xi\eta\theta}(x, y, z) \quad yR_{\xi\eta\theta}(x, y, z) = \eta R_{\xi\eta\theta}(x, y, z) \quad zR_{\xi\eta\theta}(x, y, z) = \theta R_{\xi\eta\theta}(x, y, z)$$

(Note the need in this section to use  $(\xi, \eta, \theta)$  for the measurable particle position, since  $(x, y, z)$  are already used for the eigenfunction arguments.)

To solve this eigenvalue problem, we try again separation of variables, where it is assumed that  $R_{\xi\eta\theta}(x, y, z)$  is of the form  $X(x)Y(y)Z(z)$ . Substitution gives the partial problem for  $X$  as

$$xX(x) = \xi X(x)$$

This equation implies that at all points  $x$  not equal to  $\xi$ ,  $X(x)$  will have to be zero, otherwise there is no way that the two sides can be equal. So, function  $X(x)$  can only be nonzero at the single point  $\xi$ . At that one point, it can be anything, though.

To resolve the ambiguity, the function  $X(x)$  is taken to be the “Dirac delta function,”

$$X(x) = \delta(x - \xi)$$

The delta function is, loosely speaking, sufficiently strongly infinite at the single point  $x = \xi$  that its integral over that single point is one. More precisely, the delta function is defined as the limiting case of the function shown in the left hand side of figure 6.2.

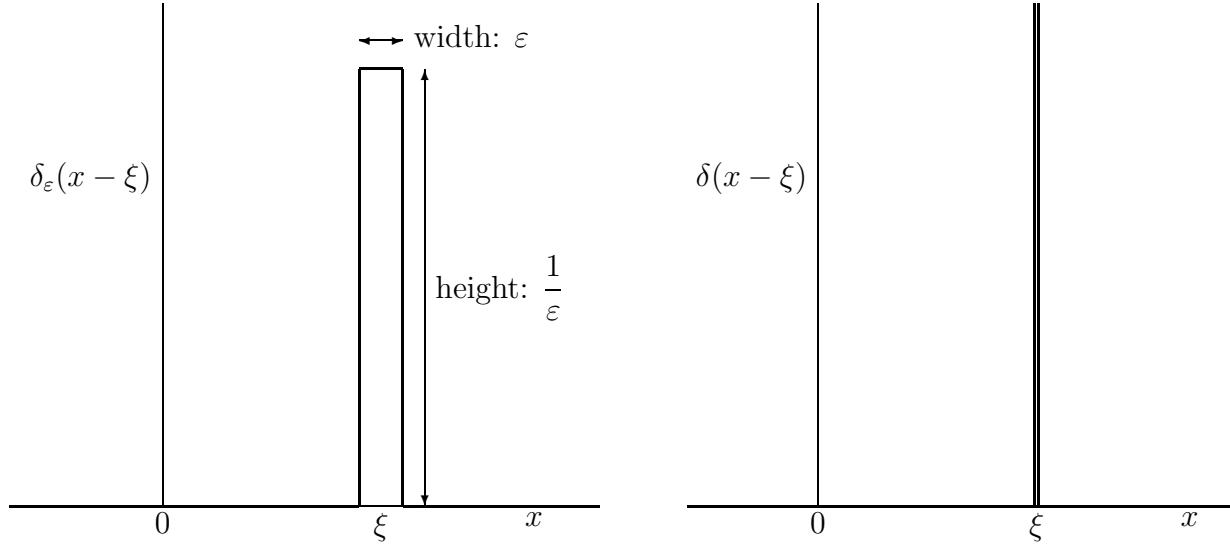


Figure 6.2: Approximate Dirac delta function  $\delta_\varepsilon(x - \xi)$  is shown left. The true delta function  $\delta(x - \xi)$  is the limit when  $\varepsilon$  becomes zero, and is an infinitely high, infinitely thin spike, shown right. It is the eigenfunction corresponding to a position  $\xi$ .

The fact that the integral is one leads to a very useful mathematical property of delta functions: they are able to pick out one specific value of any arbitrary given function  $f(x)$ . Just take an inner product of the delta function  $\delta(x - \xi)$  with  $f(x)$ . It will produce the value of  $f(x)$  at the point  $\xi$ , in other words,  $f(\xi)$ :

$$\langle \delta(x - \xi) | f(x) \rangle = \int_{x=-\infty}^{\infty} \delta(x - \xi) f(x) dx = \int_{x=-\infty}^{\infty} \delta(x - \xi) f(\xi) dx = f(\xi) \quad (6.20)$$

(Since the delta function is zero at all points except  $\xi$ , it does not make a difference whether  $f(x)$  or  $f(\xi)$  is used in the integral.)

The problems for the position eigenfunctions  $Y$  and  $Z$  are the same as the one for  $X$ , and have a similar solution. The complete eigenfunction corresponding to a measured position  $(\xi, \eta, \theta)$  is therefore:

$$R_{\xi\eta\theta}(x, y, z) = \delta(x - \xi)\delta(y - \eta)\delta(z - \theta) \quad (6.21)$$

According to the orthodox interpretation, the probability of finding the particle at  $(\xi, \eta, \theta)$  for a given wave function  $\Psi$  should be the square magnitude of the coefficient  $c_{\xi\eta\theta}$  of the eigenfunction. This coefficient can be found as an inner product:

$$c_{\xi\eta\theta}(t) = \langle \delta(x - \xi)\delta(y - \eta)\delta(z - \theta) | \Psi \rangle$$

It can be simplified to

$$c_{\xi\eta\theta}(t) = \Psi(\xi, \eta, \theta; t) \quad (6.22)$$

because of the property of the delta functions to pick out the corresponding function value.

However, the apparent conclusion that  $|\Psi(\xi, \eta, \theta; t)|^2$  gives the probability of finding the particle at  $(\xi, \eta, \theta)$  is wrong. The reason it fails is that eigenfunctions should be normalized; the integral of their square should be one. The integral of the square of a delta function is infinite, not one. That is OK, however;  $\vec{r}$  is a continuously varying variable, and the chances of finding the particle at  $(\xi, \eta, \theta)$  to *infinite* number of digits accuracy would be zero. So, the properly normalized eigenfunctions would have been useless anyway.

In fact, according to Born's statistical interpretation of chapter 2.1,  $|\Psi(\xi, \eta, \theta)|^2 d^3\vec{r}$  gives the probability of finding the particle in an infinitesimal volume  $d^3\vec{r}$  around  $(\xi, \eta, \theta)$ . In other words,  $|\Psi|^2$  is the probability of finding the particle near that location *per unit volume*.

Besides the normalization issue, another idea that needs to be somewhat modified is a strict collapse of the wave function. Any position measurement that can be done will leave some uncertainty about the precise location of the particle: it will leave the coefficient  $c_{\xi\eta\theta}$ , or in other words  $\Psi(\xi, \eta, \theta)$ , nonzero over a small range of positions, rather than just one position. Moreover, unlike energy eigenstates, position eigenstates are not stationary: after a position measurement,  $\Psi$  will again spread out as time increases.

### 6.4.2 The linear momentum eigenfunction

Turning now to linear momentum, the eigenfunction that corresponds to a precise linear momentum  $(p_x, p_y, p_z)$  will be indicated as  $P_{p_x p_y p_z}(x, y, z)$ . If we again assume that this eigenfunction is of the form  $X(x)Y(y)Z(z)$ , the partial problem for  $X$  is found to be:

$$\frac{\hbar}{i} \frac{\partial X(x)}{\partial x} = p_x X(x)$$

The solution is a complex exponential:

$$X(x) = A e^{ip_x x / \hbar}$$

where  $A$  is a constant.

This linear momentum eigenfunction too has a normalization problem: since it does not become small at large  $|x|$ , the integral of its square is infinite, not one. Again, the solution is to ignore the problem and to just take a nonzero value for  $A$ ; the choice that works out best is to take:

$$A = \frac{1}{\sqrt{2\pi\hbar}}$$

The problems for the  $y$  and  $z$ -linear momentum have similar solutions, so the full eigenfunction for linear momentum takes the form:

$$P_{p_x p_y p_z}(x, y, z) = \frac{1}{\sqrt{2\pi\hbar}^3} e^{i(p_x x + p_y y + p_z z)/\hbar} \quad (6.23)$$

Turning now to the coefficient  $c_{p_x p_y p_z}(t)$  of the eigenfunction, this coefficient is called the “momentum space wave function” and indicated by the special symbol  $\Phi(p_x, p_y, p_z; t)$ . It is again found by taking an inner product of the eigenfunction with the wave function,

$$\Phi(p_x, p_y, p_z; t) = \frac{1}{\sqrt{2\pi\hbar}^3} \langle e^{i(p_x x + p_y y + p_z z)/\hbar} | \Psi \rangle \quad (6.24)$$

Just like what was the case for position, the coefficient of the linear momentum eigenfunction does not quite give the probability for the momentum to be  $(p_x, p_y, p_z)$ . Instead it turns out that  $|\Phi(p_x, p_y, p_z; t)|^2 dp_x dp_y dp_z$  gives the probability of finding the linear momentum within an range  $dp_x dp_y dp_z$  of  $(p_x, p_y, p_z)$ . In short, the momentum space wave function  $\Phi$  is in “momentum space”  $(p_x, p_y, p_z)$  what the normal wave function  $\Psi$  is in normal space  $(x, y, z)$ .

There is even an inverse relationship to recover  $\Psi$  from  $\Phi$ , and it is easy to remember:

$$\Psi(x, y, z; t) = \frac{1}{\sqrt{2\pi\hbar}^3} \langle e^{-i(p_x x + p_y y + p_z z)/\hbar} | \Phi \rangle_{\vec{p}} \quad (6.25)$$

where the subscript on the inner product indicates that the integration is over momentum space rather than physical space.

If this inner product is written out, it reads:

$$\Psi(x, y, z; t) = \frac{1}{\sqrt{2\pi\hbar}^3} \int_{p_x=-\infty}^{\infty} \int_{p_y=-\infty}^{\infty} \int_{p_z=-\infty}^{\infty} \Phi(p_x, p_y, p_z; t) e^{i(p_x x + p_y y + p_z z)/\hbar} dp_x dp_y dp_z \quad (6.26)$$

Mathematicians prove this formula under the name “Fourier Inversion Theorem”. But it really is just the same sort of idea as writing  $\Psi$  as a sum of energy eigenfunctions  $\psi_n$  times their coefficients  $c_n$ , as in  $\Psi = \sum_n c_n \psi_n$ . In this case, the coefficients are given by  $\Phi$  and the eigenfunctions by the exponential (6.23). The only real difference is that the sum has become an integral since  $\vec{p}$  has continuous values, not discrete ones.

## 6.5 Wave Packets in Free Space

This section gives a full description of the motion of a particle according to quantum mechanics. It will be assumed that the particle is in free space, so that the potential energy is zero. In addition, to keep the analysis concise and the results easy to graph, it will be assumed that

the motion is only in the  $x$ -direction. The results may easily be extended to three dimensions, by using separation of variables.

The analysis will also show how limiting the uncertainty in both momentum and position produces the various features of classical Newtonian motion. It may be recalled that in Newtonian motion through free space, the linear momentum  $p$  is constant. (We will drop the subscript from  $p_x$  from now on, since there is only one dimension.) Further, since  $p/m$  is the velocity  $u$ , the classical particle will move at constant speed:

$$x = ut + x_0 \quad u = \frac{p}{m} = \text{constant} \quad \text{for classical Newtonian motion in free space}$$

### 6.5.1 Solution of the Schrödinger equation.

As discussed in section 6.1, the unsteady evolution of a quantum system may be determined by finding the eigenfunctions of the Hamiltonian and giving them coefficients that are proportional to  $e^{-iEt/\hbar}$ . This will be worked out in this subsection.

For a free particle, there is only kinetic energy, which leads in one dimension to the Hamiltonian eigenvalue problem:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E\psi \tag{6.27}$$

Solutions to this equation take the form of exponentials

$$\psi_E = A e^{\pm i\sqrt{2mE}x/\hbar}$$

where  $A$  is a constant.

Note that  $E$  must be positive: if the square root would be imaginary, the solution would blow up exponentially at large positive or negative  $x$ . Since the square magnitude of  $\psi$  at a point gives the probability of finding the particle near that position, blow up at infinity would imply that the particle must be at infinity with certainty.

The energy eigenfunction above is really the same as the eigenfunction of the  $x$ -momentum operator  $\hat{p}$  derived in the previous section:

$$\psi_E = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} \quad \text{with } p = \pm\sqrt{2mE} \tag{6.28}$$

The reason that the momentum eigenfunctions are also energy eigenfunctions is that the energy is all kinetic energy, and the kinetic operator equals  $\hat{T} = \hat{p}^2/2m$ . So eigenfunctions with precise momentum  $p$  have precise energy  $p^2/2m$ .

As was noted in the previous section, combinations of momentum eigenfunctions take the form of an integral rather than a sum. In this one-dimensional case that integral is:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Phi(p, t) e^{ipx/\hbar} dp$$

where  $\Phi(p, t)$  was called the momentum space wave function.

Whether a sum or an integral, the Schrödinger equation still requires that the coefficient of each energy eigenfunction varies in time proportional to  $e^{iEt/\hbar}$ . The coefficient is here the momentum space wave function  $\Phi$ , and the energy is  $E = p^2/2m = \frac{1}{2}pu$ , so the solution of the Schrödinger equation must be:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Phi_0(p) e^{ip(x - \frac{1}{2}ut)/\hbar} dp \quad (6.29)$$

where  $\Phi_0(p) \equiv \Phi(p, 0)$  is determined by whatever initial conditions are relevant to the situation we want to describe. This integral is the final solution for a particle in free space.

### 6.5.2 Component wave solutions

Before trying to interpret the complete obtained solution (6.29) for the wave function of a particle in free space, it is instructive first to have a look at the component solutions, defined by

$$\psi_w \equiv e^{ip(x - \frac{1}{2}ut)/\hbar} \quad (6.30)$$

These solutions will be called component waves; both their real and imaginary parts are sinusoidal, as can be seen from the Euler identity (1.5).

$$\psi_w = \cos(p(x - \frac{1}{2}ut)/\hbar) + i \sin(p(x - \frac{1}{2}ut)/\hbar)$$

In figure 6.3, the real part of the wave (in other words, the cosine), is sketched as the red curve; also the magnitude of the wave (which is unity) is shown as the top black line, and minus the magnitude is drawn as the bottom black line. The black lines enclose the real part

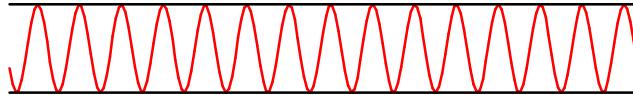


Figure 6.3: The real part (red) and envelope (black) of an example wave.

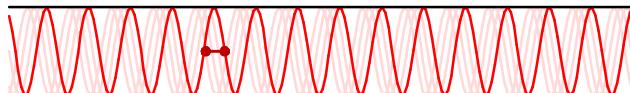
of the wave, and will be called the “envelope.” Since their vertical separation is twice the magnitude of the wave function, the vertical separation between the black lines at a point is a measure for the probability of finding the particle near that point.

The constant separation between the black lines shows that there is absolutely no localization of the particle to any particular region. The particle is equally likely to be found at every point in the infinite range. This also graphically demonstrates the normalization problem of the momentum eigenfunctions discussed in the previous section: the total probability of finding the particle just keeps getting bigger and bigger, the larger the range you look in. So

there is no way that the total probability of finding the particle can be limited to one as it should be.

The reason for the complete lack of localization is the fact that the component wave solutions have an exact momentum  $p$ . With zero uncertainty in momentum, Heisenberg's uncertainty relationship says that there must be infinite uncertainty in position. There is.

There is another funny thing about the component waves: when plotted for different times, it is seen that the real part of the wave moves towards the right with a speed  $\frac{1}{2}u$ , as illustrated in figure 6.4. This is unexpected, because classically the particle moves with speed  $u$ , not  $\frac{1}{2}u$ .



The html version of this document has an animation of the motion.

Figure 6.4: The wave moves with the phase speed.

The problem is that the speed with which the wave moves, called the “phase speed”, is not meaningful physically. In fact, without anything like a location for the particle, there is no way to define a physical velocity for a component wave.

### 6.5.3 Wave packets

As the previous section indicated, in order to get some localization of the position of a particle, some uncertainty must be allowed in momentum. That means that we must take the momentum space wave function  $\Phi_0$  in (6.29) to be nonzero over at least some small *interval* of different momentum values  $p$ . Such a combination of component waves is called a “wave packet”.

The wave function for a typical wave packet is sketched in figure 6.5. The red line is again the real part of the wave function, and the black lines are the envelope enclosing the wave; they equal plus and minus the magnitude of the wave function.

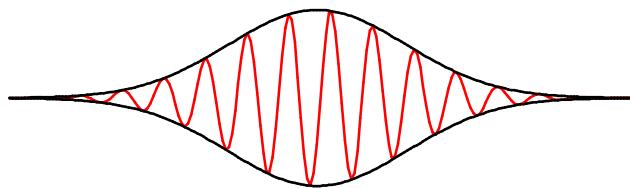


Figure 6.5: The real part (red) and magnitude or envelope (black) of a typical wave packet

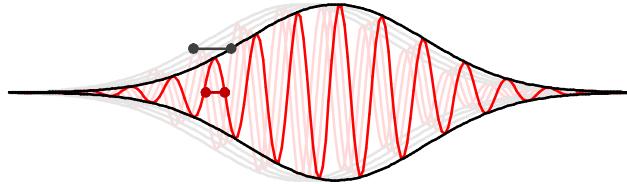
The vertical separation between the black lines is again a measure of the probability of finding the particle near that location. It is seen that the possible locations of the particle are now

restricted to a finite region, the region in which the vertical distance between the black lines is nonzero.

If the envelope changes location with time, and it does, then so does the region where the particle can be found. We now have the correct picture of motion: the region in which the particle can be found propagates through space.

The limiting case of the motion of a macroscopic Newtonian particle can now be better understood. As noted in section 6.1.5, for such a particle the uncertainty in position is negligible. The wave packet in which the particle can be found, as sketched in figure 6.5, is so small that it can be considered to be a point. To that approximation the particle then has a point position, which is the normal classical description.

The classical description also requires that the particle moves with velocity  $u = p/m$ , which is twice the speed  $\frac{1}{2}u$  of the wave. So the envelope should move twice as fast as the wave. This is indicated in figure 6.6 by the length of the bars, which show the motion of a point on the envelope and of a point on the wave during a small time interval.



The html version of this document has an animation of the motion.

Figure 6.6: The velocities of wave and envelope are not equal.

That the envelope does indeed move at speed  $p/m$  can be seen if we define the representative position of the envelope to be the expectation value of position. That position must be somewhere in the middle of the wave packet. The expectation value of position moves according to Ehrenfest's theorem of section 6.1.5 with a speed  $\langle p \rangle/m$ , where  $\langle p \rangle$  is the expectation value of momentum, which must be constant since there is no force. Since the uncertainty in momentum is also small for a macroscopic particle, the expectation value of momentum  $\langle p \rangle$  can be taken to be “the” momentum  $p$ .

#### 6.5.4 The group velocity

The previous subsection explained that the equivalent of particle motion in classical mechanics is the motion of the wave function “envelope” in quantum mechanics. The envelope is simply the magnitude of the wave function, and its motion implies that the region in which the particle can be found changes position.

An argument based on Ehrenfest's theorem showed that in the classical limit, the quantum

mechanical motion is at the same velocity as the classical one. However, that argument has some problems. First, it assumes without proof that the extent of the envelope of a wave packet remains small enough that the expectation value of position is a good enough approximation of the position of the wave packet. It also fails to say anything really useful about nonclassical motion. This subsection properly analyzes both the classical limit and true quantum motion.

First, it may be noted that the classical velocity is what mathematicians call the “group velocity”. It can be defined as the speed at which the envelope moves for a wave packet if the uncertainty in momentum is small, but not so small that there is no localization of the particle. As section 6.1.5 noted, that describes a macroscopic particle precisely.

To derive the group velocity correctly is not quite straightforward: the envelope of a wave packet extends over a finite region, and different points on it actually move at somewhat different speeds. So what do you take as the point that defines the motion in the analysis if you want to be precise? There is a trick here: consider very long times. For large times, the propagation distance is so large that it dwarfs the ambiguity about what point to take as the position of the envelope.

Using the long time idea, it is just a matter of doing a bit of analysis. The general solution of the Schrödinger equation for the wave function was already found in (6.29). That expression involved both the linear momentum  $p$  as well as the equivalent classical velocity  $u = p/m$ , and to avoid confusion it is best to write it all in terms of  $p$ :

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Phi_0(p) e^{ip(x - \frac{1}{2}pt/m)/\hbar} dp \quad (6.31)$$

This may be rewritten as:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} e^{imx^2/2\hbar t} \int_{-\infty}^{\infty} \Phi_0(p) e^{-it(p-mx/t)^2/2m\hbar} dp \quad (6.32)$$

which can easily be checked by expanding the square in the second exponential. In fact, it was obtained by “completing the square”.

Now in Newtonian mechanics, a particle with some given momentum  $p$  would travel at speed  $p/m$ , hence be at approximately  $x = pt/m$  at large times. Conversely, the particle ends up at a given  $x$  if its momentum is about  $mx/t$ . In quantum mechanics this is not necessarily true of course, but it still cannot hurt to write the momentum wave function  $\Phi_0(p)$  as its value at  $mx/t$  plus a remainder:

$$\Phi_0(p) \equiv \Phi_0(mx/t) + (\Phi_0(p) - \Phi_0(mx/t)) \quad (6.33)$$

This splits the integral for  $\Psi$  into two. The second part can be shown to be negligibly small at large times by integration by parts, assuming that the function  $f(p) = (\Phi_0(p) - \Phi_0(mx/t))/(p - (mx/t))$  is well behaved, which it normally is. The first part can be integrated exactly (it is a Fresnel integral), and results in

$$\Psi(x, t) \sim \sqrt{\frac{m}{it}} \Phi_0\left(\frac{mx}{t}\right) e^{imx^2/2\hbar t} \quad (6.34)$$

Now consider the classical case that the uncertainty in momentum is small, so that the momentum wave function  $\Phi_0(p)$  is only nonzero in a narrow range of momenta  $p_1 < p < p_2$ . Then the expression above shows that for large times the wave function will only be nonzero where  $\Phi$  is nonzero, the narrow range of  $x$  values satisfying  $p_1 < mx/t < p_2$ , {34}. Since the difference between  $p_1$  and  $p_2$  is small, we can drop the subscripts and get  $x \sim pt/m$ , which is the same as the classical speed of propagation gives.

This establishes that a wave packet with a narrow range of momenta moves at the classical velocity  $p/m$ , so by definition the group velocity is indeed the classical velocity.

It may be noted that the final result (6.34) is valid for large time whether it is the classical limit or not. In a typical true quantum mechanics case,  $\Phi$  will extend over a range of wave numbers that is not small, and may include both positive and negative values of the momentum  $p$ . So, there is no longer a meaningful velocity for the wave function: the wave function spreads out in all directions at velocities ranging from negative to positive.

For example, if the momentum space wave function  $\Phi$  consists of *two* narrow nonzero regions, one at a positive value of  $p$ , and one at a negative value, then the wave function in normal space splits into two separate wave packets. One packet moves with constant speed towards the left, the other with constant speed towards the right. The same particle is now going in two completely different directions at the same time. This would be completely impossible in classical Newtonian mechanics.

## 6.6 Motion near the Classical Limit

This section examines the motion of a particle in the presence of forces. Just like in the previous section, it will be assumed that the initial position and momentum are narrowed down sufficiently that the particle is restricted to a relatively small region called a wave packet. In addition, for the examples in this section, the forces vary slowly enough that they are approximately constant over the extent of the wave packet. Hence, according to Ehrenfest's theorem, section 6.1.5, the wave packet should move according to the classical Newtonian equations.

### 6.6.1 General procedures

This subsection describes the general procedures that were used to find the example wave packet motions described in the following subsections. It is included mainly for the curious; feel free to skip this subsection.

Each example describes motion of a wave packet under the effect of some chosen potential

$V(x)$ . In each case, it was assumed that  $V(x) = 0$  for negative  $x$ , so that the wave packet initially moves as in free space, which was discussed in section 6.5.

Similar to the case of the particle in free space, the wave function was taken to be an integral

$$\Psi = \int_0^\infty c(p)e^{-iEt/\hbar}\psi_E dp$$

where in the free space case,  $c(p)$  represents the momentum space wave function and  $\psi_E = e^{ipx/\hbar}$ . In the case of a nontrivial potential  $V(x)$ , the  $\psi_E$  are no longer exponentials, but must be found as solutions of the Hamiltonian eigenvalue problem

$$-\frac{\hbar^2}{2m} \frac{\partial \psi_E}{\partial x^2} + V(x)\psi_E = E\psi_E$$

Also,  $p$  is here no longer the momentum of the particle, but simply a computational variable representing the energy values; it is defined as  $p = \sqrt{2mE}$ .

In each example, the chosen potentials  $V(x)$  consisted of linearly varying segments only. A consequence is that the eigenvalue problem for  $\psi_E$  could be solved analytically in each segment: the solution consists of complex exponentials if  $V$  is constant and less than  $E$ , of real exponentials if  $V$  is constant and greater than  $E$ , and of “Airy functions” if  $V$  is not constant but varies linearly. The solution is linear if  $V$  is constant and equal to  $E$ .

The solutions of different segments can be tied together by demanding that adjacent segments give the same values of the wave function and its derivative at the point where they meet. However, in one case a delta function of potential energy was added to the point where two segments meet. A delta function causes a jump increase, call it  $D$ , in the value of the derivative of  $\psi_E$  at the point. It is not a big deal; the value of  $D$  can be found in terms of the strength of the delta function by integrating the Hamiltonian eigenvalue problem over a small range crossing the delta function. The solutions can then be tied together including this derivative change.

The boundary condition at large negative  $x$  was taken to be:

$$\psi_E \sim e^{ipx/\hbar} + Ae^{-ipx/\hbar}$$

in which the first term is the free space solution, and the second term represents a possible reflected wave. The value of  $A$  comes from the computation; it is not prescribed. At large positive  $x$ , if the potential was greater than  $E$  the boundary condition was that the wave function vanishes. If the potential at large  $x$  was less than  $E$ , the boundary condition was that no waves are entering from infinite positive  $x$ : the physical situation to be studied was in each case that of a wave packet entering from negative infinity, not from positive infinity.

Having found the eigenfunctions  $\psi_E$  for sufficiently many values of  $p$ , the wave function  $\Psi$  was found by numerical integration. In doing so, for the coefficient  $c(p)$  a Gaussian form was chosen:

$$c(p) = C_0 e^{-(p-p_0)^2/d^2}$$

where  $C_0$ ,  $p_0$ , and  $d$  where chosen constants. The advantage of a Gaussian is that it minimizes the initial uncertainty in momentum and position as much as the Heisenberg relation allows. However, an additional correction factor was applied to ensure that  $c(p)$  was exactly zero for negative  $p$  values.

### 6.6.2 Motion through free space

The first example will be free space, where  $V = 0$ . Classically, a particle in free space moves at a constant velocity. In quantum mechanics, the wave packet does too; figure 6.7 shows it at two different times. (The blue point indicates the position of maximum wave function magnitude.)



The html version of this document has an animation of the motion to show that it is indeed at constant speed.

Figure 6.7: A particle in free space.

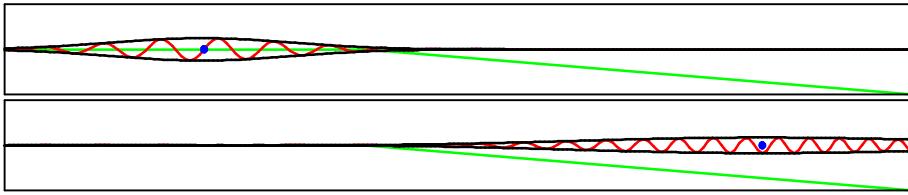
If we step back far enough that the wave packet in the figures above begins to resemble a single point, we have classical motion. A closer examination shows that the wave packet is actually expanding a bit in size in addition to translating.

### 6.6.3 Accelerated motion

Figure 6.8 shows the motion when the potential energy (shown in green) ramps down starting from some point. Physically this corresponds to a constant accelerating force beyond the point. A classical point particle would move at constant speed until it encounters the ramp, after which it would start accelerating at a constant rate. The quantum mechanical solution shows a corresponding acceleration of the wave packet, but in addition the wave packet stretches a lot.

### 6.6.4 Decelerated motion

Figure 6.9 shows the motion when the potential energy (shown in green) ramps up starting from some point. Physically this corresponds to a constant decelerating force beyond the

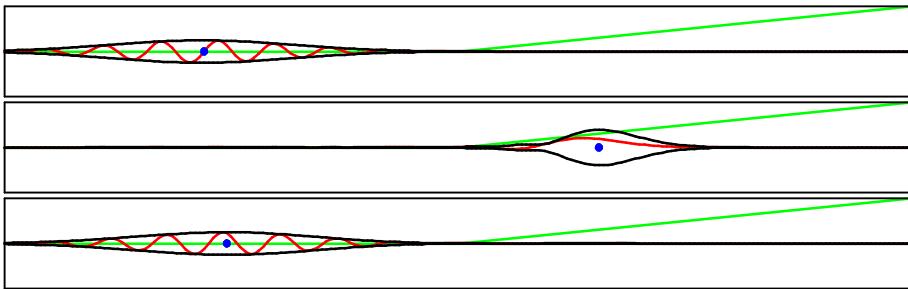


The html version of this document has an animation of the motion.

Figure 6.8: An accelerating particle.

point. A classical point particle would move at constant speed until it encounters the ramp, after which it would start decelerating until it runs out of steam and be turned back, returning to where it came from. The point where it runs out of steam is the point where the potential energy  $V$  becomes equal to the total energy  $E$  of the particle, leaving it nothing for kinetic energy.

The quantum mechanical solution shows a corresponding reflection of the wave packet back to where it came from.



The html version of this document has an animation of the motion.

Figure 6.9: An decelerating particle.

### 6.6.5 The harmonic oscillator

The harmonic oscillator was the real first quantum system that we solved, but only now, near the end of this document, are we able to recreate the classical picture of a particle actually oscillating back and forward.

There are some differences in analysis compared to the motions in the previous subsections. In particular, chapter 2.7.2 showed that the energy levels of the one-dimensional harmonic oscillator are discrete,

$$E_n = \frac{2n+1}{2}\hbar\omega \text{ for } n = 0, 1, 2, \dots$$

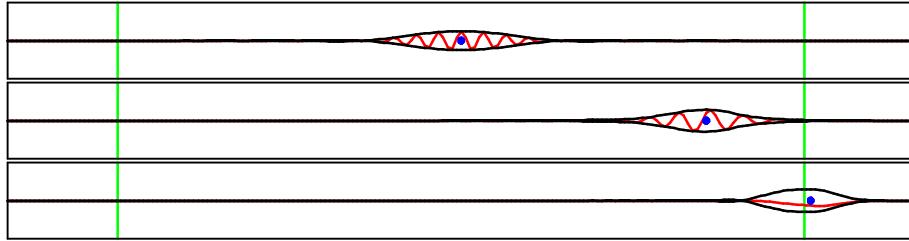
so that unlike the motions just discussed, the solution of the Schrödinger equation is a sum,

rather than an integral

$$\Psi(x, t) = \sum_{n=0}^{\infty} c_n e^{-iE_n t/\hbar} h_n(x)$$

However, for large  $n$  the difference between summation and integration is small. Also, while the energy eigenfunctions  $h_n(x)$  are not exponentials as for the free particle, for large  $n$  they can be pairwise combined to approximate such exponentials.

Hence, localized wave packets similar to the ones in free space may be formed if the range of  $n$  values is large enough, in other words, if the energy is large enough. That is done in figure 6.10, which gives the motion of a wave packet centered around  $n = 50$ .



The html version of this document has an animation of the motion.

Figure 6.10: Unsteady solution for the harmonic oscillator. The third picture shows the maximum distance from the nominal position that the wave packet reaches.

The wave packet performs a periodic oscillation back and forth just like a classical point particle would. In addition, it may be seen from the Schrödinger solution above that it oscillates at the correct classical frequency  $\omega$ . Finally, the point of maximum wave function, shown in blue, fairly closely obeys the classical limits of motion, shown in green.

Interestingly enough, the wave function does *not* return to the same values after one period: it has changed sign after one period and it takes two periods for the wave function to return to the same values. It is because the sign of the wave function cannot be observed physically that classically the particle oscillates at frequency  $\omega$ , and not at  $\frac{1}{2}\omega$  like the wave function.

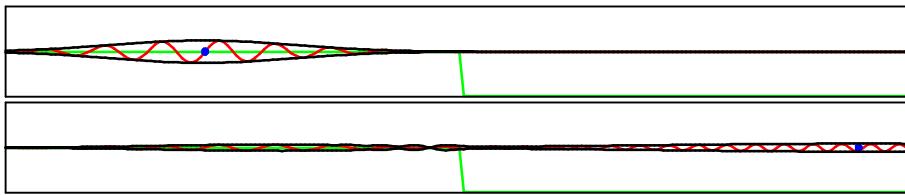
The larger the energy levels are, the more the wave packet can resemble a single point compared to the limits of motion. However, the computer program used to create the animation above evaluated the eigenfunctions using power series instead of a finite difference solver. This limited it to a maximum of about  $n = 50$  when allowing for enough uncertainty to localize the wave packet.

## 6.7 Scattering

The motion of the wave packets in the unsteady quantum systems studied in the previous section approximated that of classical Newtonian particles. However, if the potential starts varying nontrivially over distances short enough to be comparable to a quantum wave length, much more interesting behavior results, for which there is no classical equivalent. This section gives a couple of important examples.

### 6.7.1 Partial reflection

A classical particle entering a region of changing potential will keep going as long as its total energy exceeds the potential energy. Especially for a potential as shown in green in figure 6.11, it will keep advancing, since the potential only goes down.



The html version of this document has an animation of the motion.

Figure 6.11: A partial reflection.

However, the potential in this example varies so rapidly on quantum scales that the classical Newtonian picture is completely wrong. What actually happens is that the wave packet splits into two, as shown in the bottom figure. One part returns to where the packet came from, the other keeps on going.

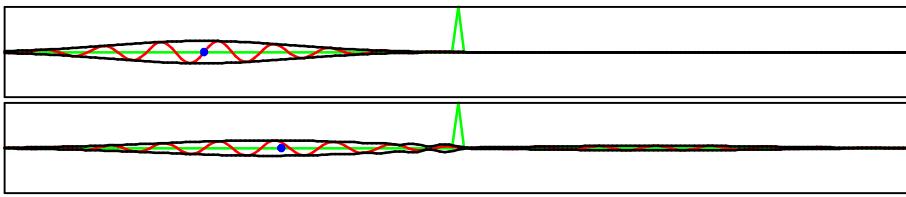
One hypothetical example used in some past sections was that of sending a single particle both to Venus and to Mars. As the current solution shows, a scattering setup gives a very real way of sending a particle in two different directions at the same time.

Partial reflections are the norm for potentials that vary nontrivially on quantum scales, but this example adds a second twist. Classically, a *decelerating* force is needed to turn a particle back, but here the force is everywhere accelerating only! As an actual physical example of this weird behavior, neutrons trying to enter nuclei experience attractive forces that come on so quickly that they may be repelled by them.

## 6.7.2 Tunneling

A classical particle will never be able to progress past a point at which the potential exceeds its total energy. It will be turned back. However, the quantum mechanical truth is, if the region in which the potential exceeds the particle's energy is narrow enough on quantum scale, the particle can go right through it. This effect is called "tunneling."

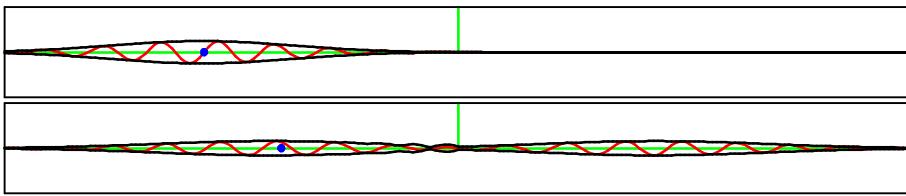
As an example, figure 6.12 shows part of the wave packet of a particle passing right through a region where the peak potential exceeds the particle's expectation energy by a factor three.



The html version of this document has an animation of the motion.

Figure 6.12: An tunneling particle.

Of course, the energy values have some uncertainty, but the example made sure that the peak potential is well above any measurable value of the energy of the particle. And if that is not convincing enough, consider the case of a delta function barrier in figure 6.13; the limit of an infinitely high, infinitely narrow barrier. Being infinitely high, classically *nothing* can get past it. But since it is also infinitely narrow, a particle will hardly notice a weak-enough delta function barrier. In figure 6.13, the strength of the delta function was chosen big enough to split the wave function into equal reflected and transmitted parts.



The html version of this document has an animation of the motion.

Figure 6.13: Penetration of an infinitely high potential energy barrier.

Curiously enough, a delta function well, (with the potential going down instead of up), reflects the same amount as the barrier version.

Tunneling has consequences for the mathematics of bound energy states. Classically, we can confine a particle by sticking it in between, say two delta function potentials, or between two other potentials that have a maximum potential energy  $V$  that exceeds the particle's energy  $E$ . But such a particle trap does not work in quantum mechanics, because given time, the particle would tunnel out over a local potential barrier. In quantum mechanics, a particle is bound only if its energy is less than the potential energy at infinite distance. Local potential

barriers only work if they have infinite energy, and that over a larger range than a delta function.

One major application of tunneling is the scanning tunneling microscope. Tunneling can also explain alpha decay of nuclei, and it is a critical part of many advanced electronics, including current leakage problems in VLSI devices.



# Chapter 7

## Some Additional Topics

This book is intended to be a learning guide to quantum mechanics, rather than a reference work. If you start working on nanotechnology, you will encounter many topics not covered in this work. Below are some introductory expositions to various areas not covered in the earlier chapters, to get you started if you need to work in them. Unlike the previous chapters, a lot of sections here use linear algebra. If you want to do some serious work in quantum mechanics, you will simply need to learn linear algebra.

### 7.1 All About Angular Momentum [Advanced]

The quantum mechanics of angular momentum is fascinating, as this chapter will show. It is also very basic to much of quantum mechanics, so you may want to browse through this section to get an idea of what is there.

In chapter 4.4, it was already mentioned that angular momentum comes in two basic kinds: orbital angular momentum, which is a result of the motion of particles, and the “built-in” angular momentum called spin.

The eigenfunctions of orbital angular momentum are the so called “spherical harmonics” of chapter 3.1, and they show that the orbital angular momentum in any arbitrarily chosen direction, we will call it the  $z$ -direction from now on, comes in whole multiples  $m$  of Planck’s constant  $\hbar$ :

$$L_z = m\hbar \quad \text{with } m \text{ an integer for orbital angular momentum}$$

Integers are whole numbers, such as  $0, \pm 1, \pm 2, \pm 3, \dots$ . The square orbital angular momentum  $L^2 = L_x^2 + L_y^2 + L_z^2$  comes in values

$$L^2 = l(l+1)\hbar^2 \quad \text{with } l \geq 0, \text{ and for orbital angular momentum } l \text{ is an integer.}$$

The numbers  $l$  and  $m$  are called the azimuthal and magnetic quantum numbers.

When spin angular momentum is included, it is conventional to still write  $L_z$  as  $m\hbar$  and  $L^2$  as  $l(l+1)\hbar^2$ , there is nothing wrong with that, but then  $m$  and  $l$  are no longer necessarily integers. The spin of common particles, such as electrons, neutrons, and protons, instead has  $m = \pm \frac{1}{2}$  and  $l = \frac{1}{2}$ . But while  $m$  and  $l$  can be half integers, we will find in this section that they can never be anything more arbitrary than that, regardless of what sort of angular momentum it is. A particle with, say, spin  $\frac{1}{3}\hbar$  cannot not exist according to the theory.

In order to have a consistent notation, from now on every angular momentum eigenstate with quantum numbers  $l$  and  $m$  will be indicated as  $|l m\rangle$  whether it is a spherical harmonic  $Y_l^m$ , a particle spin state, or a combination of angular momenta from more than one source.

### 7.1.1 The fundamental commutation relations

Analyzing nonorbital angular momentum is a challenge. How can you say anything sensible about angular momentum, the dynamic motion of masses around a given point, without a mass moving around a point? For, while a particle like an electron has spin angular momentum, trying to explain it as angular motion of the electron about some internal axis leads to gross contradictions such as the electron exceeding the speed of light [3, p. 172]. Spin is definitely part of the law of conservation of angular momentum, but it does not seem to be associated with any familiar idea of some mass moving around some axis as far as we know.

There goes the Newtonian analogy, then. We need something else to analyze spin than classical physics.

Now, the complex discoveries of mathematics are routinely deduced from apparently self-evident simple axioms, such as that a straight line will cross each of a pair of parallel lines under the same angle. Actually, such axioms are not as obvious as they seem, and mathematicians have deduced very different answers from changing the axioms into different ones. Such answers may be just as good or better than others depending on circumstances, and you can invent imaginary universes in which they are the norm.

Physics has no such latitude to invent its own universes; its mission is to describe *ours* as well as it can. But the idea of mathematics is still a good one: try to guess the simplest possible basic “law” that nature really seems to obey, and then reconstruct as much of the complexity of nature from it as we can. The more we can deduce from the law, the more ways we have to check it against a variety of facts, and the more confident we can become in it.

Physicist have found that the needed equations for angular momentum are given by the following “fundamental commutation relations.”

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \quad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \quad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y \quad (7.1)$$

They can be derived for orbital angular momentum (see chapter 3.4.4), but must be *postulated* to also apply to spin angular momentum {35}.

At first glance, these commutation relations do not look like a promising starting point for much analysis. All they say on their face is that the angular momentum operators  $\hat{L}_x$ ,  $\hat{L}_y$ , and  $\hat{L}_z$  do not commute, so that they cannot have a full set of eigenstates in common. That is hardly impressive.

But if you read the following sections, you will be astonished by what knowledge can be teased out of them. For starters, one thing that immediately follows is that the *only* eigenstates that  $\hat{L}_x$ ,  $\hat{L}_y$ , and  $\hat{L}_z$  have in common are states  $|0\ 0\rangle$  of no angular momentum at all {36}. No other common eigenstates exist.

### 7.1.2 Ladders

This section starts the quest to figure out everything that the fundamental commutation relations mean for angular momentum. We will first verify that any angular momentum can always be described using  $|l\ m\rangle$  eigenstates with definite values of square angular momentum  $L^2$  and  $z$ -angular momentum  $L_z$ . Then it will be found that these angular momentum states occur in groups called “ladders”.

To start with the first one, the mathematical condition for a complete set of eigenstates  $|l\ m\rangle$  to exist is that the angular momentum operators  $\hat{L}^2$  and  $\hat{L}_z$  commute. They do; using the commutator manipulations of chapter 3.4.4), it is easily found that:

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0 \quad \text{where } \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

So mathematics says that eigenstates  $|l\ m\rangle$  of  $\hat{L}_z$  and  $\hat{L}^2$  exist satisfying

$$\hat{L}_z|l\ m\rangle = L_z|l\ m\rangle \quad \text{where by definition } L_z = m\hbar \tag{7.2}$$

$$\hat{L}^2|l\ m\rangle = L^2|l\ m\rangle \quad \text{where by definition } L^2 = l(l+1)\hbar^2 \text{ and } l \geq 0 \tag{7.3}$$

and that are complete in the sense that any state can be described in terms of these  $|l\ m\rangle$ .

Unfortunately the eigenstates  $|l\ m\rangle$ , except for  $|0\ 0\rangle$  states, do not satisfy relations like (7.2) for  $\hat{L}_x$  or  $\hat{L}_y$ . The problem is that  $\hat{L}_x$  and  $\hat{L}_y$  do not commute with  $\hat{L}_z$ . But  $\hat{L}_x$  and  $\hat{L}_y$  *do* commute with  $\hat{L}^2$ , and you might wonder if that is still worth something. To find out, multiply, say, the zero commutator  $[\hat{L}^2, \hat{L}_x]$  by  $|l\ m\rangle$ :

$$[\hat{L}^2, \hat{L}_x]|l\ m\rangle = (\hat{L}^2\hat{L}_x - \hat{L}_x\hat{L}^2)|l\ m\rangle = 0$$

Now take the second term to the right hand side of the equation, noting that  $\hat{L}^2|l\ m\rangle = L^2|l\ m\rangle$  with  $L^2$  just a number that can be moved up-front, to get:

$$\hat{L}^2(\hat{L}_x|l\ m\rangle) = L^2(\hat{L}_x|l\ m\rangle)$$

Looking a bit closer at this equation, it shows that the combination  $\hat{L}_x|l m\rangle$  satisfies the same eigenvalue problem for  $\hat{L}^2$  as  $|l m\rangle$  itself. In other words, the multiplication by  $\hat{L}_x$  does not affect the square angular momentum  $L^2$  at all.

To be picky, that is not quite true if  $\hat{L}_x|l m\rangle$  would be zero, because zero is not an eigenstate of anything. However, such a thing only happens if there is no angular momentum; (it would make  $|l m\rangle$  an eigenstate of  $\hat{L}_x$  with eigenvalue zero in addition to an eigenstate of  $\hat{L}_z$  {36}). Except for that trivial case,  $\hat{L}_x$  does not affect square angular momentum. And neither does  $\hat{L}_y$  or any combination of the two.

Angular momentum in the  $z$ -direction is affected by  $\hat{L}_x$  and by  $\hat{L}_y$ , since they do not commute with  $\hat{L}_z$  like they do with  $\hat{L}^2$ . Nor is it possible to find any linear combination of  $\hat{L}_x$  and  $\hat{L}_y$  that does commute with  $\hat{L}_z$ . What is the next best thing? Well, it *is* possible to find two combinations, to wit

$$\hat{L}^+ \equiv \hat{L}_x + i\hat{L}_y \quad \text{and} \quad \hat{L}^- \equiv \hat{L}_x - i\hat{L}_y, \quad (7.4)$$

that satisfy the “commutator eigenvalue problems”:

$$[\hat{L}_z, \hat{L}^+] = \hbar\hat{L}^+ \quad \text{and} \quad [\hat{L}_z, \hat{L}^-] = -\hbar\hat{L}^-.$$

These two turn out to be quite remarkable operators.

Like  $\hat{L}_x$  and  $\hat{L}_y$ , their combinations  $\hat{L}^+$  and  $\hat{L}^-$  leave  $L^2$  alone. To examine what the operator  $\hat{L}^+$  does with the linear momentum in the  $z$ -direction, we multiply its commutator relation above by an eigenstate  $|l m\rangle$ :

$$(\hat{L}_z\hat{L}^+ - \hat{L}^+\hat{L}_z)|l m\rangle = \hbar\hat{L}^+|l m\rangle$$

Or, taking the second term to the right hand side of the equation and noting that by definition  $\hat{L}_z|l m\rangle = m\hbar|l m\rangle$ ,

$$\hat{L}_z(\hat{L}^+|l m\rangle) = (m+1)\hbar(\hat{L}^+|l m\rangle)$$

That is a stunning result, as it shows that  $\hat{L}^+|l m\rangle$  is an eigenstate with  $z$  angular momentum  $L_z = (m+1)\hbar$  instead of  $m\hbar$ . In other words,  $\hat{L}^+$  adds exactly one unit  $\hbar$  to the  $z$ -angular momentum, turning an  $|l m\rangle$  state into a  $|l m+1\rangle$  one!

If we apply  $\hat{L}^+$  another time, we get a state of still higher  $z$ -angular momentum  $|l m+2\rangle$ , and so on, like the rungs on a ladder. This is graphically illustrated for some examples in figures 7.1 and 7.2. The process eventually comes to an halt at some top rung  $m = m_{\max}$  where  $\hat{L}^+|l m_{\max}\rangle = 0$ . It has to, because the angular momentum in the  $z$ -direction cannot just keep growing forever: the square angular momentum in the  $z$ -direction only must stay less than the total square angular momentum in all three directions {37}.

The second “ladder operator”  $\hat{L}^-$  works in much the same way, but it goes down the ladder; its deducts one unit  $\hbar$  from the angular momentum in the  $z$ -direction at each application.  $\hat{L}^-$  provides the second stile to the ladders, and must terminate at some bottom rung  $m_{\min}$ .

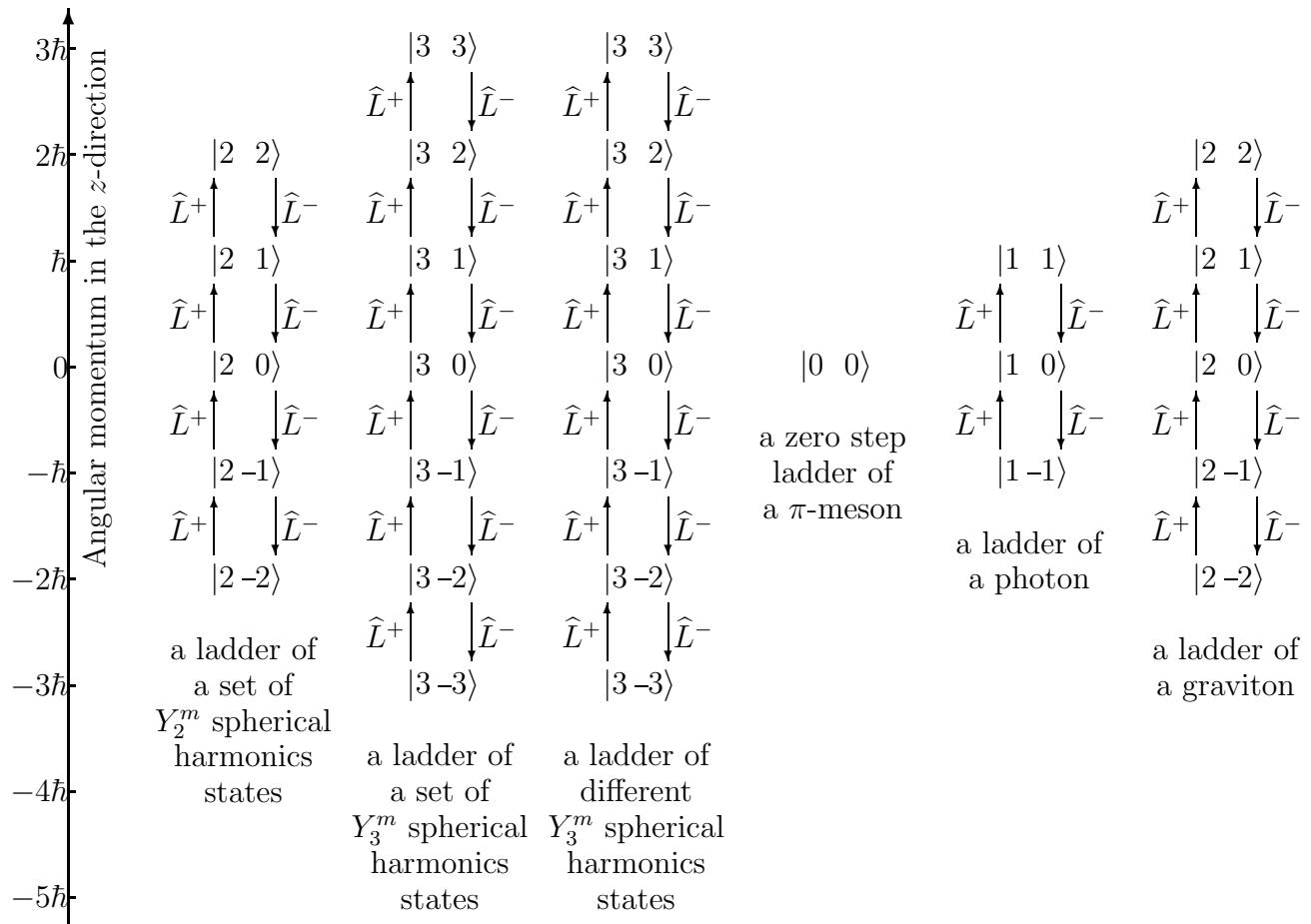


Figure 7.1: Example bosonic ladders.

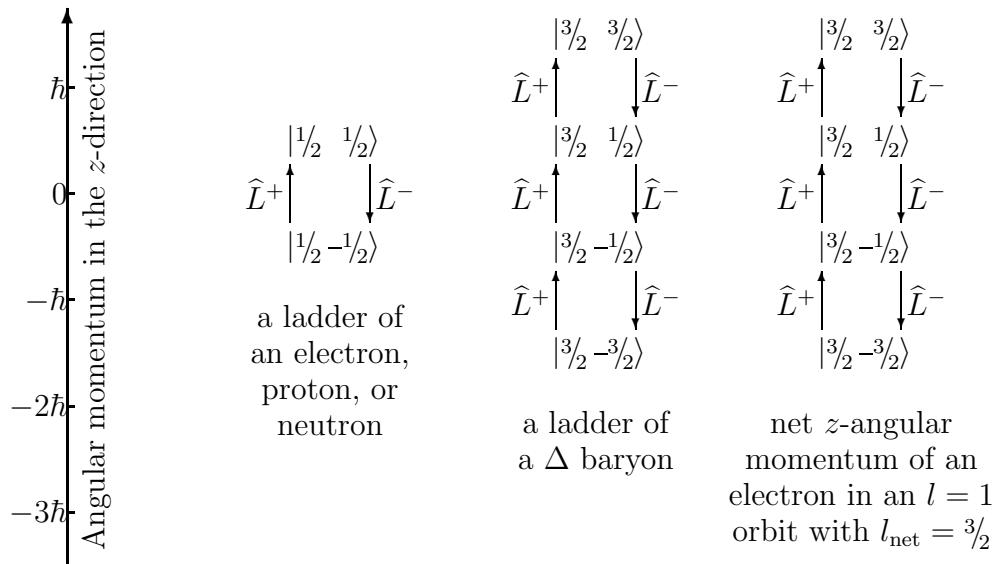


Figure 7.2: Example fermionic ladders.

### 7.1.3 Possible values of angular momentum

The fact that the angular momentum ladders of the previous section must have a top and a bottom rung restricts the possible values that angular momentum can take. In this section, we will show that the azimuthal quantum number  $l$  can either be a nonnegative whole number or half of one, but nothing else. And we will show that the magnetic quantum number  $m$  must range from  $-l$  to  $+l$  in unit increments. In other words, the bosonic and fermionic example ladders in figures 7.1 and 7.2 are representative of all that is possible.

To start, in order for a ladder to end at a top rung  $m_{\max}$ ,  $\hat{L}^+|lm\rangle$  has to be zero for  $m = m_{\max}$ . More specifically, its magnitude  $|\hat{L}^+|lm\rangle|$  must be zero. The square magnitude is given by the inner product with itself:

$$|\hat{L}^+|lm\rangle|^2 = \langle \hat{L}^+|lm\rangle | \hat{L}^+|lm\rangle \rangle = 0.$$

Now because of the complex conjugate that is used in the left hand side of an inner product, (see chapter 1.3),  $\hat{L}^+ = \hat{L}_x + i\hat{L}_y$  goes to the other side of the product as  $\hat{L}^- = \hat{L}_x - i\hat{L}_y$ , and we must have

$$|\hat{L}^+|lm\rangle|^2 = \langle |lm\rangle | \hat{L}^- \hat{L}^+ | lm \rangle \rangle$$

Let's figure out that operator product:

$$\hat{L}^- \hat{L}^+ \equiv (\hat{L}_x - i\hat{L}_y)(\hat{L}_x + i\hat{L}_y) = \hat{L}_x^2 + \hat{L}_y^2 + i(\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x),$$

but  $\hat{L}_x^2 + \hat{L}_y^2$  is the square angular momentum  $\hat{L}^2$  except for  $\hat{L}_z^2$ , and the term within the parentheses is the commutator  $[\hat{L}_x, \hat{L}_y]$  which is according to the fundamental commutation relations equal to  $i\hbar\hat{L}_z$ , so we have

$$\hat{L}^- \hat{L}^+ = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z \tag{7.5}$$

We are in luck: the effect of each of the operators in the left hand side on a state  $|lm\rangle$  is known and we can figure out our inner product:

$$|\hat{L}^+|lm\rangle|^2 = l(l+1)\hbar^2 - m^2\hbar^2 - m\hbar^2 \tag{7.6}$$

We can now answer the question where angular momentum ladders end:

$$l(l+1)\hbar^2 - m_{\max}^2\hbar^2 - m_{\max}\hbar^2 = 0$$

There are two possible solutions to this quadratic equation for  $m_{\max}$ , to wit  $m_{\max} = l$  or  $-m_{\max} = l + 1$ . The second solution is impossible since it already would have the square  $z$ -angular momentum exceed the total square angular momentum. So unavoidably,

$$m_{\max} = l.$$

That is one of the things we promised to show at the start of this section.

The lowest rung on the ladder goes the same way; we get

$$\hat{L}^+ \hat{L}^- = \hat{L}^2 - \hat{L}_z^2 + \hbar \hat{L}_z \quad (7.7)$$

and then

$$|\hat{L}^-|l m\rangle^2 = l(l+1)\hbar^2 - m^2\hbar^2 + m\hbar^2 \quad (7.8)$$

and the only acceptable solution for the lowest rung on the ladders is

$$m_{\min} = -l.$$

It is nice and symmetric; ladders run from  $m = -l$  up to  $m = l$ , as the examples in figures 7.1 and 7.2 already showed.

And in fact, it is more than that; it also limits what the quantum numbers  $l$  and  $m$  can be. For, since each step on a ladder increases the magnetic quantum number  $m$  by one unit, we have for the total number of steps up from bottom to top:

$$\text{total number of steps} = m_{\max} - m_{\min} = 2l$$

But the number of steps is a whole number, and so the azimuthal quantum  $l$  must either be a nonnegative integer, such as 0, 1, 2, ..., or half of one, such as  $\frac{1}{2}, \frac{3}{2}, \dots$ . Integer  $l$  values occur, for example, for the spherical harmonics of orbital angular momentum and for the spin of bosons like photons. Half-integer values occur, for example, for the spin of fermions such as electrons, protons, neutrons, and  $\Delta$  particles.

Note that if  $l$  is a half-integer, then so are the corresponding values of  $m$ , since  $m$  starts from  $-l$  and increases in unit steps. See again figures 7.1 and 7.2 for some examples. Also note that ladders terminate just before  $z$ -momentum would exceed total momentum.

We may also note that ladders are distinct. It is not possible to go up one ladder, like the first  $Y_3^m$  one in figure 7.1 with  $\hat{L}^+$  and then come down the second one using  $\hat{L}^-$ . The reason is that the states  $|l m\rangle$  are eigenstates of the operators  $\hat{L}^- \hat{L}^+$ , (7.5), and  $\hat{L}^+ \hat{L}^-$ , (7.7), so going up with  $\hat{L}^+$  and then down again with  $\hat{L}^-$ , or vice-versa, returns to the same state. For similar reasons, if the tops of two ladders are orthonormal, then so is the rest of their rungs.

#### 7.1.4 A warning about angular momentum

Normally, eigenstates are indeterminate by a complex number of magnitude one. If you so desire, you can multiply any normalized eigenstate by a number of unit magnitude of your own choosing, and it is still a normalized eigenstate. It is important to remember that in analytical expressions involving angular momentum, you are *not* allowed to do this.

As an example, consider a pair of spin 1/2 particles, call them  $a$  and  $b$ , in the “singlet state”, in which their spins cancel and there is no net angular momentum. It was noted in chapter

4.6.5 that this state takes the form

$$|0\ 0\rangle_{ab} = \frac{|1/2\ 1/2\rangle_a |1/2\ -1/2\rangle_b - |1/2\ -1/2\rangle_a |1/2\ 1/2\rangle_b}{\sqrt{2}}$$

(we use kets rather than arrows in this section for spin states.) But if we were allowed to arbitrarily change the definition of say the spin state  $|1/2\ -1/2\rangle_a$  by a minus sign, then the minus sign in the singlet state above would turn in a plus sign. The given expression for the singlet state, with its minus sign, is only correct if we use the right normalization factors for the individual states.

It all has to do with the ladder operators  $\hat{L}^+$  and  $\hat{L}^-$ . They are very convenient for analysis, but to make that easiest, we would like to know *exactly* what they do to our angular momentum states  $|l\ m\rangle$ . What we have seen so far is that  $\hat{L}^+|l\ m\rangle$  produces a state with the same square angular momentum, and with angular momentum in the  $z$ -direction equal to  $(m + 1)\hbar$ . In other words,  $\hat{L}^+|l\ m\rangle$  is some multiple of a suitably normalized eigenstate  $|l\ m+1\rangle$ ;

$$\hat{L}^+|l\ m\rangle = C|l\ m+1\rangle$$

where the number  $C$  is the multiple. What *is* that multiple? Well, from the magnitude of  $\hat{L}^+|l\ m\rangle$ , derived earlier in (7.6) we know that its square magnitude is

$$|C|^2 = l(l + 1)\hbar^2 - m^2\hbar^2 - m\hbar^2.$$

But that still leaves  $C$  indeterminate by a factor of unit magnitude. Which would be very inconvenient in the analysis of angular momentum.

To resolve this conundrum, we will restrict the normalization factors of the angular momentum states  $|l\ m\rangle$  in ladders. We will require that the normalization factors are chosen such that the ladder operator constants are positive real numbers. That really leaves only *one* normalization factor in an entire ladder freely selectable, say the one of the top rung.

Most of the time, this is not a big deal. Only when you start trying to get too clever with angular momentum normalization factors, then you want to remember that you cannot really choose them to your own liking.

The good news is that in this convention, we know *precisely* what the ladder operators do {38}:

$$\hat{L}^+|l\ m\rangle = \hbar\sqrt{l(l + 1) - m(1 + m)}|l\ m+1\rangle \quad (7.9)$$

$$\hat{L}^-|l\ m\rangle = \hbar\sqrt{l(l + 1) + m(1 - m)}|l\ m-1\rangle \quad (7.10)$$

### 7.1.5 Triplet and singlet states

With the ladder operators, we can determine how different angular momenta add up to net angular momentum. As an example, this section will examine what net spin values can be

produced by two particles, each with spin  $1/2$ . They may be the proton and electron in a hydrogen atom, or the two electrons in the hydrogen molecule, or whatever. The actual result will be to rederive the triplet and singlet states described in chapter 4.6.5, but it will also be an example for how more complex angular momentum states can be combined.

The particles involved will be denoted as  $a$  and  $b$ . Since each particle can have two different spin states  $|1/2\ 1/2\rangle$  and  $|1/2\ -1/2\rangle$ , there are four different combined “product” states:

$$|1/2\ 1/2\rangle_a |1/2\ 1/2\rangle_b, |1/2\ 1/2\rangle_a |1/2\ -1/2\rangle_b, |1/2\ -1/2\rangle_a |1/2\ 1/2\rangle_b, \text{ and } |1/2\ -1/2\rangle_a |1/2\ -1/2\rangle_b.$$

In these product states, each particle is in a single individual spin state. The question is, what is the combined angular momentum of these four product states? And what combination states have definite net values for square and  $z$  angular momentum?

The angular momentum in the  $z$ -direction is simple; it is just the sum of those of the individual particles. For example, the  $z$ -momentum of the  $|1/2\ 1/2\rangle_a |1/2\ 1/2\rangle_b$  state follows from

$$(\hat{L}_{za} + \hat{L}_{zb}) |1/2\ 1/2\rangle_a |1/2\ 1/2\rangle_b = \frac{1}{2}\hbar |1/2\ 1/2\rangle_a |1/2\ 1/2\rangle_b + |1/2\ 1/2\rangle_a |1/2\ \hbar |1/2\ 1/2\rangle_b = \hbar |1/2\ 1/2\rangle_a |1/2\ 1/2\rangle_b$$

which makes the net angular momentum in the  $z$  direction  $\hbar$ , or  $1/2\hbar$  from each particle. Note that the  $z$  angular momentum operators of the two particles simply add up and that  $\hat{L}_{za}$  only acts on particle  $a$ , and  $\hat{L}_{zb}$  only on particle  $b$  {39}. In terms of quantum numbers, the magnetic quantum number  $m_{ab}$  is the sum of the individual quantum numbers  $m_a$  and  $m_b$ ;  $m_{ab} = m_a + m_b = 1/2 + 1/2 = 1$ .

The net total angular momentum is not so obvious; we cannot just add total angular momenta. To figure out the total angular momentum of  $|1/2\ 1/2\rangle_a |1/2\ 1/2\rangle_b$  anyway, there is a dirty trick: multiply it with the combined step-up operator

$$\hat{L}_{ab}^+ = \hat{L}_a^+ + \hat{L}_b^+$$

Each part returns zero:  $\hat{L}_a^+$  because particle  $a$  is at the top of its ladder and  $\hat{L}_b^+$  because particle  $b$  is. So the combined state  $|1/2\ 1/2\rangle_a |1/2\ 1/2\rangle_b$  must be at the top of the ladder too; there is no higher rung. That must mean  $l_{ab} = m_{ab} = 1$ ; the combined state must be a  $|1\ 1\rangle$  state. We will *define* it as *the* combination  $|1\ 1\rangle$  state:

$$|1\ 1\rangle_{ab} \equiv |1/2\ 1/2\rangle_a |1/2\ 1/2\rangle_b \tag{7.11}$$

As mentioned earlier, eigenstates are indeterminate by a factor of magnitude one; we could just as well have defined  $|1\ 1\rangle_{ab}$  as  $-|1/2\ 1/2\rangle_a |1/2\ 1/2\rangle_b$  or  $i|1/2\ 1/2\rangle_a |1/2\ 1/2\rangle_b$ , say. But why drag along a minus sign or  $i$  if you do not have to? We have found our first triplet state.

You will surely admit it was a smart idea to multiply with  $\hat{L}_{ab}^+$  to figure out the total angular momentum of the  $|1/2\ 1/2\rangle_a |1/2\ 1/2\rangle_b$  state. But I have another great idea: multiply by  $\hat{L}_{ab}^-$ : that will go one step down the combined states ladder and produce a combination state  $|1\ 0\rangle_{ab}$ :

$$\hat{L}_{ab}^- |1\ 1\rangle_{ab} = \hbar \sqrt{1(1+1) + 1(1-1)} |1\ 0\rangle_{ab} = \hat{L}_a^- |1/2\ 1/2\rangle_a |1/2\ 1/2\rangle_b + \hat{L}_b^- |1/2\ 1/2\rangle_a |1/2\ 1/2\rangle_b$$

or

$$\hbar\sqrt{2}|10\rangle_{ab} = \hbar|1/2 -1/2\rangle_a|1/2 1/2\rangle_b + \hbar|1/2 1/2\rangle_a|1/2 -1/2\rangle_b$$

where the effects of the ladder-down operators were taken from (7.10). (Note that this requires that the individual particle spin states are normalized consistent with the ladder operators.) The second triplet state is therefor:

$$|10\rangle_{ab} \equiv \sqrt{1/2}|1/2 1/2\rangle_a|1/2 -1/2\rangle_b + \sqrt{1/2}|1/2 -1/2\rangle_a|1/2 1/2\rangle_b \quad (7.12)$$

But this gives only *one*  $|l m\rangle$  combination state for the *two* product states  $|1/2 1/2\rangle_a|1/2 -1/2\rangle_b$  and  $|1/2 -1/2\rangle_a|1/2 1/2\rangle_b$  with zero net  $z$ -momentum. If I want to describe unequal combinations of them, like  $|1/2 1/2\rangle_a|1/2 -1/2\rangle_b$  by itself, it cannot be just a multiple of  $|10\rangle_{ab}$ . This suggests that there may be another  $|l 0\rangle_{ab}$  combination state involved here. How do I get this second state?

Well, I am out of fresh ideas, but I can reuse an old one. If I construct a combination of the two product states that steps up to zero, it must be a state with zero  $z$ -angular momentum that is at the end of its ladder, a  $|00\rangle_{ab}$  state. Consider an arbitrary combination of the two product states with as yet unknown numerical coefficients  $C_1$  and  $C_2$ :

$$C_1|1/2 1/2\rangle_a|1/2 -1/2\rangle_b + C_2|1/2 -1/2\rangle_a|1/2 1/2\rangle_b$$

For this combination to step up to zero,

$$(\hat{L}_a^+ + \hat{L}_b^+) (C_1|1/2 1/2\rangle_a|1/2 -1/2\rangle_b + C_2|1/2 -1/2\rangle_a|1/2 1/2\rangle_b) = \hbar C_1|1/2 1/2\rangle_a|1/2 1/2\rangle_b + \hbar C_2|1/2 1/2\rangle_a|1/2 1/2\rangle_b$$

must be zero, which requires  $C_2 = -C_1$ , leaving  $C_1$  undetermined.  $C_1$  must be chosen such that the state is normalized, but that still leaves a constant of magnitude one undetermined. We will take  $C_1$  real and positive, and then

$$|00\rangle_{ab} = \sqrt{1/2}|1/2 1/2\rangle_a|1/2 -1/2\rangle_b - \sqrt{1/2}|1/2 -1/2\rangle_a|1/2 1/2\rangle_b \quad (7.13)$$

We have found the singlet state.

To find the remaining triplet state, just apply  $\hat{L}_{ab}^-$  once more, to  $|10\rangle_{ab}$  above. It gives:

$$|1-1\rangle_{ab} = |1/2 -1/2\rangle_a|1/2 -1/2\rangle_b \quad (7.14)$$

Of course, the normalization factor of this bottom state had to turn out to be one; all three step-down operators produce only positive real factors.

Figure 7.3 shows the results graphically in terms of ladders. The two possible spin states of each of the two electrons produce 4 combined product states indicated using up and down arrows. These product states are then combined to produce triplet and singlet states that have definite values for both  $z$ - and total net angular momentum, and can be shown as rungs on ladders.

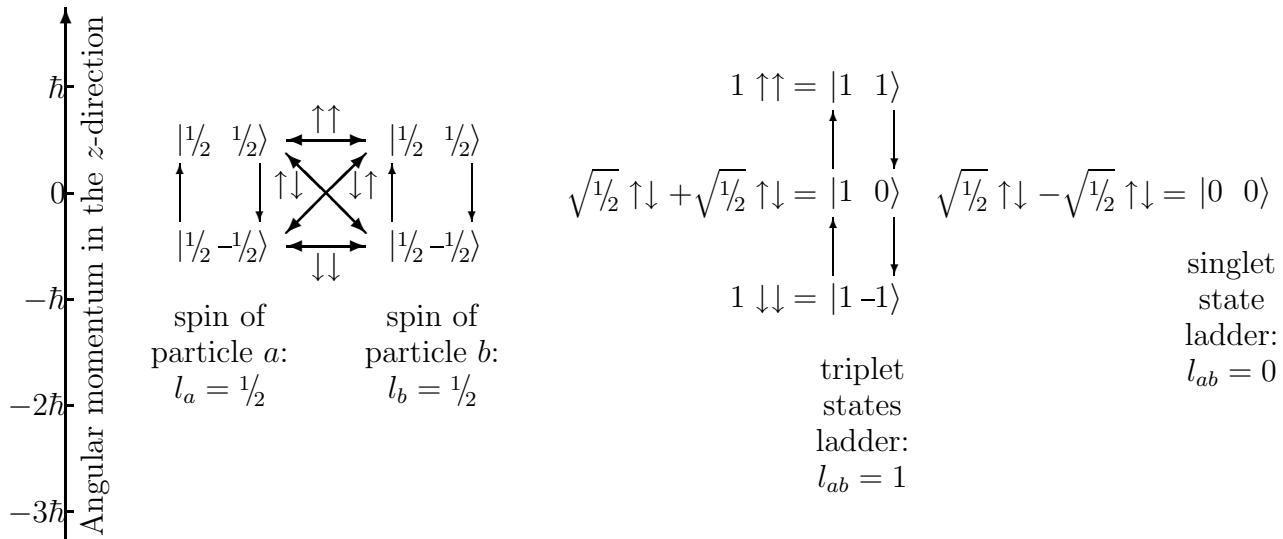


Figure 7.3: Triplet and singlet states in terms of ladders

Note that a product state like  $|\frac{1}{2} \frac{1}{2}\rangle_a |\frac{1}{2} -\frac{1}{2}\rangle_b$  cannot be shown as a rung on a ladder. In fact, from adding (7.12) and (7.13) it is seen that

$$|\frac{1}{2} \frac{1}{2}\rangle_a |\frac{1}{2} -\frac{1}{2}\rangle_b = \sqrt{\frac{1}{2}}|1 0\rangle_{ab} + \sqrt{\frac{1}{2}}|0 0\rangle_{ab}$$

which makes it a combination of the middle rungs of the triplet and singlet ladders, rather than a single rung.

### 7.1.6 Clebsch-Gordan coefficients

In classical physics, combining angular momentum from different sources is easy; the net components in the  $x$ ,  $y$ , and  $z$  directions are simply the sum of the individual components. In quantum mechanics, things are trickier, because if the component in the  $z$ -direction exists, those in the  $x$  and  $y$  directions do not. But the previous subsection showed how the spin angular momenta of two spin  $\frac{1}{2}$  particles could be combined. In similar ways, the angular momentum states of any two ladders, whatever their origin, can be combined into net angular momentum ladders. And then those ladders can in turn be combined with still other ladders, allowing net angular momentum states to be found for systems of arbitrary complexity.

The key is to be able to combine the angular momentum ladders from two different sources into net angular momentum ladders. To do so, the net angular momentum can in principle be described in terms of product states in which each source is on a single rung of its ladder. But as the example of the last section illustrated, such product states give incomplete information about the net angular momentum; they do not tell us what square net angular momentum is. We need to know what combinations of product states produce rungs on the ladders of the

net angular momentum, like the ones illustrated in figure 7.3. In particular, we need to know the coefficients that multiply the product states in those combinations.

			$ 1\rangle_{ab}$
		$ 0\rangle_{ab}$	$ 1\rangle_{ab}$
	$ 0\rangle_{ab}$	$ 0\rangle_{ab}$	$ 1\rangle_{ab}$
$ 0\rangle_{ab}$	$ 0\rangle_{ab}$	$ 1\rangle_{ab}$	$ 1\rangle_{ab}$
$ 1\rangle_{ab}$	$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$	$ 1\rangle_{ab}  1\rangle_{ab}  1\rangle_{ab}  1\rangle_{ab}$
$ 1\rangle_{ab}$	$-\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$	$ 1\rangle_{ab}  1\rangle_{ab}  1\rangle_{ab}  1\rangle_{ab}$
$ 1\rangle_{ab}$	$1$	$1$	$ 1\rangle_{ab}  1\rangle_{ab}  1\rangle_{ab}  1\rangle_{ab}$

Figure 7.4: Clebsch-Gordan coefficients of two spin  $\frac{1}{2}$  particles.

These coefficients are called “Clebsch-Gordan” coefficients. Figure 7.4 shows the ones from figure 7.3 tabulated. Note that there are really three tables of numbers; one for each rung level. The top, single number, “table” says that the  $|1 1\rangle$  net momentum state is found in terms of product states as:

$$|1 1\rangle_{ab} = 1 \times |1/2 1/2\rangle_a |1/2 1/2\rangle_b$$

The second table gives the states with zero net angular momentum in the  $z$ -direction. For example, the first column of the table says that the  $|0 0\rangle$  singlet state is found as:

$$|0 0\rangle_{ab} = \sqrt{\frac{1}{2}} |1/2 1/2\rangle_a |1/2 -1/2\rangle_b - \sqrt{\frac{1}{2}} |1/2 -1/2\rangle_a |1/2 1/2\rangle_b$$

Similarly the second column gives the middle rung  $|1 0\rangle$  on the triplet ladder. The bottom “table” gives the bottom rung of the triplet ladder.

You can also read the tables horizontally {40}. For example, the first row of the middle table says that the  $|1/2 1/2\rangle_a |1/2 -1/2\rangle_b$  product state equals

$$|1/2 1/2\rangle_a |1/2 -1/2\rangle_b = \sqrt{\frac{1}{2}} |0 0\rangle_{ab} + \sqrt{\frac{1}{2}} |1 0\rangle_{ab}$$

That in turn implies that if the net square angular momentum of this product state is measured, there is a 50/50 chance of it turning out to be either zero, or the  $l = 1$  (i.e.  $2\hbar^2$ ) value. The  $z$ -momentum will always be zero.

How about the Clebsch-Gordan coefficients to combine other ladders than the spins of two spin  $\frac{1}{2}$  particles? Well, the same procedures used in the previous section work just as well to combine the angular momenta of any two angular momentum ladders, whatever their size. Just the thing for a long winter night. Or, if you live in Florida, you just might want to write a little computer program that does it for you {41} and outputs the tables in human-readable form {42}, like figures 7.5 and 7.6.

$l_a = 1, l_b = \frac{1}{2}$ $ 1\ 1\rangle_a  1/2\ 1/2\rangle_b$ $\begin{pmatrix} \sqrt{2/3} & \sqrt{1/3} \\ -\sqrt{1/3} & \sqrt{2/3} \end{pmatrix}$	$l_a = \frac{1}{2}, l_b = \frac{1}{2}$ $ 1/2\ 1/2\rangle_{ab}$ $ 1\ 0\rangle_a  1/2\ -1/2\rangle_b$ $\begin{pmatrix} \sqrt{1/3} & \sqrt{2/3} \\ -\sqrt{2/3} & \sqrt{1/3} \end{pmatrix}$
$l_a = 1, l_b = \frac{1}{2}$ $ 1/2\ -1/2\rangle_{ab}$ $ 1\ -1\rangle_a  1/2\ -1/2\rangle_b$ $\begin{pmatrix} \sqrt{1/3} & \sqrt{2/3} \\ -\sqrt{2/3} & \sqrt{1/3} \end{pmatrix}$	$l_a = \frac{1}{2}, l_b = \frac{1}{2}$ $ 0\ 0\rangle_{ab}$ $ 1/2\ 1/2\rangle_a  1/2\ 1/2\rangle_b$ $\begin{pmatrix} \sqrt{1/2} & \sqrt{1/2} \\ -\sqrt{1/2} & \sqrt{1/2} \end{pmatrix}$
$l_a = \frac{3}{2}, l_b = \frac{1}{2}$ $ 2\ 2\rangle_{ab}$ $ 1\ -1\rangle_a  1/2\ -1/2\rangle_b$ $\begin{pmatrix} \sqrt{3/4} & \sqrt{1/4} \\ -\sqrt{1/4} & \sqrt{3/4} \end{pmatrix}$	$l_a = 2, l_b = \frac{1}{2}$ $ 2\ 0\rangle_{ab}$ $ 2\ 1\rangle_a  1/2\ 1/2\rangle_b$ $ 3/2\ 3/2\rangle_a  1/2\ -1/2\rangle_b$ $\begin{pmatrix} \sqrt{4/5} & \sqrt{1/5} \\ -\sqrt{1/5} & \sqrt{4/5} \end{pmatrix}$
$l_a = \frac{3}{2}, l_b = \frac{1}{2}$ $ 2\ -1\rangle_{ab}$ $ 1\ -1\rangle_a  1/2\ -1/2\rangle_b$ $ 3/2\ 1/2\rangle_a  1/2\ -1/2\rangle_b$ $\begin{pmatrix} \sqrt{1/2} & \sqrt{1/2} \\ -\sqrt{1/2} & \sqrt{1/2} \end{pmatrix}$	$l_a = 2, l_b = \frac{1}{2}$ $ 2\ 2\rangle_a  1/2\ 1/2\rangle_b$ $ 3/2\ 3/2\rangle_a  1/2\ -1/2\rangle_b$ $ 5/2\ 5/2\rangle_a  1/2\ -1/2\rangle_b$ $\begin{pmatrix} \sqrt{3/5} & \sqrt{2/5} \\ -\sqrt{2/5} & \sqrt{3/5} \end{pmatrix}$
$l_a = \frac{3}{2}, l_b = \frac{1}{2}$ $ 2\ -2\rangle_{ab}$ $ 1\ -2\rangle_a  1/2\ -1/2\rangle_b$ $ 3/2\ -3/2\rangle_a  1/2\ -1/2\rangle_b$ $\begin{pmatrix} \sqrt{1/4} & \sqrt{3/4} \\ -\sqrt{3/4} & \sqrt{1/4} \end{pmatrix}$	$l_a = 2, l_b = \frac{1}{2}$ $ 2\ 1\rangle_a  1/2\ 1/2\rangle_b$ $ 2\ 0\rangle_a  1/2\ 1/2\rangle_b$ $ 3/2\ -1/2\rangle_a  1/2\ -1/2\rangle_b$ $\begin{pmatrix} \sqrt{2/5} & \sqrt{3/5} \\ -\sqrt{3/5} & \sqrt{2/5} \end{pmatrix}$
$l_a = \frac{5}{2}, l_b = \frac{1}{2}$ $ 2\ -3\rangle_{ab}$ $ 1\ -3\rangle_a  1/2\ -1/2\rangle_b$ $ 5/2\ -3/2\rangle_a  1/2\ -1/2\rangle_b$ $\begin{pmatrix} \sqrt{1/5} & \sqrt{4/5} \\ -\sqrt{4/5} & \sqrt{1/5} \end{pmatrix}$	$l_a = 2, l_b = \frac{1}{2}$ $ 2\ -1\rangle_a  1/2\ -1/2\rangle_b$ $ 2\ -2\rangle_a  1/2\ 1/2\rangle_b$ $ 2\ -2\rangle_a  1/2\ -1/2\rangle_b$ $ 5/2\ -5/2\rangle_a  1/2\ -1/2\rangle_b$ $\begin{pmatrix} \sqrt{2/5} & \sqrt{3/5} \\ -\sqrt{3/5} & \sqrt{2/5} \end{pmatrix}$
$l_a = \frac{5}{2}, l_b = \frac{1}{2}$ $ 2\ -2\rangle_{ab}$ $ 1\ -2\rangle_a  1/2\ -1/2\rangle_b$ $ 5/2\ -5/2\rangle_a  1/2\ -1/2\rangle_b$ $\begin{pmatrix} \sqrt{1/5} & \sqrt{4/5} \\ -\sqrt{4/5} & \sqrt{1/5} \end{pmatrix}$	

Figure 7.5: Clebsch-Gordan coefficients for  $l_b = \frac{1}{2}$ .

Figure 7.6: Clebsch-Gordan coefficients for  $l_b = 1$ .

From the figures you may note that when two states with total angular momentum quantum numbers  $l_a$  and  $l_b$  are combined, the combinations have total angular quantum numbers ranging from  $l_a + l_b$  to  $|l_a - l_b|$ . This is similar to the fact that when in classical mechanics two angular momentum vectors are combined, the combined total angular momentum  $L_{ab}$  is at most  $L_a + L_b$  and at least  $|L_a - L_b|$ . (The so-called “triangle inequality” for combining vectors.) But of course,  $l$  is not quite a proportional measure of  $L$  unless  $L$  is large; in fact,  $L = \sqrt{l(l+1)}\hbar$  {43}.

### 7.1.7 Pauli spin matrices

Let's go back to the simple two rung spin ladder of an electron, or any other spin  $1/2$  particle for that matter, and try to tease out some more information about the spin. While we have so far made statements about the angular momentum in the arbitrarily chosen  $z$ -direction, you often also need information about the spin in the corresponding  $x$  and  $y$  directions. This section will find it.

But before getting at it, a matter of notations. It is customary to indicate angular momentum that is due to spin not by a capital  $L$ , but by a capital  $S$ . Similarly, the azimuthal quantum number is then indicated by  $s$  instead of  $l$ . In this subsection we will follow this convention.

Now, suppose we know that the particle is in the “spin-up” state with  $S_z = 1/2\hbar$  angular momentum in a chosen  $z$  direction; in other words that it is in the  $|1/2\ 1/2\rangle$ , or  $\uparrow$ , state. We want the effect of the  $\hat{S}_x$  and  $\hat{S}_y$  operators on this state. In the absence of a physical model for the motion that gives rise to the spin, this may seem like a hard question indeed. But again the faithful ladder operators  $\hat{S}^+$  and  $\hat{S}^-$  clamber up and down to our rescue!

Assuming that the normalization factor of the  $\downarrow$  state is chosen in terms of the one of the  $\uparrow$  state consistent with the ladder relations (7.9) and (7.10), we have:

$$\hat{S}^+ \uparrow = (\hat{S}_x + i\hat{S}_y) \uparrow = 0 \quad \hat{S}^- \uparrow = (\hat{S}_x - i\hat{S}_y) \uparrow = \hbar \downarrow$$

By adding or subtracting the two equations, we find the effects of  $\hat{S}_x$  and  $\hat{S}_y$  on the spin-up state:

$$\hat{S}_x \uparrow = \frac{1}{2}\hbar \downarrow \quad \hat{S}_y \uparrow = \frac{1}{2}i\hbar \downarrow$$

It works the same way for the spin-down state  $\downarrow = |1/2\ -1/2\rangle$ :

$$\hat{S}_x \downarrow = \frac{1}{2}\hbar \uparrow \quad \hat{S}_y \downarrow = -\frac{1}{2}i\hbar \uparrow$$

We now know the effect of the  $x$ - and  $y$ -angular momentum operators on our  $z$ -direction spin states. Chalk one up for the ladder operators.

Next, assume that you have some spin state that is an arbitrary combination of spin-up and spin-down:

$$a \uparrow + b \downarrow$$

Then, according to the expressions above, application of the  $x$ -spin operator  $\hat{S}_x$  will turn it into:

$$\hat{S}_x (a \uparrow + b \downarrow) = a \left( 0 \uparrow + \frac{1}{2} \hbar \downarrow \right) + b \left( \frac{1}{2} \hbar \uparrow + 0 \downarrow \right)$$

while the operator  $\hat{S}_y$  turns it into

$$\hat{S}_y (a \uparrow + b \downarrow) = a \left( 0 \uparrow + \frac{1}{2} \hbar i \downarrow \right) + b \left( -\frac{1}{2} \hbar i \uparrow + 0 \downarrow \right)$$

And of course, since  $\uparrow$  and  $\downarrow$  are the eigenstates of  $\hat{S}_z$ ,

$$\hat{S}_z (a \uparrow + b \downarrow) = a \left( \frac{1}{2} \hbar \uparrow + 0 \downarrow \right) + b \left( 0 \uparrow - \frac{1}{2} \hbar \downarrow \right)$$

If we put the coefficients in the formula above, except for the common factor  $\frac{1}{2}\hbar$ , in little  $2 \times 2$  tables, we get the so-called “Pauli spin matrices”:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (7.15)$$

where the convention is that  $a$  multiplies the first column of the matrices and  $b$  the second. Also, the top rows in the matrices produce the spin-up part of the result and the bottom rows the spin down part. In linear algebra, we also put the coefficients  $a$  and  $b$  together in a vector:

$$a \uparrow + b \downarrow \equiv \begin{pmatrix} a \\ b \end{pmatrix}$$

We can now go further and find the eigenstates of the  $\hat{S}_x$  and  $\hat{S}_y$ -operators in terms of the eigenstates  $\uparrow$  and  $\downarrow$  of the  $\hat{S}_z$  operator. You can use the techniques of linear algebra, but we will just guess: for example, if we guess  $a = b = 1$ ,

$$\hat{S}_x \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{2} \hbar \sigma_x \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{2} \hbar \begin{pmatrix} 0 \times 1 + 1 \times 1 \\ 1 \times 1 + 0 \times 1 \end{pmatrix} = \frac{1}{2} \hbar \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

so  $a = b = 1$  is an eigenstate of  $\hat{S}_x$  with eigenvalue  $\frac{1}{2}\hbar$ , call it  $a \rightarrow$ , “spin-right”, state. To normalize the state, we still need to divide by  $\sqrt{2}$ :

$$\rightarrow = \frac{1}{\sqrt{2}} \uparrow + \frac{1}{\sqrt{2}} \downarrow$$

Similarly, we can guess the other eigenstates, and we get in total:

$$\rightarrow = \frac{1}{\sqrt{2}} \uparrow + \frac{1}{\sqrt{2}} \downarrow \quad \leftarrow = -\frac{i}{\sqrt{2}} \uparrow + \frac{i}{\sqrt{2}} \downarrow \quad \otimes = \frac{1}{\sqrt{2}} \uparrow + \frac{i}{\sqrt{2}} \downarrow \quad \odot = \frac{1}{\sqrt{2}} \uparrow - \frac{i}{\sqrt{2}} \downarrow \quad (7.16)$$

Note that the square magnitudes of the coefficients of the states are all one half, giving a 50/50 chance of finding the  $z$ -momentum up or down. Since the choice of the axis system is

arbitrary, this can be generalized to mean that if the spin in a given direction has a definite value, then there will be a 50/50 chance of the spin in any orthogonal direction turning out to be  $\frac{1}{2}\hbar$  or  $-\frac{1}{2}\hbar$ .

You might wonder about the choice of normalization factors in the spin states (7.16). For example, why not leave out the common factor  $i$  in the  $\leftarrow$ , (negative  $x$ -spin, or spin-left), state? The reason is to ensure that the  $x$ -direction ladder operator  $\hat{S}_y \pm i\hat{S}_z$  and the  $y$ -direction one  $\hat{S}_z \pm i\hat{S}_x$ , as obtained by cyclic permutation of the ones for  $z$ , produce real, positive multiplication factors. This allows relations valid in the  $z$ -direction (like the expressions for triplet and singlet states) to also apply in the  $x$  and  $y$ -directions. In addition, with this choice, if we do a simple change in the labeling of our axes, from  $xyz$  to  $yzx$  or  $zxy$ , the form of the Pauli spin matrices remains unchanged. The  $\rightarrow$  and  $\otimes$  states of positive  $x$ -, respectively  $y$ -momentum were chosen a different way: if you rotate the axis system 90° around the  $y$  or  $x$  axis, these are the spin-up states along the new  $z$ -axes, the  $x$  or  $y$  axis in the system we are looking at now {44}.

## 7.2 The Relativistic Dirac Equation [Advanced]

Relativity threw up some road blocks when quantum mechanics was first formulated, especially for the electrically charged particles physicist wanted to look at most, electrons. This section explains some of the ideas. You will need a good understanding of linear algebra to really follow the reasoning.

### 7.2.1 The Dirac idea

For zero spin particles, including relativity appears to be simple. The classical kinetic energy Hamiltonian we have been using for a particle in free space,

$$H = \frac{1}{2m} \sum_{i=1}^3 \hat{p}_i^2 \quad \hat{p}_i = \frac{\hbar}{i} \frac{\partial}{\partial x_i}$$

can be replaced by Einstein's relativistic expression

$$H = \sqrt{(m_0 c^2)^2 + \sum_{i=1}^3 (\hat{p}_i c)^2}$$

where  $m_0$  is the rest mass of the particle and  $m_0 c^2$  is the energy this mass is equivalent to. We can again write  $H\psi = E\psi$ , or squaring the operators in both sides to get rid of the square root:

$$\left[ (m_0 c^2)^2 + \sum_{i=1}^3 (\hat{p}_i c)^2 \right] \psi = E^2 \psi$$

This is the “Klein-Gordon” relativistic version of the Hamiltonian eigenvalue problem, and with a bit of knowledge of partial differential equations, you can check that the unsteady version, chapter 6.1, obeys the speed of light as the maximum propagation speed, as you would expect, section 7.6.2.

Unfortunately, throwing a dash of spin into this recipe simply does not seem to work in a convincing way. Apparently, that very problem led Schrödinger to limit himself to the nonrelativistic case. It is hard to formulate simple equations with an ugly square root in your way, and surely, you will agree, the relativistic equation for something so very fundamental as an electron in free space should be simple and beautiful like other fundamental equations in physics. (Can you be more concise than  $\vec{F} = m\vec{a}$  or  $E = mc^2$ ?).

So P.A.M. Dirac boldly proposed that for a particle like an electron, (and other spin  $1/2$  elementary particles like quarks, it turned out,) the square root produces a simple linear combination of the individual square root terms:

$$\sqrt{(m_0c^2)^2 + \sum_{i=1}^3 (\hat{p}_i c)^2} = \alpha_0 m_0 c^2 + \sum_{i=1}^3 \alpha_i \hat{p}_i c \quad (7.17)$$

for suitable coefficients  $\alpha_0$ ,  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$ . Now, if you know a little bit of algebra, you will quickly recognize that there is absolutely no way this can be true. The teacher will have told you that, say, a function like  $\sqrt{x^2 + y^2}$  is definitely not the same as the function  $\sqrt{x^2} + \sqrt{y^2} = x + y$ , otherwise the Pythagorean theorem would look a lot different, and adding coefficients as in  $\alpha_1 x + \alpha_2 y$  does not do any good at all.

But here is the key: while this does not work for plain numbers, Dirac showed it *is* possible if we are dealing with matrices, tables of numbers. In particular, it works if the coefficients are given by

$$\alpha_0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \alpha_1 = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} \quad \alpha_2 = \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix} \quad \alpha_3 = \begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix}$$

This looks like  $2 \times 2$  size matrices, but actually they are  $4 \times 4$  matrices since all elements are  $2 \times 2$  matrices themselves: the ones stand for  $2 \times 2$  unit matrices, the zeros for  $2 \times 2$  zero matrices, and the  $\sigma_x$ ,  $\sigma_y$  and  $\sigma_z$  are the so-called  $2 \times 2$  Pauli spin matrices that also pop up in the theory of spin angular momentum, section 7.1.7. The square root cannot be eliminated with matrices smaller than  $4 \times 4$  in actual size.

Now if the Hamiltonian is a  $4 \times 4$  matrix, the wave function at any point must have four components. As you might guess from the appearance of the spin matrices, half of the explanation of the wave function splitting into four is the two spin states of the electron. How about the other half? It turns out that the Dirac equation brings with it states of negative total energy, in particular negative rest mass energy.

That was of course a curious thing. Consider an electron in what otherwise is an empty vacuum. What prevents the electron from spontaneously transitioning to the negative rest

mass state, releasing twice its rest mass in energy? Dirac concluded that what we call empty vacuum should in the mathematics of quantum mechanics be taken to be a state in which all negative energy states are already filled with electrons. Clearly, that requires the Pauli exclusion principle to be valid for electrons, otherwise our electron could still transition into such a state. According to this idea, nature really does not have a free choice in whether to apply the exclusion principle to electrons if it wants to create a universe as we know it.

But now consider the vacuum without the electron. What prevents us from adding a big chunk of energy and lifting an electron out of a negative rest-mass state into a positive one? Nothing, really. We will end up with a normal electron and a place in the vacuum where an electron is missing, a “hole”. And here finally Dirac’s boldness appears to have deserted him; he shrank from proposing that this hole would physically show up as the exact antithesis, or anti-particle of the electron, the positively charged positron, instead weakly pointing the finger at the proton as a possibility. “Pure cowardice,” he called it later. The positron that his theory really predicted was subsequently discovered anyway. (It had already been observed earlier, but was not recognized.)

The reverse of the production of an electron/positron pair is pair annihilation, in which a positron and an electron eliminate each other, creating two gamma-ray photons. There must be two, because viewed from the combined center of mass, the net momentum of the pair is zero, and momentum conservation says it must still be zero after the collision. A single photon would have nonzero momentum, we need two photons coming out in opposite directions. However, pairs can be created from a single photon with enough energy if it happens in the vicinity of, say, a heavy nucleus: a heavy nucleus can absorb the momentum of the photon without picking up much velocity, so without absorbing too much of the photon’s energy.

The Dirac equation also gives a very accurate prediction of the magnetic moment of the electron, section 7.3.3, though the quantum electromagnetic field affects the electron and introduces a correction of about a tenth of a percent. But the importance of the Dirac equation was much more than that: it was the clue to our understanding how quantum mechanics can be reconciled with relativity, where particles are no longer absolute, but can be created out of nothing or destroyed according to Einstein’s relation  $E = mc^2$ .

Dirac was a theoretical physicist at Cambridge University, but he moved to Florida in his later life to be closer to his elder daughter, and was a professor of physics at the Florida State University when I got there. So it gives me some pleasure to include the Dirac equation in my text as the corner stone of relativistic quantum mechanics.

### 7.2.2 Emergence of spin from relativity

In this subsection we will give a (relatively) simple derivation of the Dirac equation to show how relativity naturally gives rise to spin. We will derive the equation without ever mentioning the word spin while doing it, just to prove it can be done. We will only use Dirac’s assumption

that Einstein's square root disappears,

$$\sqrt{(m_0c^2)^2 + \sum_{i=1}^3 (\hat{p}_i c)^2} = \alpha_0 m_0 c^2 + \sum_{i=1}^3 \alpha_i \hat{p}_i c$$

and a few other assumptions that have nothing to do with spin.

The conditions on the coefficient matrices  $\alpha_i$  for the linear combination to equal the square root can be found by squaring both sides in the equation above and then comparing sides. They turn out to be:

$$\alpha_i^2 = 1 \text{ for every } i \quad \alpha_i \alpha_j + \alpha_j \alpha_i = 0 \text{ for } i \neq j \quad (7.18)$$

Now assume that the matrices  $\alpha_i$  are Hermitian, as appropriate for measurable energies, and choose to describe the wave function vector in terms of the eigenvectors of matrix  $\alpha_0$ . Under those conditions  $\alpha_0$  will be a diagonal matrix, and its diagonal elements must be  $\pm 1$  for its square to be the unit matrix. So, choosing the order of the eigenvectors suitably,

$$\alpha_0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

where the sizes of the positive and negative unit matrices in  $\alpha_0$  are still undecided; one of the two could in principle be of zero size.

However, since  $\alpha_0 \alpha_i + \alpha_i \alpha_0$  must be zero for the three other Hermitian  $\alpha_i$  matrices, it is seen from multiplying that out that they must be of the form

$$\alpha_1 = \begin{pmatrix} 0 & \sigma_1^H \\ \sigma_1 & 0 \end{pmatrix} \quad \alpha_2 = \begin{pmatrix} 0 & \sigma_2^H \\ \sigma_2 & 0 \end{pmatrix} \quad \alpha_3 = \begin{pmatrix} 0 & \sigma_3^H \\ \sigma_3 & 0 \end{pmatrix}.$$

The  $\sigma_i$  matrices, whatever they are, must be square in size or the  $\alpha_i$  matrices would be singular and could not square to one. This then implies that the positive and negative unit matrices in  $\alpha_0$  must be the same size.

Now let's try to satisfy the remaining conditions on  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  using just complex numbers, rather than matrices, for the  $\sigma_i$ . By multiplying out the conditions (7.18), it is seen that

$$\alpha_i \alpha_i = 1 \implies \sigma_i^H \sigma_i = \sigma_i \sigma_i^H = 1 \quad \alpha_i \alpha_j + \alpha_j \alpha_i = 0 \implies \sigma_i^H \sigma_j + \sigma_j^H \sigma_i = \sigma_i \sigma_j^H + \sigma_j \sigma_i^H = 0.$$

The first condition above would require each  $\sigma_i$  to be a number of magnitude one, in other words, a number that can be written as  $e^{i\phi_i}$  for some real angle  $\phi_i$ . The second condition is then according to the Euler identity (1.5) equivalent to the requirement that

$$\cos(\phi_i - \phi_j) = 0 \text{ for } i \neq j;$$

this implies that all three angles would have to be 90 degrees apart. That is impossible: if  $\phi_2$  and  $\phi_3$  are each 90 degrees apart from  $\phi_1$ , then  $\phi_2$  and  $\phi_3$  are either the same or apart by 180 degrees; not by 90 degrees.

It follows that the components  $\sigma_i$  cannot be numbers, and must be matrices too. Assume, reasonably, that they correspond to some measurable quantity and are Hermitian. In that case the conditions above on the  $\sigma_i$  are the same as those on the  $\alpha_i$ , with one critical difference: there are only three  $\sigma_i$  matrices, not four. And so the analysis repeats.

Choose to describe the wave function in terms of the eigenvectors of the  $\sigma_3$  matrix; this does not conflict with the earlier choice since all half wave function vectors are eigenvectors of the positive and negative unit matrices in  $\alpha_0$ . So we have

$$\sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

and the other two matrices must then be of the form

$$\sigma_1 = \begin{pmatrix} 0 & \tau_1^H \\ \tau_1 & 0 \end{pmatrix} \quad \sigma_2 = \begin{pmatrix} 0 & \tau_2^H \\ \tau_2 & 0 \end{pmatrix}.$$

But now the components  $\tau_1$  and  $\tau_2$  can indeed be just complex numbers, since there are only two, and two angles can be apart by 90 degrees. We can take  $\tau_1 = e^{i\phi_1}$  and then  $\tau_2 = e^{i(\phi_1+\pi/2)}$  or  $e^{i(\phi_1-\pi/2)}$ . The existence of two possibilities for  $\tau_2$  implies that on the wave function level, nature is not mirror symmetric; momentum in the positive  $y$ -direction interacts differently with the  $x$ - and  $z$  momenta than in the opposite direction. Since the observable effects are mirror symmetric, we will not worry about it and just take the first possibility.

So, we have achieved our goal of finding a formulation in which Einstein's square root falls apart. However, we can clean up some more, by redefining the value of  $\tau_1$  away. If our 4-dimensional wave function vector takes the form  $(a_1, a_2, a_3, a_4)$ , define  $\bar{a}_1 = e^{i\phi_1/2}a_1$ ,  $\bar{a}_2 = e^{-i\phi_1/2}a_2$  and similar for  $\bar{a}_3$  and  $\bar{a}_4$ .

In that case, our final cleaned-up  $\sigma$  matrices are

$$\sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (7.19)$$

The “s” word has not been mentioned even once in this derivation. So, now please express audible surprise that the  $\sigma_i$  matrices turn out to be the Pauli (we can say it now) spin matrices of section 7.1.7.

But there is more. Suppose we define a new coordinate system rotated 90 degrees around the  $z$ -axis. This turns the old  $y$ -axis into a new  $x$ -axis. Since  $\tau_2$  has an additional factor  $e^{i\pi/2}$ , to get our normalized coefficients, we must include an additional factor  $e^{i\pi/4}$  in  $\bar{a}_1$ , which by the fundamental definition of angular momentum discussed in chapter 6.3 means that it describes a state with angular momentum  $1/2\hbar$ . Similarly  $a_3$  corresponds to a state with angular momentum  $1/2\hbar$  and  $a_2$  and  $a_4$  to ones with  $-1/2\hbar$ .

For nonzero momentum, the relativistic evolution of spin and momentum becomes coupled. But still, if you look at the eigenstates of positive energy, they take the form:

$$\begin{pmatrix} \vec{a} \\ \varepsilon(\vec{p} \cdot \vec{\sigma})\vec{a} \end{pmatrix}$$

where  $\varepsilon p$  is a small number in the nonrelativistic limit and  $\vec{a}$  is the two-component vector  $(a_1, a_2)$ . The operator corresponding to rotation of the coordinate system around the momentum vector commutes with  $\vec{p} \cdot \vec{\sigma}$ , hence the entire four-dimensional vector transforms as a combination of a spin  $1/2\hbar$  state and a spin  $-1/2\hbar$  state for rotation around the momentum vector.

## 7.3 The Electromagnetic Field [Advanced]

This section gives some very basic ideas of how electromagnetism fits into quantum mechanics. However, electromagnetism is fundamentally relativistic; its carrier, the photon, readily emerges or disappears, and a solid coverage is far beyond the scope of this text.

### 7.3.1 The Hamiltonian

In classical electromagnetics, the force on a particle like an electron with charge  $q = -e$  in a field with electric strength  $\vec{E}$  and magnetic strength  $\vec{B}$  is given by the Lorentz force law

$$m \frac{d\vec{v}}{dt} = q (\vec{E} + \vec{v} \times \vec{B}) \quad (7.20)$$

where  $\vec{v}$  is the velocity of the particle.

Unfortunately, quantum mechanics uses neither forces nor velocities. In fact, we have repeatedly used the fact that the electric field is described by the corresponding potential energy  $V$ , see for example the Hamiltonian of the hydrogen atom. The magnetic field must appear differently in the Hamiltonian; as the Lorentz force law shows, it couples with velocity. One would expect that still the Hamiltonian would be relatively simple, and the simplest idea is then that any potential corresponding to the magnetic field moves in together with momentum. Since the momentum is a vector quantity, then so must be the magnetic potential. So, your simplest guess would be that the Hamiltonian takes the form

$$H = \frac{1}{2m} (\hat{\vec{p}} - q\vec{A})^2 + q\phi \quad (7.21)$$

where  $\phi = V/q$  is the “electric potential” per unit charge, and  $\vec{A}$  is the “magnetic vector potential” per unit charge. And this simplest guess is in fact right.

The relationship between the vector potential  $\vec{A}$  and the magnetic field strength  $\vec{B}$  can be found from requiring that the classical Lorentz force law is obtained in the classical limit that the quantum uncertainty in position and momentum are small. In that case, we can use expectation values to characterize them, and also use the fact that the field strengths  $\vec{E}$  and  $\vec{B}$  will be constant on the small quantum scales. That means that the derivatives of  $\phi$  will be

constant, (since  $\vec{E}$  is the negative gradient of  $\phi$ ,) and presumably the same for the derivatives of  $\vec{A}$ .

To start this classical-limit analysis, according to chapter 6.1.4, the evolution of the expectation value of position is found as

$$\frac{d\langle \hat{\vec{r}} \rangle}{dt} = \left\langle \frac{i}{\hbar} [H, \hat{\vec{r}}] \right\rangle$$

Working out the commutator with the Hamiltonian above and the help of chapter 3.4.4, we get

$$\frac{d\langle \hat{\vec{r}} \rangle}{dt} = \frac{1}{m} \left\langle \hat{\vec{p}} - q\vec{A} \right\rangle$$

This is unexpected; it shows that  $\hat{\vec{p}}$ , i.e.  $\hbar\nabla/i$ , is no longer the operator of the normal momentum  $m\vec{v}$  when there is a magnetic field,  $\hat{\vec{p}} - q\vec{A}$  is. The momentum represented by  $\hat{\vec{p}}$  is called “canonical” momentum to distinguish it from normal momentum. (Actually, it was not that unexpected to physicists, since the same happens in the classical description of electromagnetics using the so-called Lagrangian approach.)

Anyway, to find the evolution of the expectation value of normal momentum, we need to put its operator  $\hat{\vec{p}} - q\vec{A}$  in the formula of chapter 6.1.4, giving:

$$m \frac{d\langle \vec{v} \rangle}{dt} = \left\langle \frac{i}{\hbar} [H, \hat{\vec{p}} - q\vec{A}] \right\rangle - q \left\langle \frac{\partial A}{\partial t} \right\rangle$$

After a lot of grinding down commutators with the tricks of chapter 3.4.4, and using the vectorial triple product properties {46}, we get

$$m \frac{d\langle \vec{v} \rangle}{dt} = q (\vec{E} + \langle \vec{v} \rangle \times \vec{B})$$

where

$$\vec{E} = -\nabla\phi - \frac{\partial \vec{A}}{\partial t} \quad \vec{B} = \nabla \times \vec{A} \quad (7.22)$$

So the magnetic field is found as the curl of the vector potential  $\vec{A}$ . And the electric field is no longer just the negative gradient of the scalar potential  $\phi$  if the vector potential varies with time.

These results are not new. The electric scalar potential  $\phi$  and the magnetic vector potential  $\vec{A}$  are the same in classical physics, though they are a lot less easy to guess than we did here. Moreover, in classical physics they are just convenient mathematical quantities to simplify analysis. In quantum mechanics they appear as central to the formulation.

And it can make a difference. Suppose we do an experiment where we pass electron wave functions around both sides of a very thin magnet: we will get a wave interference pattern behind the magnet. The classical expectation is that this interference pattern will be independent of

the magnet strength: the magnetic field  $\vec{B}$  outside a very thin and long ideal magnet is zero, so there is no force on the electron. But the magnetic vector potential  $\vec{A}$  is *not* zero outside the magnet, and Aharonov and Bohm argued that the interference pattern would therefore change with magnet strength. So it turned out to be in experiments done subsequently. The conclusion is clear; nature really goes by the vector potential  $\vec{A}$  and not the magnetic field  $\vec{B}$  in its actual workings.

### 7.3.2 Maxwell's equations

Maxwell's equations are commonly not covered in a typical engineering program. While these laws are not directly related to quantum mechanics, they do tend to pop up in nanotechnology. This subsection intends to give you some of the ideas. The description is based on the divergence and curl spatial derivative operators, and the related Gauss and Stokes theorems commonly found in calculus courses (Calculus III in the US system.)

Skipping the first equation for now, the second of Maxwell's equations comes directly out of the quantum mechanical description of the previous subsection. Consider the expression for the magnetic field  $\vec{B}$  "derived" (guessed) there, (7.22). If we take its divergence, (premultiply by  $\nabla \cdot$ ), we get rid of the vector potential  $\vec{A}$ , since the divergence of any curl is always zero, so we get

$$\text{Maxwell's second equation: } \nabla \cdot \vec{B} = 0 \quad (7.23)$$

and that is the second of Maxwell's four beautifully concise equations. (The compact modern notation using divergence and curl is really due to Heaviside and Gibbs, though.)

The first of Maxwell's equations is a similar expression for the electric field  $\vec{E}$ , but its divergence is *not* zero:

$$\text{Maxwell's first equation: } \nabla \cdot \vec{E} = \frac{\rho}{\epsilon_0} \quad (7.24)$$

where  $\rho$  is the electric charge per unit volume that is present and  $\epsilon_0$  is just a constant, the permittivity of vacuum.

What does it all mean? Well, the first thing I want to convince you of is that Maxwell's first equation is just a very clever way to write Coulomb's law for the electric field of a point charge. Consider therefore an electric point charge of strength  $q$ , and imagine this charge surrounded by a translucent sphere of radius  $r$ , as shown in figure 7.7. By symmetry, the electric field at all points on the spherical surface is radial, and everywhere has the same magnitude  $E = |\vec{E}|$ ; figure 7.7 shows it for eight selected points.

Now watch what happens if we integrate both sides of Maxwell's first equation (7.24) over the interior of this sphere. Starting with the right hand side, since the charge density is the charge per unit volume, by definition its integral over the volume is the charge  $q$ . So the right hand side integrates simply to  $q/\epsilon_0$ . How about the left hand side? Well, the Gauss, or divergence,

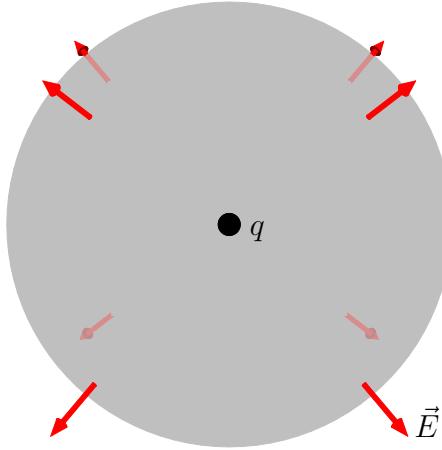


Figure 7.7: Relationship of Maxwell's first equation to Coulomb's law.

theorem of calculus says that the divergence of any vector,  $\vec{E}$  in this case, integrated over the *volume* of the sphere, equals the radial electric field  $E$  integrated over the *surface* of the sphere. Since  $E$  is constant on the surface, and the surface of a sphere is just  $4\pi r^2$ , the right hand side integrates to  $4\pi r^2 E$ . So in total, we get for the integrated first Maxwell's equation that  $4\pi r^2 E = q/\epsilon_0$ . Take the  $4\pi r^2$  to the other side and there you have the Coulomb electric field of a point charge:

$$\text{Coulomb's law: } E = \frac{q}{4\pi r^2 \epsilon_0} \quad (7.25)$$

Multiply by  $-e$  and you have the electrostatic force on an electron in that field according to the Lorentz equation (7.20). Integrate with respect to  $r$  and you have the potential energy  $V = -qe/4\pi\epsilon_0 r$  that we have been using for the atoms and molecules we have looked at.

Of course, all this raises the question, why bother? If Maxwell's first equation is just a rewrite of Coulomb's law, why not simply stick with Coulomb's law in the first place? Well, to describe the electric field at a given point using Coulomb's law requires you to consider every charge everywhere else. In contrast, Maxwell's equation only involves *local* quantities at the given point, to wit, the derivatives of the local electric field and the local charge per unit volume. It so happens that in numerical or analytical work, most of the time it is much more convenient to deal with local quantities, even if those are derivatives, than with global ones.

Of course, we can also integrate Maxwell's first equation over more general regions than a sphere centered around a charge. For example figure 7.8 shows a sphere with an off-center charge. But the electric field strength is no longer constant over the surface, and divergence theorem now requires us to integrate the component of the electric field normal to the surface over the surface. Clearly, that does not have much intuitive meaning. However, if you are willing to loosen up a bit on mathematical precision, there is a better way to look at it. It is in terms of the “electric field lines”, the lines that everywhere trace the direction of the electric field. The left figure in figure 7.8 shows the field lines through our selected points; a single charge has radial field lines.

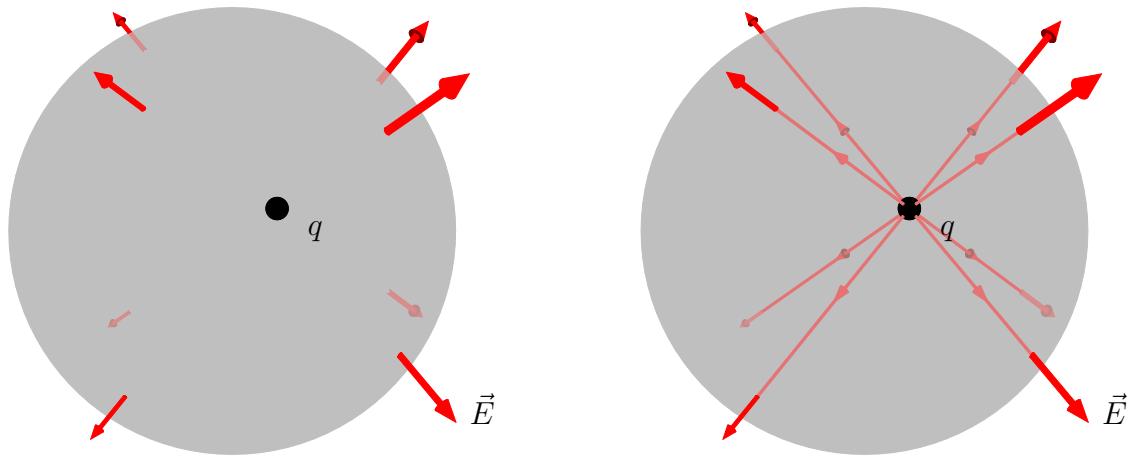


Figure 7.8: Maxwell's first equation for a more arbitrary region. The figure to the right includes the field lines through the selected points.

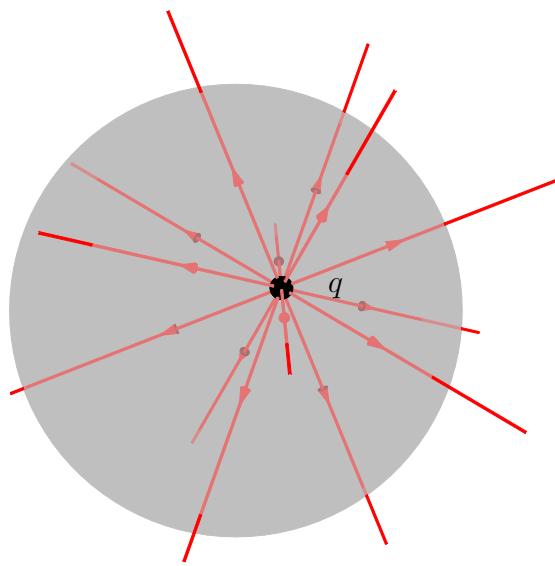


Figure 7.9: The net number of field lines leaving a region is a measure for the net charge inside that region.

Now assume that we draw the field lines densely, more like figure 7.9 say, and moreover, that we make the number of field lines coming out of a charge proportional to the strength of that charge. In that case, the local density of field lines at a point becomes a measure of the strength of the electric field at that point, and in those terms, Maxwell's integrated first equation says that the net number of field lines *leaving* a region is proportional to the net charge *inside* that region. That remains true when we add more charges inside the region. In that case the field lines will no longer be straight, but the net number going out will still be a multiple of the net charge inside.

Now we are ready to consider the question why Maxwell's *second* equation says that the divergence of the magnetic field is zero. For the electric field we can shove, say, some electrons in our region to create a net negative charge, or we can shove in some ionized molecules to create a net positive charge. But the magnetic equivalents to such particles, called "magnetic monopoles", being separate magnetic north pole particles or magnetic south pole particles, simply do not exist. It might *appear* that your bar magnet has a north pole and a south pole, but if you take it apart into little pieces, you do not end up with north pole pieces and south pole pieces. Each little piece by itself is still a little magnet, with equally strong north and south poles. The only reason the combined magnet *seems* to have a north pole is that all the microscopic magnets of which it consists have their north poles preferentially pointed in that direction.

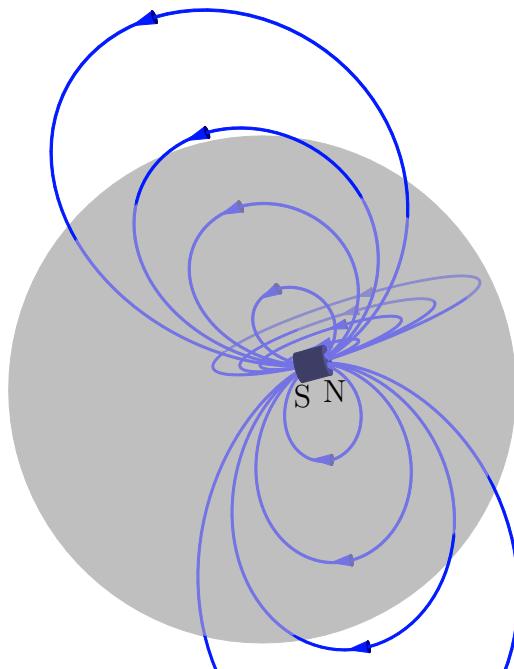


Figure 7.10: Since magnetic monopoles do not exist, the net number of magnetic field lines leaving a region is always zero.

If all microscopic magnets have equal strength north and south poles, then the same magnetic field lines that come out of the north poles go back into the south poles, as figure 7.10 illustrates. So the *net* magnetic field lines leaving a given region will be zero; whatever goes

out comes back in. True, if you enclose the north pole of a long bar magnet by an imaginary sphere, you can get a pretty good magnetic approximation of the electrical case of figure 7.7, but even then, if you look *inside* the magnet where it sticks through the spherical surface, the field lines will be found to go *in* towards the north pole, instead of away from it. You see why Maxwell's second equation is also called "absence of magnetic monopoles." And why, say, electrons can have a net negative charge, but have zero magnetic pole strength; their spin and orbital angular momenta produce equally strong magnetic north and south poles, a magnetic "dipole" (di meaning two.)

We can get Maxwell's third equation from the electric field "derived" in the previous subsection. If we take its curl, (premultiply by  $\nabla \times$ ), we get rid of the potential  $\phi$ , since the curl of any gradient is always zero, and the curl of  $\vec{A}$  is the magnetic field. So the third of Maxwell's equations is:

$$\text{Maxwell's third equation: } \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (7.26)$$

The "curl",  $\nabla \times$ , is also often indicated as "rot".

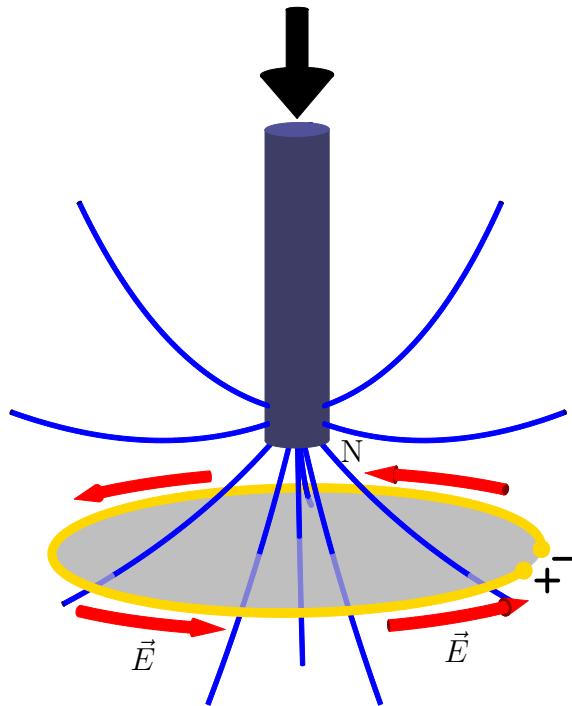


Figure 7.11: Electric power generation.

Now what does that one mean? Well, I want to convince you that this is just a clever rewrite of Faraday's law of induction, governing electric power generation. Let's assume that you want to create a voltage to drive some load (a bulb or whatever, we will not worry what the load is, just how to get the voltage for it.) Just take a piece of copper wire and bend it into a circle, as shown in figure 7.11. If you can create a voltage difference between the ends of the wire you are in business; just hook your bulb or whatever to the ends of the wire and it will light up. But to get such a voltage, you will need an electric field as shown in figure 7.11

because the voltage difference between the ends is the integral of the electric field strength along the length of the wire. Now Stokes' theorem of calculus says that the electric field strength along the wire integrated over the *length* of the wire equals the integral of the curl of the electric field strength integrated over the *inside* of the wire, in other words over the imaginary translucent circle in figure 7.11. So to get our voltage, we need a nonzero curl of the electric field on the translucent circle. And Maxwell's third equation above says that this means a time-varying magnetic field on the translucent circle. Moving the end of a strong magnet closer to the circle should do it, as suggested by figure 7.11. You better not make that a big bulb unless you make some further improvements, but anyway {47}.

Maxwell's fourth and final equation is a similar expression for the curl of the magnetic field:

$$\text{Maxwell's fourth equation: } c^2 \nabla \times \vec{B} = \frac{\vec{J}}{\epsilon_0} + \frac{\partial \vec{E}}{\partial t} \quad (7.27)$$

where  $\vec{J}$  is the “electric current density,” the charge flowing per unit cross sectional area, and  $c$  is the speed of light. (It is possible to rescale  $\vec{B}$  by a factor  $c$  to get the speed of light to show up equally in the equations for the curl of  $\vec{E}$  and the curl of  $\vec{B}$ , but then the Lorentz force law must be adjusted too.)

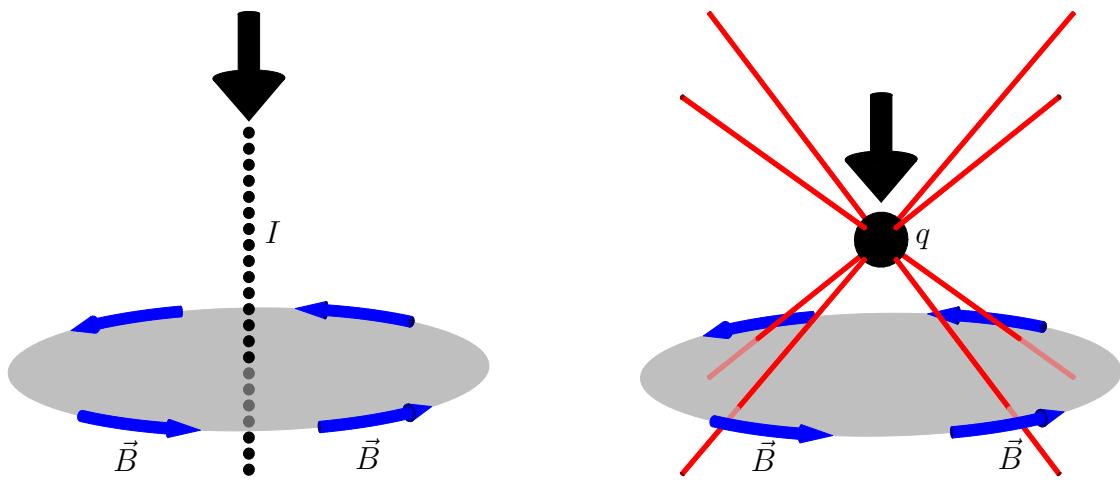


Figure 7.12: Two ways to generate a magnetic field: using a current (left) or using a varying electric field (right).

The big difference from the third equation is the appearance of the current density  $\vec{J}$ . So, there are two ways to create a circulatory magnetic field, as shown in figure 7.12: (1) pass a current through the enclosed circle (the current density integrates over the circle into the current through the circle), and (2) by creating a varying electric field over the circle, much like we did for the electric field in figure 7.11.

The fact that a current creates a surrounding magnetic field was already known as Ampere's law when Maxwell did his analysis. Maxwell himself however added the time derivative of the electric field to the equation to have the mathematics make sense. The problem was that the

divergence of any curl must be zero, and by itself, the divergence of the current density in the right hand side of the fourth equation is *not* zero. Just like the divergence of the electric field is the net field lines coming out of a region per unit volume, the divergence of the current density is the net current coming out. And it is perfectly OK for a net charge to flow out of a region: it simply reduces the charge remaining within the region by that amount. This is expressed by the “continuity equation:”

$$\text{Maxwell's continuity equation: } \nabla \cdot \vec{J} = -\frac{\partial \rho}{\partial t} \quad (7.28)$$

So Maxwell’s fourth equation without the time derivative of the electrical field is mathematically impossible. But after he added it, if we take the divergence of the total right hand side then we do indeed get zero as we should. To check that, use the continuity equation above and the first equation.

In empty space, Maxwell’s equations simplify: there are no charges so both the charge density  $\rho$  and the current density  $\vec{J}$  will be zero. In that case, the solutions of Maxwell’s equations are simply combinations of “traveling waves.” A traveling wave takes the form

$$\vec{E} = \hat{k}E_0 \cos(\omega(t - y/c) - \phi) \quad \vec{B} = \hat{i}\frac{1}{c}E_0 \cos(\omega(t - y/c) - \phi). \quad (7.29)$$

where for simplicity, we aligned the  $y$ -axis of our coordinate system with the direction in which the wave travels, and the  $z$ -axis with the amplitude  $\hat{k}E_0$  of the electric field of the wave. The constant  $\omega$  is the natural frequency of the wave, equal to  $2\pi$  times its frequency in cycles per second, and is related to its wave length  $\lambda$  by  $\omega\lambda/c = 2\pi$ . The constant  $\phi$  is just a phase factor. For these simple waves, the magnetic and electric field must be normal to each other, as well as to the direction of wave propagation.

You can plug the above wave solution into Maxwell’s equations and so verify that it satisfies them all. The point is that it travels with the speed  $c$ . When Maxwell wrote down his equations,  $c$  was just a constant to him, but when the propagation speed of electromagnetic waves matched the experimentally measured speed of light, it was just too much of a coincidence and he correctly concluded that light must be traveling electromagnetic waves.

It was a great victory of mathematical analysis. Long ago, the Greeks had tried to use mathematics to make guesses about the physical world, and it was an abysmal failure. You do not want to hear about it. Only when the Renaissance started *measuring* how nature really works, the correct laws were discovered for people like Newton and others to put into mathematical form. But here, Maxwell successfully amends Ampere’s *measured* law, just because *the mathematics did not make sense*. Moreover, by deriving how fast electromagnetic waves move, he discovers the very fundamental nature of the then mystifying *physical* phenomenon we call light.

You will usually not find Maxwell’s equations in the exact form described here. To explain what is going on inside materials, you would have to account for the electric and magnetic fields of every electron and proton (and neutron!) of the material. That is just an impossible

task, so physicists have developed ways to average away all those effects by messing with Maxwell's equations. But then the messed-up  $\vec{E}$  in one of Maxwell's equations is not longer the same as the messed-up  $\vec{E}$  in another, and the same for  $\vec{B}$ . So physicists rename one messed-up  $\vec{E}$  as, maybe, the “electric flux density”  $\vec{D}$ , and a messed up magnetic field as, maybe, “the auxiliary field”. And they define many other symbols, and even refer to the auxiliary field as being the magnetic field, all to keep engineers out of nanotechnology. Don't let them! When you need to understand the messed-up Maxwell equations, Wikipedia has a list of the countless definitions.

### 7.3.3 Electrons in magnetic fields

According to the Maxwell equations, a charged particle spinning around an axis acts as a little electromagnet. (Think of a version of figure 7.12 using a circular path.) The question in this section is, since electrons have spin angular momentum, do they too act like little magnets? The answer derived in this section will turn out to be yes.

In particular, a little magnet wants to align itself with an ambient magnetic field, just like a compass needle, and that means that the energy of the electron depends on how its spin is aligned with the magnetic field. Curiously, the energy involved pops out of Dirac's relativistic description of the electron, and the energy that an electron picks up in a magnetic field is:

$$H_{SB} = -\frac{q}{m} \hat{\vec{S}} \cdot \vec{B} \quad (7.30)$$

where  $q = -e$  is the charge of the electron,  $m$  its mass,  $\hat{\vec{S}}$  its spin, and  $\vec{B}$  the magnetic field. (We use again  $S$  rather than  $L$  to indicate spin angular momentum.) The electron-dependent part in the expression is called the electron's “magnetic dipole moment”:

$$\vec{\mu} = \frac{q}{m} \hat{\vec{S}} \quad (7.31)$$

and the scalar  $q/m$ -part of that in turn is called the “gyromagnetic ratio”

$$\gamma = \frac{q}{m} \quad (7.32)$$

The found magnetic dipole moment is very accurate, though interaction with the quantum electromagnetic field does change it by about 0.1%.

You might think that the same formula would apply to protons and neutrons, since they too are spin  $\frac{1}{2}$  particles. However, this turns out to be untrue. Protons and neutrons are not elementary particles, but consist of three quarks. Still, for both electron and proton we can write the gyromagnetic ratio as

$$\gamma = \frac{gq}{2m} \quad (7.33)$$

where  $g$  is a dimensionless constant called the “ $g$ -factor”. But while the  $g$ -factor of the electron according to the above is 2, the measured one for the proton is 5.59. Note that due to the

much larger mass of the proton, the actual magnetic dipole moment is much less despite the larger  $g$ -factor.

For the neutron, the charge is zero, but the magnetic moment is not, which would make its  $g$ -factor infinite! The problem is that the quarks that make up the neutron *do* have charge, and so the neutron can interact with a magnetic field even though its *net* charge is zero. When we arbitrarily use the *proton* mass and charge in the formulae, the neutron's  $g$  factor is -3.83.

If you are curious how the magnetic dipole strength of the electron can just pop out of the relativistic equation, in the rest of this section we give a quick derivation. But before we can get at that, we need to address a problem. Dirac's equation, section 7.2, assumes that Einstein's energy square root falls apart in a linear combination of terms:

$$H = \sqrt{(m_0 c^2)^2 + \sum_{i=1}^3 (\hat{p}_i c)^2} = \alpha_0 m_0 c^2 + \sum_{i=1}^3 \alpha_i \hat{p}_i c$$

which works for the  $4 \times 4 \alpha$  matrices given in that section. For an electron in a magnetic field, we want to replace  $\hat{\vec{p}}$  with  $\hat{\vec{p}} - q\vec{A}$  where  $\vec{A}$  is the magnetic vector potential. But where should we do that, in the square root or in the linear combination? It turns out that the answer you get for the electron energy is *not* the same.

If we believe that the Dirac linear combination is the way physics really works, and its description of spin leaves little doubt about that, then the answer is clear: we need to put  $\hat{\vec{p}} - q\vec{A}$  in the linear combination, not in the square root.

So, what are now the energy levels? That would be hard to say directly from the linear form, so we square it down to  $H^2$ , using the properties of the  $\alpha$  matrices, section 7.2.2. We get, in index notation,

$$H^2 = (m_0 c^2)^2 I + \sum_{i=1}^3 ((\hat{p}_i - qA_i)c)^2 I + \sum_{i=1}^3 [\hat{p}_{\bar{i}} - qA_{\bar{i}}, \hat{p}_{\bar{i}} - qA_{\bar{i}}] c^2 \alpha_{\bar{i}} \alpha_{\bar{i}}$$

where  $I$  is the four by four unit matrix,  $\bar{i}$  is the index following  $i$  in the sequence 123123..., and  $\bar{\bar{i}}$  is the one preceding  $i$ . The final sum represents the additional squared energy that we get by substituting  $\hat{\vec{p}} - q\vec{A}$  in the linear combination instead of the square root. The commutator arises because  $\alpha_{\bar{i}} \alpha_{\bar{i}} + \alpha_{\bar{i}} \alpha_{\bar{i}} = 0$ , giving the terms with the indices reversed the opposite sign. Working out the commutator using the formulae of chapter 3.4.4, and the definition of the vector potential  $\vec{A}$ ,

$$H^2 = (m_0 c^2)^2 I + \sum_{i=1}^3 ((\hat{p}_i - qA_i)c)^2 I + q\hbar c^2 i \sum_{i=1}^3 B_i \alpha_{\bar{i}} \alpha_{\bar{i}}$$

By multiplying out the expressions for the  $\alpha_i$  of section 7.2, using the fundamental commutation relation for the Pauli spin matrices that  $\sigma_{\bar{i}} \sigma_{\bar{i}} = i\sigma_i$ ,

$$H^2 = (m_0 c^2)^2 I + \sum_{i=1}^3 ((\hat{p}_i - qA_i)c)^2 I - q\hbar c^2 \sum_{i=1}^3 B_i \begin{pmatrix} \sigma_i & 0 \\ 0 & \sigma_i \end{pmatrix}$$

It is seen that due to the interaction of the spin with the magnetic field, the square energy changes by an amount  $-qhc^2\sigma_iB_i$ . Since  $\frac{1}{2}\hbar$  times the Pauli spin matrices gives the spin  $\hat{\vec{S}}$ , the square energy due to the magnetic field acting on the spin is  $-2qc^2\hat{\vec{S}} \cdot \vec{B}$ .

In the nonrelativistic case, the rest mass energy  $m_0c^2$  is much larger than the other terms, and in that case, if the change in square energy is  $-2qc^2\hat{\vec{S}} \cdot \vec{B}$ , the change in energy itself is smaller by a factor  $2m_0c^2$ , so

$$H_{SB} = -\frac{q}{m}\hat{\vec{S}} \cdot \vec{B} \quad (7.34)$$

which is what we claimed at the start of this section.

## 7.4 Nuclear Magnetic Resonance [Advanced]

Nuclear magnetic resonance, or NMR, is a valuable tool for examining nuclei, for probing the structure of molecules, in particular organic ones, and for medical diagnosis, as MRI. This section will give a basic quantum description of the idea. Linear algebra will be used.

### 7.4.1 Description of the method

First demonstrated independently by Bloch and Purcell in 1946, NMR probes nuclei with net spin, in particular hydrogen nuclei or other nuclei with spin  $1/2$ . Various common nuclei, like carbon and oxygen do not have net spin; this can be a blessing since they cannot mess up the signals from the hydrogen nuclei, or a limitation, depending on how you want to look at it. In any case, if necessary isotopes such as carbon 13 can be used which do have net spin.

It is not actually the spin, but the associated magnetic dipole moment of the nucleus that is relevant, for that allows the nuclei to be manipulated by magnetic fields. First the sample is placed in an extremely strong steady magnetic field. Typical fields are in terms of teslas. (A tesla is about 20,000 times the strength of the magnetic field of the earth.) In the field, the nucleus has two possible energy states; a ground state in which the spin component in the direction of the magnetic field is aligned with it, and an elevated energy state in which the spin is opposite {48}. (Despite the large field strength, the energy difference between the two states is extremely small compared to the thermal kinetic energy at room temperature. The number of nuclei in the ground state may only exceed those in the elevated energy state by say one in 100,000, but that is still a large absolute number of nuclei in a sample.)

Now we perturb the nuclei with a second, much smaller and radio frequency, magnetic field. If the radio frequency is just right, the excess ground state nuclei can be lifted out of the lowest energy state, absorbing energy that can be observed. The “resonance” frequency at which this happens then gives information about the nuclei. In order to observe the resonance

frequency very accurately, the perturbing rf field must be very weak compared to the primary steady magnetic field.

In Continuous Wave NMR, the perturbing frequency is varied and the absorption examined to find the resonance. (Alternatively, the strength of the primary magnetic field can be varied, that works out to the same thing using the appropriate formula.)

In Fourier Transform NMR, the perturbation is applied in a brief pulse just long enough to fully lift the excess nuclei out of the ground state. Then the decay back towards the original state is observed. An experienced operator can then learn a great deal about the environment of the nuclei. For example, a nucleus in a molecule will be shielded a bit from the primary magnetic field by the rest of the molecule, and that leads to an observable frequency shift. The amount of the shift gives a clue about the molecular structure at the nucleus, so information about the molecule. Additionally, neighboring nuclei can cause resonance frequencies to split into several through their magnetic fields. For example, a single neighboring perturbing nucleus will cause a resonance frequency to split into two, one for spin up of the neighboring nucleus and one for spin down. It is another clue about the molecular structure. The time for the decay back to the original state to occur is another important clue about the local conditions the nuclei are in, especially in MRI. The details are beyond this author's knowledge; the purpose here is only to look at the basic quantum mechanics behind NMR.

#### 7.4.2 The Hamiltonian

The magnetic fields will be assumed to be of the form

$$\vec{B} = B_0 \hat{k} + B_1 (\hat{i} \cos \omega t - \hat{j} \sin \omega t) \quad (7.35)$$

where  $B_0$  is the tesla-strength primary magnetic field,  $B_1$  the very weak perturbing field strength, and  $\omega$  is the frequency of the perturbation.

The component of the magnetic field in the  $xy$ -plane,  $B_1$ , rotates around the  $z$ -axis at angular velocity  $\omega$ . Such a rotating magnetic field can be achieved using a pair of properly phased coils placed along the  $x$  and  $y$  axes. (In Fourier Transform NMR, a single perturbation pulse actually contains a range of different frequencies  $\omega$ , and Fourier transforms are used to take them apart.) Since the apparatus and the wave length of a radio frequency field is very large on the scale of a nucleus, spatial variations in the magnetic field can be ignored.

Now suppose we place a spin  $1/2$  nucleus in the center of this magnetic field. As discussed in section 7.3.3, a particle with spin will act as a little compass needle, and its energy will be lowest if it is aligned with the direction of the ambient magnetic field. In particular, the energy is given by

$$H = -\vec{\mu} \cdot \vec{B}$$

where  $\vec{\mu}$  is called the magnetic dipole strength of the nucleus. This dipole strength is proportional to its spin angular momentum  $\hat{\vec{S}}$ :

$$\vec{\mu} = \gamma \hat{\vec{S}}$$

where the constant of proportionality  $\gamma$  is called the gyromagnetic ratio. The numerical value of the gyromagnetic ratio can be found as

$$\gamma = \frac{gq}{2m}$$

In case of a hydrogen nucleus, a proton, the mass  $m_p$  and charge  $q_p = e$  can be found in the notations section, and the proton's experimentally found  $g$ -factor is  $g_p = 5.59$ .

The bottom line is that we can write the Hamiltonian of the interaction of the nucleus with the magnetic field in terms of a numerical gyromagnetic ratio value, spin, and the magnetic field:

$$H = -\gamma \hat{\vec{S}} \cdot \vec{B} \quad (7.36)$$

Now turning to the wave function of the nucleus, it can be written as a combination of the spin-up and spin-down states,

$$\Psi = a \uparrow + b \downarrow,$$

where  $\uparrow$  has spin  $\frac{1}{2}\hbar$  in the  $z$ -direction, along the primary magnetic field, and  $\downarrow$  has  $-\frac{1}{2}\hbar$ . Normally,  $a$  and  $b$  would describe the spatial variations, but spatial variations are not relevant to our analysis, and  $a$  and  $b$  can be considered to be simple numbers.

We can use the concise notations of linear algebra by combining  $a$  and  $b$  in a two-component column vector (more precisely, a spinor),

$$\Psi = \begin{pmatrix} a \\ b \end{pmatrix}$$

In those terms, the spin operators become matrices, the so-called Pauli spin matrices of section 7.1.7,

$$\hat{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \hat{S}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \hat{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (7.37)$$

Substitution of these expressions for the spin, and (7.35) for the magnetic field into (7.36) gives after cleaning up the final Hamiltonian:

$$H = -\frac{\hbar}{2} \begin{pmatrix} \omega_0 & \omega_1 e^{i\omega t} \\ \omega_1 e^{-i\omega t} & -\omega_0 \end{pmatrix} \quad \omega_0 = \gamma B_0 \quad \omega_1 = \gamma B_1 \quad (7.38)$$

The constants  $\omega_0$  and  $\omega_1$  have the dimensions of a frequency;  $\omega_0$  is called the "Larmor frequency." As far as  $\omega_1$  is concerned, the important thing to remember is that it is much smaller than the Larmor frequency  $\omega_0$  because the perturbation magnetic field is small compared to the primary one.

### 7.4.3 The unperturbed system

Before looking at the perturbed case, it helps to first look at the unperturbed solution. If there is just the primary magnetic field affecting the nucleus, with no radio-frequency perturbation  $\omega_1$ , the Hamiltonian derived in the previous subsection simplifies to

$$H = -\frac{\hbar}{2} \begin{pmatrix} \omega_0 & 0 \\ 0 & -\omega_0 \end{pmatrix}$$

The energy eigenstates are the spin-up state, with energy  $-\frac{1}{2}\hbar\omega_0$ , and the spin-down state, with energy  $\frac{1}{2}\hbar\omega_0$ .

The difference in energy is in relativistic terms exactly equal to a photon with the Larmor frequency  $\omega_0$ . While the treatment of the electromagnetic field in this discussion will be classical, rather than relativistic, it seems clear that the Larmor frequency must play more than a superficial role.

The unsteady Schrödinger equation tells us that the wave function evolves in time like  $i\hbar\dot{\Psi} = H\Psi$ , so if  $\Psi = a \uparrow + b \downarrow$ ,

$$i\hbar \begin{pmatrix} \dot{a} \\ \dot{b} \end{pmatrix} = -\frac{\hbar}{2} \begin{pmatrix} \omega_0 & 0 \\ 0 & -\omega_0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix}$$

The solution for the coefficients  $a$  and  $b$  of the spin-up and -down states is:

$$a = a_0 e^{i\omega_0 t/2} \quad b = b_0 e^{-i\omega_0 t/2}$$

if  $a_0$  and  $b_0$  are the values of these coefficients at time zero.

Since  $|a|^2 = |a_0|^2$  and  $|b|^2 = |b_0|^2$  at all times, the probabilities of measuring spin-up or spin-down do not change with time. This was to be expected, since spin-up and spin-down are energy states for the steady system. To get more interesting physics, we really need the unsteady perturbation.

But first, to understand the quantum processes better in terms of the ideas of nonquantum physics, it will be helpful to write the unsteady quantum evolution in terms of the *expectation values* of the angular momentum components. The expectation value of the  $z$ -component of angular momentum is

$$\langle S_z \rangle = |a|^2 \frac{\hbar}{2} - |b|^2 \frac{\hbar}{2}$$

To more clearly indicate that the value must be in between  $-\hbar/2$  and  $\hbar/2$ , we can write the magnitude of the coefficients in terms of an angle  $\alpha$ , the “precession angle”,

$$|a| = |a_0| \equiv \cos(\alpha/2) \quad |b| = |b_0| \equiv \sin(\alpha/2)$$

In terms of the so-defined  $\alpha$ , we simply have, using the half-angle trig formulae,

$$\langle S_z \rangle = \frac{\hbar}{2} \cos \alpha$$

The expectation values of the angular momenta in the  $x$ - and  $y$ -directions can be found as the inner products  $\langle \Psi | \hat{S}_x \Psi \rangle$  and  $\langle \Psi | \hat{S}_y \Psi \rangle$ , chapter 3.3.3. Substituting the representation in terms of spinors and Pauli spin matrices, and cleaning up using the Euler identity (1.5), we get

$$\langle S_x \rangle = \frac{\hbar}{2} \sin \alpha \cos(\omega_0 t + \phi) \quad \langle S_y \rangle = -\frac{\hbar}{2} \sin \alpha \sin(\omega_0 t + \phi)$$

where  $\phi$  is some constant phase angle that is further unimportant.

The first thing that can be seen from these results is that the length of the expectation angular momentum vector is  $\hbar/2$ . Next, the component with the  $z$ -axis, the direction of the primary magnetic field, is at all times  $\frac{1}{2}\hbar \cos \alpha$ . That implies that the expectation angular momentum vector is under a constant angle  $\alpha$  with the primary magnetic field.

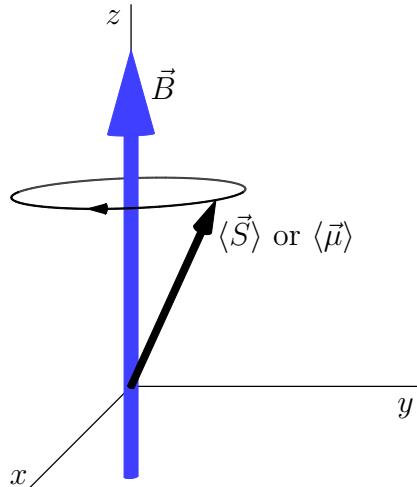


Figure 7.13: Larmor precession of the expectation spin (or magnetic moment) vector around the magnetic field.

The component in the  $x, y$ -plane is  $\frac{1}{2}\hbar \sin \alpha$ , and this component rotates around the  $z$ -axis, as shown in figure 7.13, causing the end point of the expectation angular momentum vector to sweep out a circular path around the magnetic field  $\vec{B}$ . This rotation around the  $z$ -axis is called “Larmor precession.” Since the magnetic dipole moment is proportional to the spin, it traces out the same conical path.

Caution should be used against attaching too much importance to this classical picture of a precessing magnet. The expectation angular momentum vector is not a physically measurable quantity. One glaring inconsistency in the expectation angular momentum vector versus the true angular momentum is that the square magnitude of the expectation angular momentum vector is  $\hbar^2/4$ , three times smaller than the true square magnitude of angular momentum.

### 7.4.4 Effect of the perturbation

In the presence of the perturbing magnetic field, the unsteady Schrödinger equation  $i\hbar\dot{\Psi} = H\Psi$  becomes

$$i\hbar \begin{pmatrix} \dot{a} \\ \dot{b} \end{pmatrix} = -\frac{\hbar}{2} \begin{pmatrix} \omega_0 & \omega_1 e^{i\omega t} \\ \omega_1 e^{-i\omega t} & -\omega_0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} \quad (7.39)$$

where  $\omega_0$  is the Larmor frequency,  $\omega$  is the frequency of the perturbation, and  $\omega_1$  is a measure of the strength of the perturbation and small compared to  $\omega_0$ .

The above equations can be solved exactly using standard linear algebra procedures, though the algebra is fairly stifling {49}. The analysis brings in an additional quantity that we will call the “resonance factor”

$$f = \sqrt{\frac{\omega_1^2}{(\omega - \omega_0)^2 + \omega_1^2}} \quad (7.40)$$

Note that  $f$  has its maximum value, one, at “resonance,” i.e. when the perturbation frequency  $\omega$  equals the Larmor frequency  $\omega_0$ .

The analysis finds the coefficients of the spin-up and spin-down states to be:

$$a = \left[ a_0 \left( \cos \left( \frac{\omega_1 t}{2f} \right) - i f \frac{\omega - \omega_0}{\omega_1} \sin \left( \frac{\omega_1 t}{2f} \right) \right) + b_0 i f \sin \left( \frac{\omega_1 t}{2f} \right) \right] e^{i\omega t/2} \quad (7.41)$$

$$b = \left[ b_0 \left( \cos \left( \frac{\omega_1 t}{2f} \right) + i f \frac{\omega - \omega_0}{\omega_1} \sin \left( \frac{\omega_1 t}{2f} \right) \right) + a_0 i f \sin \left( \frac{\omega_1 t}{2f} \right) \right] e^{-i\omega t/2} \quad (7.42)$$

where  $a_0$  and  $b_0$  are the initial coefficients of the spin-up and spin-down states.

This solution looks pretty forbidding, but it is not that bad in application. We are primarily interested in nuclei that start out in the spin-up ground state, so we can set  $|a_0| = 1$  and  $b_0 = 0$ . Also, the primary interest is in the probability that the nuclei may be found at the elevated energy level, which is

$$|b|^2 = f^2 \sin^2 \left( \frac{\omega_1 t}{2f} \right) \quad (7.43)$$

That is a pretty simple result. When we start out, the nuclei we look at are in the ground state, so  $|b|^2$  is zero, but with time the rf perturbation field increases the probability of finding the nuclei in the elevated energy state eventually to a maximum of  $f^2$  when the sine becomes one.

Continuing the perturbation beyond that time is bad news; it decreases the probability of elevated states again. As figure 7.14 shows, over extended times, there is a flip-flop between the nuclei being with certainty in the ground state, and having a probability of being in the elevated state. The frequency at which the probability oscillates is called the “Rabi flopping frequency”. My sources differ about the precise definition of this frequency, but the one that makes most sense to me is  $\omega_1/f$ .

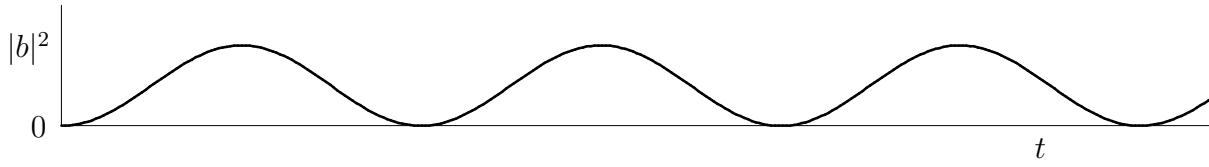


Figure 7.14: Probability of being able to find the nuclei at elevated energy versus time for a given perturbation frequency  $\omega$ .

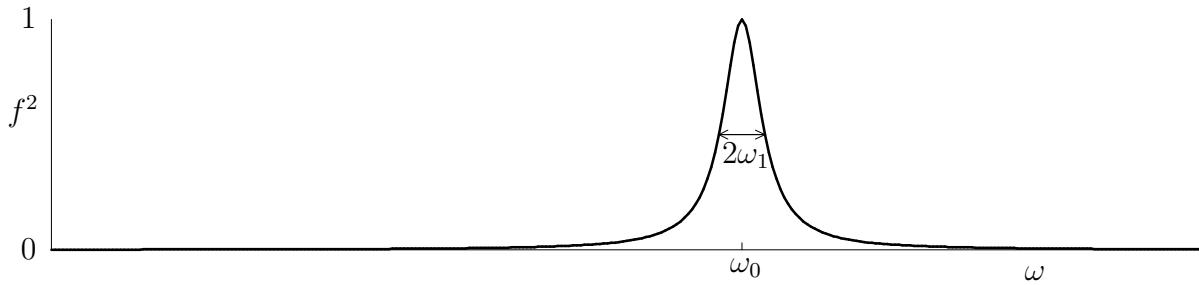


Figure 7.15: Maximum probability of finding the nuclei at elevated energy.

Anyway, by keeping up the perturbation for the right time we can raise the probability of elevated energy to a maximum of  $f^2$ . A plot of  $f^2$  against the perturbing frequency  $\omega$  is called the “resonance curve,” shown in figure 7.15. For the perturbation to have maximum effect, its frequency  $\omega$  must equal the nuclei’s Larmor frequency  $\omega_0$ . Also, for this frequency to be very accurately observable, the “spike” in figure 7.15 must be narrow, and since its width is proportional to  $\omega_1 = \gamma B_1$ , that means the perturbing magnetic field must be very weak compared to the primary magnetic field.

There are two qualitative ways to understand the need for the frequency of the perturbation to equal the Larmor frequency. One is geometrical and classical: as noted in the previous subsection, the expectation magnetic moment precesses around the primary magnetic field with the Larmor frequency. In order for the small perturbation field to exert a long-term downward “torque” on this precessing magnetic moment as in figure 7.16, it must rotate along with it. If it rotates at any other frequency, the torque will quickly reverse direction compared to the magnetic moment, and the vector will start going up again. The other way to look at it is from a relativistic quantum perspective: if the magnetic field frequency equals the Larmor frequency, its photons have exactly the energy required to lift the nuclei from the ground state to the excited state.

At the Larmor frequency, it would naively seem that the optimum time to maintain the perturbation is until the expectation spin vector is vertically down; then the nucleus is in the excited energy state with certainty. If we then allow nature the time to probe its state, every nucleus will be found to be in the excited state, and will emit a photon. (If not

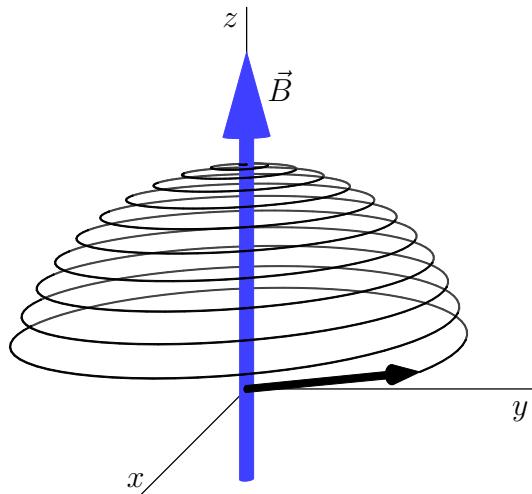


Figure 7.16: A perturbing magnetic field, rotating at precisely the Larmor frequency, causes the expectation spin vector to come cascading down out of the ground state.

messed up by some collision or whatever, little in life is ideal, is it?) However, according to actual descriptions of NMR devices, it is better to stop the perturbation earlier, when the expectation spin vector has become horizontal, rather than fully down. In that case, nature will only find half the nuclei in the excited energy state after the perturbation, presumably decreasing the radiation yield by a factor 2. The classical explanation that is given is that when the (expectation) spin vector is precessing at the Larmor frequency in the horizontal plane, the radiation is most easily detected by the coils located in that same plane. And that closes this discussion.

## 7.5 Some Topics Not Covered [Advanced]

This work is not intended as a comprehensive coverage of quantum mechanics, not even of classical quantum mechanics. Its purpose is to introduce engineers to the most basic ideas, so that they will be able to follow expositions in other, specialized, texts when the need arises.

Yet, it is helpful to have a general idea what physicists are talking about when they use certain phrases, so below is a list of some common terms. I probably should be adding more; suggestions are welcome.

**The hydrogen atom fine structure** We have talked about the hydrogen atom as “the exact solution we could do.” But even that is only true in the most strict classical description, in which relativity effects, including spin, are strictly ignored. (And even so, the solution is only exact if we correct for proton motion by using the effective electron

mass). To be really accurate, the hydrogen energies must be corrected for a variety of relativistic effects.

Before doing so, however, it is helpful to re-express the energy levels that we got for the hydrogen atom electron in terms of its rest mass energy  $m_e c^2$ . Rewriting (3.21),

$$E_n = \frac{\alpha^2}{2n^2} m_e c^2 \quad \text{where } \alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}$$

The constant  $\alpha$  is called the “fine structure constant.” It combines constants from electromagnetism,  $e^2/\epsilon_0$ , quantum mechanics,  $\hbar$ , and relativity,  $c$ , in one dimensionless combination. Nobody knows why it has the value that it has, but obviously it is a measurable value. So, following the stated ideas of quantum mechanics, maybe the universe “measured” this value during its early formation by a process that we may never understand, (since we do not have other measured values for  $\alpha$  to deduce any properties of that process from.) If you have a demonstrably better explanation, Sweden awaits you. Anyway, for engineering purposes, it is a small constant, less than 1%. That makes the hydrogen energy levels really small compared to the rest mass of the electron, because they are proportional to the square of  $\alpha$ .

Now let’s turn to the corrections we need to make to the energy levels to account for various relativistic effects. They are, in order of decreasing magnitude:

- *Fine structure.*

The electron should really be described relativistically using the Dirac equation instead of classically. In classical terms, that will introduce two corrections to the energy levels:

- Einstein’s relativistic correction to the classical expression  $p^2/2m_e$  for the kinetic energy of the electron.
- “Spin-orbit interaction”, due to the fact that the spin of the moving electron changes the energy levels. Think of the magnetic dipole moment of the electron spin as being due to a pair of positive and negative magnetic monopoles. Following the symmetry of Maxwell’s equations, moving magnetic monopoles produce an electric field just like moving electric charges produce a magnetic field. The electric fields generated by the moving monopoles are opposite in strength, but not quite centered at the same position, so they correspond to an electric dipole strength. And just like the energy of a magnetic dipole depends on how it aligns with an ambient magnetic field, the energy of the electron’s electric dipole moment depends on how it aligns with the proton’s electric field.

Fortunately, both of these effects are very small; they are smaller than the energy levels we derived by a factor of order  $\alpha^2$ , which is less than 0.01%. So, our “exact” solution is, by engineering standards, pretty exact after all. But fine structure leads to small variations in energy levels that in our derivation are the same, hence fine structure shows up experimentally as a splitting of single spectral lines into more than one when examined closely.

- *Lamb shift.* Relativistically, the electromagnetic field is quantized too, its particle being the photon. It adds a correction of relative magnitude  $\alpha^3$  to the energy levels, which means a factor 100 or so smaller still than the fine structure corrections.
- *Hyperfine structure.* The proton has a magnetic dipole moment too, which means that it generates a magnetic field. The electron's energy depends on how its magnetic moment aligns with the proton's magnetic field. This is called "spin-spin coupling." Its magnitude is a factor  $m_e/m_p$ , or in the order of a thousand times, smaller still than the fine structure corrections. Hyperfine structure couples the spins of proton and electron, and in the ground state, they combine in the singlet state. A slightly higher energy level occurs when they are in a spin one triplet state; transitions between these states radiate very low energy photons with a wave length of 21 cm.

This is the source of the "21 centimeter line" or "hydrogen line" radiation that is of great importance in cosmology. For example, it has been used to analyze the spiral arms of the galaxy, and the hope at the time of this writing is that it can shed light on the so called "dark ages" that the universe went through. The transition is highly forbidden in the sense of chapter 6.2, and takes on the order of 10 million years, but that is a small time on the scale of the universe.

The message to take away from it is that even errors in the ground state energy of hydrogen that are 10 million times smaller than the energy itself can be of critical importance under the right conditions.

**Zeeman and Stark** An external magnetic field will perturb the energy levels of the hydrogen too; that is called the Zeeman effect. Perturbation by an external electric field is the Stark effect.

**Electron diffraction experiments** When electron wave functions of a given momentum are passed through two closely spaced slits, an interference pattern results, in which the probability of finding the electrons behind the slits goes up and down with location in a periodic, wave-like, fashion.

This effect is frequently discussed at length in expositions of quantum mechanics in the popular press. The idea is that the reader will be intuitive enough to recognize the difficulty of explaining such a wavy pattern without wave motion, and that as a result, the reader will now be solidly convinced that the whole of quantum mechanics in the gullible Copenhagen type interpretation favored by the author is absolutely correct, and that the dreaded hidden variable theories are not. (The multi-world interpretation will not even be mentioned.)

Personally, it never did much to convince me that quantum mechanics was correct; it just got me into trying to think up ways to explain the thing without quantum mechanics. Just because there seems to be some wave motion involved here does not prove that the electron is the wave. Nor that cats in boxes are dead and alive at the same time. I think people get convinced about quantum mechanics not from electrons ending up in bands behind two slits, but by the preponderance of the evidence, by the countless very

concrete and precise things quantum mechanics can predict from a few basic formulae and ideas.

**Stern-Gerlach apparatus** A constant magnetic field will exert a torque, but no net force on a magnetic dipole like an electron; if you think of the dipole as a magnetic north pole and south pole close together, the magnetic forces on north pole and south pole will be opposite and produce no net deflection of the dipole. However, if the magnetic field strength varies with location, the two forces will be different and a net force will result.

The Stern-Gerlach apparatus exploits this process by sending a beam of atoms through a magnetic field with spatial variation, causing the atoms to deflect upwards or downwards relative to the field depending on their magnetic dipole strength. Since the magnetic dipole strength will be proportional to a relevant electron angular momentum, the beam will split into distinct beams corresponding to the quantized values of the angular momentum  $m\hbar$ ,  $(m - 1)\hbar$ ,  $\dots$ ,  $-m\hbar$  in the direction of the magnetic field.

The experiment was a great step forward in the development of quantum mechanics, because there is really no way that classical mechanics can explain the splitting into separate beams; classical mechanics just has to predict a smeared-out beam. Moreover, by capturing one of the split beams, we have a source of particles all in the *same* spin state, for other experiments or practical applications such as masers.

Stern and Gerlach used a beam of silver atoms in their experiment, and the separated beams deposited this silver on a plate. Initially, Gerlach had difficulty seeing any deposited silver on those plates because the layer was extremely thin. But fortunately for quantum mechanics, Stern was puffing his usual cheap cigars when he had a look, and the large amount of sulphur in the smoke was enough to turn some of the silver into jet-black silver sulfide, making it show clearly.

An irony is that that Stern and Gerlach assumed that they had verified Bohr's orbital momentum. But actually, they had discovered spin. The net magnetic moment of silver's inner electrons is zero, and the lone valence electron is in an orbit with zero angular momentum; it was the spin of the valence electron that caused the splitting. While spin has half the strength of orbital angular momentum, its magnetic moment is about the same due to its *g*-factor being two rather than one.

To use the Stern Gerlach procedure with charged particles such as electrons, a transverse electric field must be provided to counteract the large Lorentz force the magnet imparts on the moving electrons.

## 7.6 The Meaning of Quantum Mechanics [Background]

The following sections examine what is the nature of the universe under the laws of quantum mechanics. The conclusion may be disquieting, but it is what the evidence says.

### 7.6.1 Failure of the Schrödinger Equation?

Chapter 4.5 briefly mentioned sending half of the wave function of an electron to Venus, and half to Mars. A scattering setup as described in the previous chapter provides a practical means for actually doing this, (at least, for taking the wave function apart in two separate parts.) The obvious question is now: can the Schrödinger equation also describe the physically observed “collapse of the wave function”, where the electron changes from being on both Venus and Mars with a 50/50 probability to, say, being on Mars with absolute certainty?

The answer we will obtain in this and the next subsection will be most curious: no, the Schrödinger equation flatly *contradicts* that the wave function collapses, but yes, it *requires* that measurement leads to the experimentally observed collapse. The analysis will take us to a mind-boggling but really unavoidable conclusion about the very nature of our universe.

This subsection will examine the problem the Schrödinger equation has with describing a collapse. First of all, the solutions of the linear Schrödinger equation do not allow a mathematically exact collapse like some nonlinear equations do. But that does not necessarily imply that solutions would not be able to collapse physically. It would be conceivable that the solution could evolve to a state where the electron is on Mars with such high probability that it can be taken to be certainty. In fact, a common notion is that, somehow, interaction with a macroscopic “measurement” apparatus could lead to such an end result.

Of course, the constituent particles that make up such a macroscopic measurement apparatus still need to satisfy the laws of physics. So let’s make up a reasonable model for such a complete macroscopic system, and see what we then can say about the possibility for the wave function to evolve towards the electron being on Mars.

In the model, we will ignore the existence of anything beyond the Venus, Earth, Mars system. It will be assumed that the three planets consist of a humongous, but finite, number of conserved classical particles 1, 2, 3, 4, 5, . . . , with a supercolossal wave function:

$$\Psi(\vec{r}_1, S_{z1}, \vec{r}_2, S_{z2}, \vec{r}_3, S_{z3}, \vec{r}_4, S_{z4}, \vec{r}_5, S_{z5}, \dots)$$

Particle 1 will be taken to be the scattered electron. We will assume that the wave function satisfies the Schrödinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = - \sum_i \sum_{j=1}^3 \frac{\hbar^2}{2m_i} \frac{\partial^2 \Psi}{\partial r_{i,j}^2} + V(\vec{r}_1, S_{z1}, \vec{r}_2, S_{z2}, \vec{r}_3, S_{z3}, \vec{r}_4, S_{z4}, \dots) \Psi \quad (7.44)$$

Trying to write the solution to this problem would of course be prohibitive, but the evolution of the probability of the electron to be on Venus can still be extracted from it with some fairly standard manipulations. First, taking the combination of the Schrödinger equation times  $\Psi^*$  minus the complex conjugate of the Schrödinger equation times  $\Psi$  produces after some further

manipulation an equation for the time derivative of the probability:

$$i\hbar \frac{\partial \Psi^* \Psi}{\partial t} = - \sum_i \sum_{j=1}^3 \frac{\hbar^2}{2m_i} \frac{\partial}{\partial r_{i,j}} \left( \Psi^* \frac{\partial \Psi}{\partial r_{i,j}} - \Psi \frac{\partial \Psi^*}{\partial r_{i,j}} \right) \quad (7.45)$$

We are interested in the probability for the electron to be on Venus, and we can get that by integrating the probability equation above over all possible positions and spins of the particles *except* for particle 1, for which we restrict the spatial integration to Venus and its immediate surroundings. If we do that, the left hand side becomes the rate of change of the probability for the electron to be on Venus, regardless of the position and spin of all the other particles.

Interestingly, assuming times at which the Venus part of the scattered electron wave is definitely at Venus, the right hand side integrates to zero: the wave function is supposed to disappear at large distances from this isolated system, and whenever particle 1 would be at the border of the surroundings of Venus.

It follows that the probability for the electron to be at Venus cannot change from 50%. A true collapse of the wave function of the electron as postulated in the orthodox interpretation, where the probability to find the electron at Venus changes to 100% or 0% cannot occur.

Of course, our model was simple; one might therefore conjecture that a true collapse could occur if additional physics is included, such as nonconserved particles like photons, or other relativistic effects. But that would obviously be a moving target. We made a good-faith effort to examine whether including macroscopic effects may cause the observed collapse of the wave function, and the answer we got was no. Having a scientifically open mind requires us to at least follow our model to its logical end; nature might be telling us something here.

Is it really true that our results disagree with the observed physics? We need to be careful. There is no reasonable doubt that if a measurement is performed about the presence of the electron on Venus, the wave function will be observed to collapse. But all we established above is that the wave function does not collapse; we did not establish whether or not it will be *observed* to collapse. To answer the question whether a collapse will be *observed*, we will need to include the observers in our reasoning.

The problem is with the innocuous looking phrase *regardless of the position and spin of all the other particles* in our arguments above. Even while the total probability for the electron to be at Venus must stay at 50% in this example system, it is still perfectly possible for the probability to become 100% for one state of the particles that make up the observer and her tools, and to be 0% for another state of the observer and her tools.

It is perfectly possible to have a state of the observer with brain particles, ink-on-paper particles, tape recorder particles, that all say that the electron is on Venus, combined with 100% probability that the electron is on Venus, and a second state of the observer with brain particles, ink-on-paper particles, tape recorder particles, that all say the electron must be on

Mars, combined with 0% probability for the electron to be on Venus. Such a scenario is called a “relative state interpretation;” the states of the observer and the measured object become entangled with each other.

The state of the electron does not change to a single state of presence or absence; instead two states of the macroscopic universe develop, one with the electron absent, the other with it present. As explained in the next subsection, the Schrödinger equation does not just *allow* this to occur, it *requires* this to occur. So, far from being in conflict with the observed collapse, our model above requires it. Our model produces the right physics: observed collapse is a consequence of the Schrödinger equation, not of something else.

But all this leaves us with the rather disturbing thought that we have now ended up with two states of the universe, and the two are different in what they think about the electron. We did not ask for this conclusion; it was forced upon us as the unavoidable consequence of the mathematical equations that we abstracted for the way nature operates.

### 7.6.2 The Many-Worlds Interpretation

The Schrödinger equation has been enormously successful, but it describes the wave function as always smoothly evolving in time, in apparent contradiction to its postulated collapse in the orthodox interpretation. So, it would seem to be extremely interesting to examine the solution of the Schrödinger equation for measurement processes more closely, to see whether and how a collapse might occur.

Of course, if a true solution for a single arsenic atom already presents an unsurmountable problem, it may seem insane to try to analyze an entire macroscopic system such as a measurement apparatus. But in a brilliant Ph.D. thesis with Wheeler at Princeton, Hugh Everett, III did exactly that. He showed that the wave function does *not* collapse. However it *seems* to us that it does, so we *are* correct in applying the rules of the orthodox interpretation anyway. This subsection explains briefly how this works.

Let us return to the experiment of chapter 4.5, where we send a positron to Venus and an electron to Mars, as in figure 7.17. The spin states are uncertain when the two are send from



Figure 7.17: Bohm’s version of the Einstein, Podolski, Rosen Paradox

Earth, but when Venus measures the spin of the positron, it miraculously causes the spin state of the electron on Mars to collapse too. For example, if the Venus positron collapses to the spin-up state in the measurement, the Mars electron *must* collapse to the spin-down state.

The problem, however, is that there is nothing in the Schrödinger equation to describe such a collapse, nor the superluminal communication between Venus and Mars it implies.

The reason that the collapse and superluminal communication are needed is that the two particles are entangled in the singlet spin state of chapter 4.6.5. This is a 50% / 50% probability state of (electron up and positron down) / (electron down and positron up).

It would be easy if the positron would just be spin up and the electron spin down, as in figure 7.18. I would still not want to write down the supercolossal wave function of *everything*, the



Figure 7.18: Non entangled positron and electron spins; up and down.

particles along with the observers and their equipment for this case. But I do know what it describes. It will simply describe that the observer on Venus measures spin up, and the one on Mars, spin down. There is no ambiguity.

The same way, there is no question about the opposite case, figure 7.19. It will produce a



Figure 7.19: Non entangled positron and electron spins; down and up.

wave function of everything describing that the observer on Venus measures spin down, and the one on Mars, spin up.

Everett, III recognized that the answer for the entangled case is blindingly simple. Since the Schrödinger equation is *linear*, the wave function for the entangled case must simply be the sum of the two non entangled ones above, as shown in figure 7.20. If the wave function in each

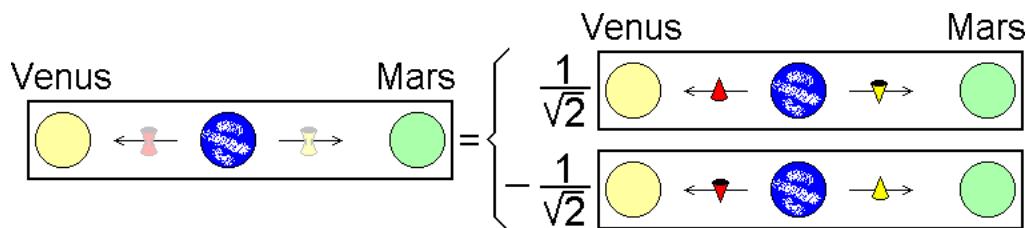


Figure 7.20: The wave functions of two universes combined

non entangled case describes a universe in which a particular state is solidly established for the spins, then the conclusion is undeniable: the wave function in the entangled case describes

*two universes, each of which solidly establishes states for the spins, but which end up with opposite results.*

We now have the explanation for the claim of the orthodox interpretation that only eigenvalues are measurable. The linearity of the Schrödinger equation leaves no other option:

*Assume that any measurement device at all is constructed that for a spin-up positron results in a universe that has absolutely no doubt that the spin is up, and for a spin-down positron results in a universe that has absolutely no doubt that the spin is down. In that case a combination of spin up and spin down states must unavoidably result in a combination of two universes, one in which there is absolutely no doubt that the spin is up, and one in which there is absolutely no doubt that it is down.*

Note that this observation does not depend on the details of the Schrödinger equation, just on its linearity. For that reason it stays true even including relativity.

The two universes are completely unaware of each other. It is the very nature of linearity that if two solutions are combined, they do not affect each other at all: neither universe would change in the least whether the other universe is there or not. For each universe, the other universe “exists” only in the sense that the Schrödinger equation must have created it given the initial entangled state.

Nonlinearity would be needed to allow the solutions of the two universes to couple together to produce a single universe with a combination of the two eigenvalues, and there is none. A universe measuring a combination of eigenvalues is made impossible by linearity.

While the wave function has not collapsed, what has changed is *the most meaningful way to describe it*. The wave function still by its very nature assigns a value to every possible configuration of the universe, in other words, to every possible universe. That has never been a matter of much controversy. And after the measurement it is still perfectly *correct* to say that the Venus observer has marked down in her notebook that the positron was up and down, and has transmitted a message to earth that the positron was up and down, and earth has marked on in its computer disks and in the brains of the assistants that the positron was found to be up and down, etcetera.

But it is *much more precise* to say that after the measurement there are two universes, one in which the Venus observer has observed the positron to be up, has transmitted to earth that the positron was up, and in which earth has marked down on its computer disks and in the brains of the assistants that the positron was up, etcetera; and a second universe in which the same happened, but with the positron everywhere down instead of up. This description is much more precise since it notes that up always goes with up, and down with down. As noted before, this more precise way of describing what happens is called the “relative state formulation.”

Note that in each universe, it *appears* that the wave function has collapsed. Both universes agree on the fact that the decay of the  $\pi$ -meson creates an electron/positron pair in a singlet state, but after the measurement, the notebook, radio waves, computer disks, brains in one universe all say that the positron is up, and in the other, all down. Only the unobservable full wave function “knows” that the positron is still both up and down.

And there is no longer a spooky superluminal action: in the first universe, the electron was already down when send from earth. In the other universe, it was send out as up. Similarly, for the case of the last subsection, where half the wave function of an electron was send to Venus, the Schrödinger equation does not fail. There is still half a chance of the electron to be on Venus; it just gets decomposed into one universe with one electron, and a second one with zero electron. In the first universe, earth send the electron to Venus, in the second to Mars. The contradictions of quantum mechanics just melt away when the *complete* solution of the Schrödinger equation is examined.

Next, let us examine why the results would seem to be covered by rules of chance, even though the Schrödinger equation is fully deterministic. To do so, we will instruct earth to keep on sending entangled positron and electron pairs. When the third pair is on its way, the situation looks as shown in the third column of figure 7.21. The wave function now describes 8 universes.

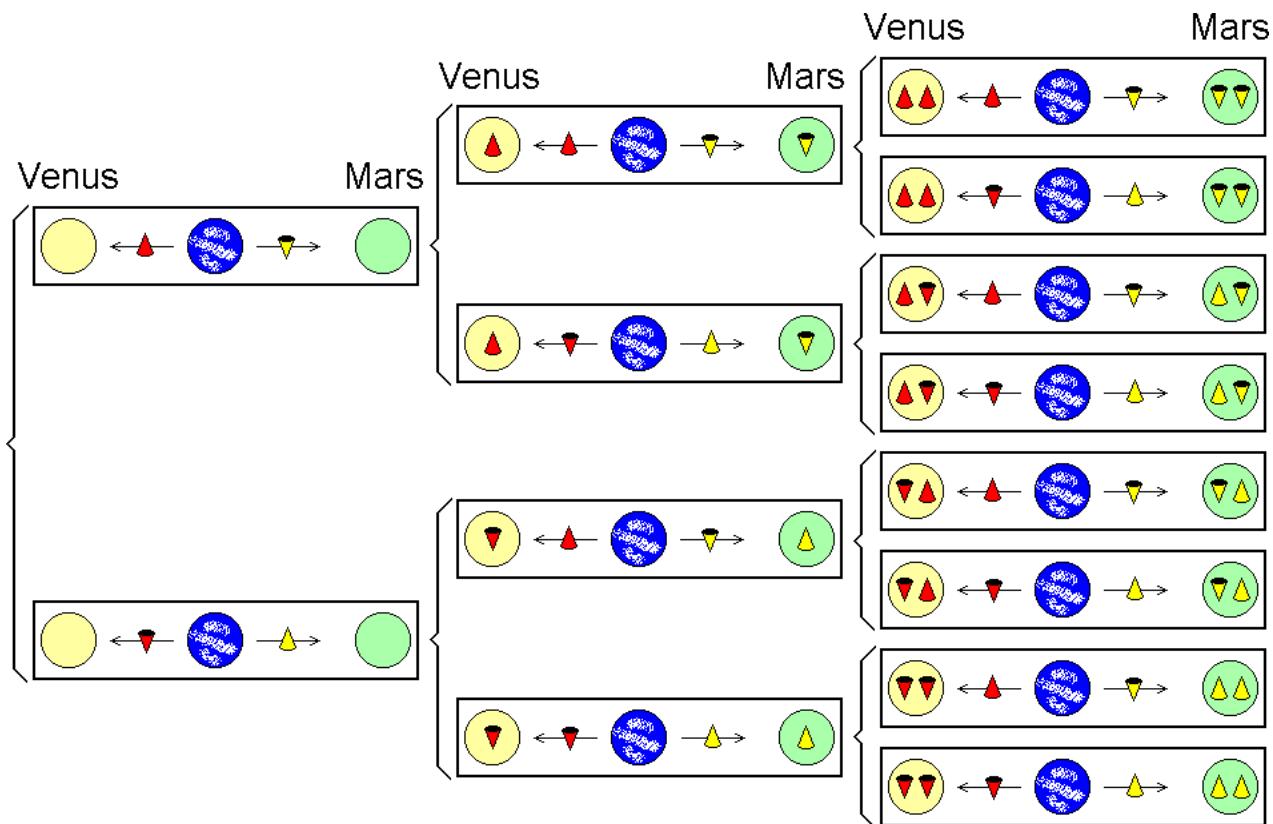


Figure 7.21: The Bohm experiment repeated.

Note that in *most* universes the observer starts seeing an apparently random sequence of up

and down spins. When repeated enough times, the sequences appear random in practically speaking every universe. Unable to see the other universes, the observer in each universe has no choice but to call her results random. Only the full wave function knows better.

Everett, III also derived that the statistics of the apparently random sequences are proportional to the absolute squares of the eigenfunction expansion coefficients, as the orthodox interpretation says.

How about the uncertainty relationship? For spins, the relevant uncertainty relationship states that it is impossible for the spin in the up/down directions and in the front/back directions to be certain at the same time. Measuring the spin in the front/back direction will make the up/down spin uncertain. But if the spin was always up, how can it change?

This is a bit more tricky. Let's have the Mars observer do a couple of additional experiments on one of her electrons, first one front/back, and then another again up/down, to see what happens. To be more precise, let's also ask her to write the result of each measurement on a blackboard, so that we have a good record of what was found. Figure 7.22 shows what happens.

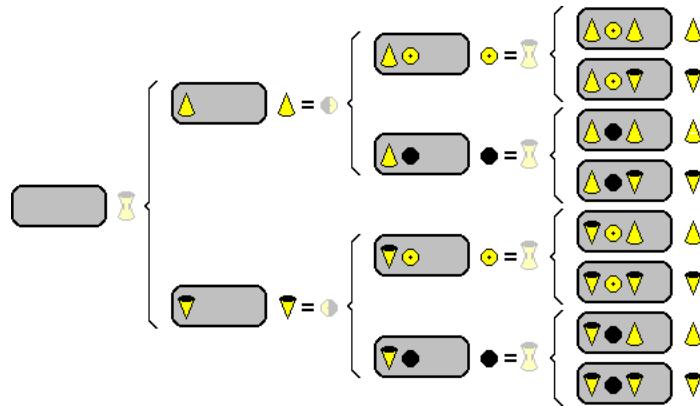


Figure 7.22: Repeated experiments on the same electron.

When the electron is send from Earth, we can distinguish two universes, one in which the electron is up, and another in which it is down. In the first one, the Mars observer measures the spin to be up and marks so on the blackboard. In the second, she measures and marks the spin to be down.

Next the observer in each of the two universes measures the spin front/back. Now it can be shown that the spin-up state in the first universe is a linear combination of equal amounts of spin-front and spin-back. So the second measurement splits the wave function describing the first universe into two, one with spin-front and one with spin-back.

Similarly, the spin-down state in the second universe is equivalent to equal amounts of spin-front and spin-back, but in this case with opposite sign. Either way, the wave function of the

second universe still splits into a universe with spin front and one with spin back.

Now the observer in each universe does her third measurement. The front electron consists of equal amounts of spin up and spin down electrons, and so does the back electron, just with different sign. So, as the last column in figure 7.22 shows, in the third measurement, as much as half the eight universes measure the vertical spin to be the opposite of the one they got in the first measurement!

The full wave function knows that if the first four of the final eight universes are summed together, the net spin is still down (the two down spins have equal and opposite amplitude). But the observers have only their blackboard (and what is recorded in their brains, etcetera) to guide them. And that information seems to tell them unambiguously that the front-back measurement “destroyed” the vertical spin of the electron. (The four observers that measured the spin to be unchanged can repeat the experiment a few more times and are sure to eventually find that the vertical spin does change.)

The unavoidable conclusion is that the Schrödinger equation does *not* fail. It describes exactly what we observe, in full agreement with the orthodox interpretation, without any collapse. The *appearance* of a collapse is actually just a limitation of our observational capabilities.

Of course, in other cases than the spin example above, there are more than just two symmetric states, and it becomes much less self-evident what the proper partial solutions are. However, it does not seem hard to make some conjectures. For Schrödinger’s cat, we might model the radioactive decay that gives rise to the Geiger counter going off as due to a nucleus with a neutron wave packet rattling around in it, trying to escape. As chapter 6.7.1 showed, in quantum mechanics each rattle will fall apart into a transmitted and a reflected wave. The transmitted wave would describe the formation of a universe where the neutron escapes at that time to set off the Geiger counter which kills the cat, and the reflected wave a universe where the neutron is still contained.

For the standard quantum mechanics example of an excited atom emitting a photon, a model would be that the initial excited atom is perturbed by the ambient electromagnetic field. The perturbations will turn the atom into a linear combination of the excited state with a bit of a lower energy state thrown in, surrounded by a perturbed electromagnetic field. Presumably this situation can be taken apart in a universe with the atom still in the excited state, and the energy in the electromagnetic field still the same, and another universe with the atom in the lower energy state with a photon escaping in addition to the energy in the original electromagnetic field. Of course, the process would repeat for the first universe, producing an eventual series of universes in almost all of which the atom has emitted a photon and thus transitioned to a lower energy state.

So this is where we end up. Our equations of quantum mechanics describe the physics we observe perfectly well. Yet they have forced us to the uncomfortable conclusion that, mathematically speaking, we are not at all unique. Beyond our universe, the mathematics of quantum mechanics requires an infinity of unobservable other universes that are nontrivially

different from us.

Note that the existence of an infinity of universes is not the issue. They are already required by the very formulation of quantum mechanics. The wave function of say an arsenic atom already assigns a nonzero probability to every possible configuration of the positions of the electrons. Similarly, a wave function of the universe will assign a nonzero probability to every possible configuration of the universe, in other words, to every possible universe. The existence of an infinity of universes is therefore not something that should be ascribed to Everett, III {50}.

However, when quantum mechanics was first formulated, people quite obviously believed that, practically speaking, there would be just one universe, the one we observe. No serious physicist would deny that the monitor on which you may be reading this has uncertainty in its position, yet the uncertainty you are dealing with here is so astronomically small that it can be ignored. Similarly it might appear that all the other substantially different universes should have such small probabilities that they can be ignored. The actual contribution of Everett, III was to show that this idea is not tenable. Nontrivial universes *must* develop that are substantially different.

Formulated in 1957 and then largely ignored, Everett's work represents without doubt one of the human race's greatest accomplishments; a stunning discovery of what we are and what is our place in the universe.

# Notes

This section gives various derivations of claims made, for those who are interested. They may help understand the various aspects better.

1. To verify the Euler identity, write all three functions involved in terms of their Taylor series, [5, p. 136]
2. The major difference between real and complex numbers is that real numbers can be ordered from smaller to larger. So you might speculate that the fact that the numbers of our world are real may favor a human tendency towards simplistic rankings where one item is “worse” or “better” than the other. What if your grade for a quantum mechanics test was  $55 + 90i$  and someone else had a  $70 + 65i$ ? It would be logical in a world in which the important operators would not be Hermitian.
3. A mathematician might choose to phrase the problem of Hermitian operators having or not having eigenvalues and eigenfunctions in a suitable space of permissible functions and then find, with some justification, that some operators in quantum mechanics, like the position or momentum operators do not have any permissible eigenfunctions. Let alone a complete set. The approach of this text is to simply follow the formalism anyway, and then fix the problems that arise as they arise.
4. Let  $\Psi_1$  and  $\Psi_2$  be any two proper, reasonably behaved, wave functions, then by definition:

$$\langle \Psi_1 | \hat{p}_x \Psi_2 \rangle = \int_{x=-\infty}^{\infty} \int_{y=-\infty}^{\infty} \int_{z=-\infty}^{\infty} \Psi_1^* \frac{\hbar}{i} \frac{\partial \Psi_2}{\partial x} dx dy dz$$
$$\langle \hat{p}_x \Psi_1 | \Psi_2 \rangle = \int_{x=-\infty}^{\infty} \int_{y=-\infty}^{\infty} \int_{z=-\infty}^{\infty} \left( \frac{\hbar}{i} \frac{\partial \Psi_1}{\partial x} \right)^* \Psi_2 dx dy dz$$

The two must be equal for  $\hat{p}_x$  to be an Hermitian operator. That they are indeed equal may be seen from integration by parts in the  $x$ -direction, noting that by definition  $i^* = -i$  and that  $\Psi_1$  and  $\Psi_2$  must be zero at infinite  $x$ : if they were not, their integral would be infinite, so that they could not be normalized.

5. You might well ask why we cannot have a wave function that has a discontinuity at the ends of the pipe. In particular, you might ask what is wrong with a wave function that

is a nonzero constant inside the pipe and zero outside it. Since the second derivative of a constant is zero, this (incorrectly) appears to satisfy the Hamiltonian eigenvalue problem with an energy eigenvalue equal to zero.

The problem is that this wave function has “jump discontinuities” at the ends of the pipe where the wave function jumps from the constant value to zero. Suppose we approximate such a wave function with a smooth one whose value merely drops down steeply rather than jumps down to zero. The steep fall-off produces a first order derivative that is very large in the fall-off regions, and a second derivative that is much larger still. Therefor, including the fall-off regions, the average kinetic energy is not close to zero, as the constant part alone would suggest, but actually almost infinitely large. And in the limit of a real jump, such eigenfunctions produce infinite energy, so they are not physically acceptable.

The bottom line is that jump discontinuities in the wave function are not acceptable. However, the solutions we will obtain have jump discontinuities in the *derivative* of the wave function, where it jumps from a nonzero value to zero at the pipe walls. Such discontinuities in the derivative correspond to “kinks” in the wave function. These kinks are acceptable; they naturally form when the walls are made more and more impenetrable. Jumps are wrong, but kinks are fine.

For more complicated cases, it may be less trivial to figure out what singularities are acceptable or not. In general, you want to check the “expectation value,” as defined later, of the energy of the almost singular case, using integration by parts to remove difficult-to-estimate higher derivatives, and then check that this energy remains bounded in the limit to the fully singular case. That is mathematics far beyond what we want to cover here, but in general you want to make singularities as minor as possible.

6. Maybe you have some doubt whether we really can just multiply one-dimensional eigenfunctions together, and add one-dimensional energy values to get the three-dimensional ones. Would a book that you find for free on the Internet lie? OK, let’s look at the details then. First, the three-dimensional Hamiltonian, (really just the kinetic energy operator), is the sum of the one-dimensional ones:

$$H = H_x + H_y + H_z$$

where the one-dimensional Hamiltonians are:

$$H_x = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad H_y = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} \quad H_z = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2}.$$

To check that any product of one-dimensional eigenfunctions,  $\psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$ , is an eigenfunction of the combined Hamiltonian  $H$ , note that the partial Hamiltonians only act on their own eigenfunction, multiplying it by the corresponding eigenvalue:

$$\begin{aligned} & (H_x + H_y + H_z)\psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z) \\ &= E_x\psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z) + E_y\psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z) + E_z\psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z). \end{aligned}$$

or

$$H\psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z) = (E_x + E_y + E_z)\psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z).$$

This shows, by the very definition of an eigenvalue problem, that  $\psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$  is an eigenfunction of the three-dimensional Hamiltonian, and that the eigenvalue is the sum of the three one-dimensional ones.

But there is still the question of completeness. Maybe the above eigenfunctions are not complete, which would mean a need for additional eigenfunctions that are not products of one-dimensional ones. Well, the one dimensional eigenfunctions  $\psi_{n_x}(x)$  are complete, see [5, p. 141] and earlier exercises in this book. So, we can write any wave function  $\Psi(x, y, z)$  at given values of  $y$  and  $z$  as a combination of  $x$ -eigenfunctions:

$$\Psi(x, y, z) = \sum_{n_x} c_{n_x} \psi_{n_x}(x),$$

but the coefficients  $c_{n_x}$  will be different for different values of  $y$  and  $z$ ; in other words they will be functions of  $y$  and  $z$ :  $c_{n_x} = c_{n_x}(y, z)$ . So, more precisely, we have

$$\Psi(x, y, z) = \sum_{n_x} c_{n_x}(y, z) \psi_{n_x}(x),$$

But since the  $y$ -eigenfunctions are also complete, at any given value of  $z$ , we can write each  $c_{n_x}(y, z)$  as a sum of  $y$ -eigenfunctions:

$$\Psi(x, y, z) = \sum_{n_x} \left( \sum_{n_y} c_{n_x n_y} \psi_{n_y}(y) \right) \psi_{n_x}(x),$$

where the coefficients  $c_{n_x n_y}$  will be different for different values of  $z$ ,  $c_{n_x n_y} = c_{n_x n_y}(z)$ . So, more precisely,

$$\Psi(x, y, z) = \sum_{n_x} \left( \sum_{n_y} \left( \sum_{n_z} c_{n_x n_y n_z}(z) \psi_{n_z}(z) \right) \psi_{n_y}(y) \right) \psi_{n_x}(x),$$

But since the  $z$ -eigenfunctions are also complete, we can write  $c_{n_x n_y}(z)$  as a sum of  $z$ -eigenfunctions:

$$\Psi(x, y, z) = \sum_{n_x} \left( \sum_{n_y} \left( \sum_{n_z} c_{n_x n_y n_z} \psi_{n_z}(z) \right) \psi_{n_y}(y) \right) \psi_{n_x}(x).$$

Since the order of doing the summation does not make a difference,

$$\Psi(x, y, z) = \sum_{n_x} \sum_{n_y} \sum_{n_z} c_{n_x n_y n_z} \psi_{n_x}(x) \psi_{n_y}(y) \psi_{n_z}(z).$$

So, any wave function  $\Psi(x, y, z)$  can be written as a sum of products of one-dimensional eigenfunctions; these products are complete.

7. If you really must know, here is a sketch of how the solution process works. Read at your own risk. The ODE (ordinary differential equation) to solve is

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_x}{\partial x^2} + \frac{1}{2} m \omega^2 x^2 \psi_x = E_x \psi_x$$

where I rewrote the spring constant  $c$  as the equivalent expression  $m\omega^2$ .

Now the first thing you always want to do with this sort of problems is to simplify it as much as possible. In particular, get rid of as much dimensional constants as you can by rescaling the variables: define a new scaled  $x$ -coordinate  $\xi$  and a scaled energy  $\epsilon$  by

$$x \equiv \ell\xi \quad E_x \equiv E_0\epsilon.$$

If you make these replacements into the ODE above, you can make the coefficients of the two terms in the left hand side equal by choosing  $\ell = \sqrt{\hbar/m\omega}$ . In that case both terms will have the same net coefficient  $\frac{1}{2}\hbar\omega$ . Then if you cleverly choose  $E_0 = \frac{1}{2}\hbar\omega$ , the right hand side will have that coefficient too, and you can divide it away and end up with no coefficients at all:

$$-\frac{\partial^2\psi_x}{\partial\xi^2} + \xi^2\psi_x = \epsilon\psi_x$$

Looks a lot cleaner, not?

Now examine this equation for large values of  $\xi$  (i.e. large  $x$ ). You get approximately

$$\frac{\partial^2\psi_x}{\partial\xi^2} \approx \xi^2\psi_x + \dots$$

If you write the solution as an exponential, you can ball park that it must take the form

$$\psi_x = e^{\pm\frac{1}{2}\xi^2+\dots}$$

where the dots indicate terms that are small compared to  $\frac{1}{2}\xi^2$  for large  $\xi$ . The form of the solution is important, since  $e^{+\frac{1}{2}\xi^2}$  becomes infinitely large at large  $\xi$ . That is unacceptable: the probability of finding the particle cannot become infinitely large at large  $x$ : the total probability of finding the particle must be one, not infinite. The *only* solutions that are acceptable are those that behave as  $e^{-\frac{1}{2}\xi^2+\dots}$  for large  $\xi$ .

Let's split off the leading exponential part by defining a new unknown  $h(\xi)$  by

$$\psi_x \equiv e^{-\frac{1}{2}\xi^2} h(\xi)$$

Substituting this in the ODE and dividing out the exponential, we get:

$$-\frac{\partial^2 h}{\partial\xi^2} + 2\xi\frac{\partial h}{\partial\xi} + h = \epsilon h$$

Now try to solve this by writing  $h$  as a power series, (say, a Taylor series):

$$h = \sum_p c_p \xi^p$$

where the values of  $p$  run over whatever the appropriate powers are and the  $c_p$  are constants. If we plug this into the ODE, we get

$$\sum_p p(p-1)c_p \xi^{p-2} = \sum_p (2p+1-\epsilon)c_p \xi^p$$

For the two sides to be equal, they must have the same coefficient for every power of  $\xi$ .

There must be a lowest value of  $p$  for which there is a nonzero coefficient  $c_p$ , for if  $p$  took on arbitrarily large negative values,  $h$  would blow up strongly at the origin, and the probability to find the particle near the origin would then be infinite. Let's denote the lowest value of  $p$  by  $q$ . This lowest power produces a power of  $\xi^{q-2}$  in the left hand side of the equation above, but there is no corresponding power in the right hand side. So, the coefficient  $q(q-1)c_q$  of  $\xi^{q-2}$  will need to be zero, and that means either  $q = 0$  or  $q = 1$ . So the power series for  $h$  will need to start as either  $c_0 + \dots$  or  $c_1\xi + \dots$ . The constant  $c_0$  or  $c_1$  is allowed to have any nonzero value.

But note that the  $c_q\xi^q$  term normally produces a term  $(2q+1-\epsilon)c_q\xi^q$  in the right hand side of the equation above. For the left hand side to have a matching  $\xi^q$  term, there will need to be a further  $c_{q+2}\xi^{q+2}$  term in the power series for  $h$ ,

$$h = c_q\xi^q + c_{q+2}\xi^{q+2} + \dots$$

where  $(q+2)(q+1)c_{q+2}$  will need to equal  $(2q+1-\epsilon)c_q$ , so  $c_{q+2} = (2q+1-\epsilon)c_q/(q+2)(q+1)$ . This term in turn will normally produce a term  $(2(q+2)+1-\epsilon)c_{q+2}\xi^{q+2}$  in the right hand side which will have to be cancelled in the left hand side by a  $c_{q+4}\xi^{q+4}$  term in the power series for  $h$ . And so on.

So, if the power series starts with  $q = 0$ , the solution will take the general form

$$h = c_0 + c_2\xi^2 + c_4\xi^4 + c_6\xi^6 + \dots$$

while if it starts with  $q = 1$  we will get

$$h = c_1\xi + c_3\xi^3 + c_5\xi^5 + c_7\xi^7 + \dots$$

In the first case, we have a symmetric solution, one which remains the same when we flip over the sign of  $\xi$ , and in the second case we have an antisymmetric solution, one which changes sign when we flip over the sign of  $\xi$ .

You can find a general formula for the coefficients of the series by making the change in notations  $p = 2 + \bar{p}$  in the left hand side sum:

$$\sum_{\bar{p}=q}(\bar{p}+2)(\bar{p}+1)c_{\bar{p}+2}\xi^{\bar{p}} = \sum_{p=q}(2p+1-\epsilon)c_p\xi^p$$

Note that we can start summing at  $\bar{p} = q$  rather than  $q - 2$ , since the first term in the sum is zero anyway. Next note that we can again forget about the difference between  $\bar{p}$  and  $p$ , because it is just a symbolic summation variable. The symbolic sum writes out to the exact same actual sum whether you call the symbolic summation variable  $p$  or  $\bar{p}$ .

So for the powers in the two sides to be equal, we must have

$$c_{p+2} = \frac{2p+1-\epsilon}{(p+2)(p+1)}c_p$$

In particular, for large  $p$ , by approximation

$$c_{p+2} \approx \frac{2}{p} c_p$$

Now if you check out the Taylor series of  $e^{\xi^2}$ , (i.e. the Taylor series of  $e^x$  with  $x$  replaced by  $\xi^2$ ), you find it satisfies the exact same equation. So, normally the solution  $h$  blows up something like  $e^{\xi^2}$  at large  $\xi$ . And since  $\psi_x$  was  $e^{-\frac{1}{2}\xi^2} h$ , normally  $\psi_x$  takes on the unacceptable form  $e^{+\frac{1}{2}\xi^2+\dots}$ . (If you must have rigor here, estimate  $h$  in terms of  $Ce^{\alpha\xi^2}$  where  $\alpha$  is a number slightly less than one, plus a polynomial. That is enough to show unacceptability of such solutions.)

What are the options for acceptable solutions? The only possibility is that the power series terminates. There must be a highest power  $p$ , call it  $p = n$ , whose term in the right hand side is zero

$$0 = (2n + 1 - \epsilon) c_n \xi^n$$

In that case, there is no need for a further  $c_{n+2}\xi^{n+2}$  term, the power series will remain a polynomial of degree  $n$ . But note that all this requires the scaled energy  $\epsilon$  to equal  $2n+1$ , and the actual energy  $E_x$  is therefore  $(2n+1)\hbar\omega/2$ . Different choices for the power at which the series terminates produce different energies and corresponding eigenfunctions. But they are discrete, since  $n$ , as any power  $p$ , must be a nonnegative integer.

With  $\epsilon$  identified as  $2n+1$ , you can find the ODE for  $h$  listed in table books, like [5, 29.1], under the name “Hermite’s differential equation.” They then identify our polynomial solutions as the so-called “Hermite polynomials,” except for a normalization factor. To find the normalization factor, i.e.  $c_0$  or  $c_1$ , demand that the total probability of finding the particle anywhere is one,  $\int_{-\infty}^{\infty} |\psi_x|^2 dx = 1$ . You should be able to find the value for the appropriate integral in your table book, like [5, 29.15].

Like I said at the beginning, read at your own risk. If you know the right tricks, there is a much neater approach to find the eigenfunctions, {38}.

8. These qualitative arguments should be justified. In particular, position, linear momentum, potential energy, and kinetic energy are not defined for the ground state. However, as explained more fully in chapter 3.3, we can define the “expectation value” of kinetic energy to be the average predicted result for kinetic energy measurements. Similarly, we can define the expectation value of potential energy to be the average predicted result for potential energy measurements. Quantum mechanics does require the total energy of the ground state to be the sum of the kinetic and potential energy expectation values. Now if there would be an almost infinite uncertainty in linear momentum, then typical measurements would find a large momentum, hence a large kinetic energy. So the kinetic energy expectation value would then be large; that would be nowhere close to any ground state. Similarly, if there would be a large uncertainty in position, then typical measurements will find the particle at large distance from the nominal position, hence at large potential energy. Not good either.

It so happens that the ground state of the harmonic oscillator manages to obtain the absolute minimum in combined position and momentum uncertainty that the uncertainty

relationship, given in chapter 3.4.3, allows. This can be verified using the fact that the two uncertainties,  $\sigma_x$  and  $\sigma_{px}$ , as defined in chapter 3.3, are directly related to the expectation values for potential energy, respectively kinetic energy in the  $x$ -direction, each of which equals  $\frac{1}{4}\hbar\omega$ . (One sixth the total energy, since each coordinate direction contributes an equal share to the potential and kinetic energies.)

The fact that the expectation values of kinetic and potential energy for the harmonic oscillator eigenstates are the same follows from the virial theorem of chapter 6.1.4.

9. The elementary equality required is not in [5] in any form. In the absence of tensor algebra, it is best to just grind it out. Define  $\vec{f} \equiv (\vec{r} \times \nabla)\Psi$ . Then  $(\vec{r} \times \nabla) \cdot \vec{f}$  equals

$$y \frac{\partial f_x}{\partial z} - z \frac{\partial f_x}{\partial y} + z \frac{\partial f_y}{\partial x} - x \frac{\partial f_y}{\partial z} + x \frac{\partial f_z}{\partial y} - y \frac{\partial f_z}{\partial x}$$

On the other hand,  $\vec{r} \cdot (\nabla \times \vec{f})$  is

$$x \frac{\partial f_z}{\partial y} - x \frac{\partial f_y}{\partial z} + y \frac{\partial f_x}{\partial z} - y \frac{\partial f_z}{\partial x} + z \frac{\partial f_y}{\partial x} - z \frac{\partial f_x}{\partial y}$$

which is the same.

10. Here we go again. This analysis will use similar techniques as for the harmonic oscillator solution, {7}. The requirement that the spherical harmonics  $Y_l^m$  are eigenfunctions of  $L_z$  means that they are of the form  $\Theta_l^m(\theta)e^{im\phi}$  where function  $\Theta_l^m(\theta)$  is still to be determined. (There is also an arbitrary dependence on the radius  $r$ , but it does not have anything to do with angular momentum, hence is ignored when people define the spherical harmonics.) Substitution into  $\hat{L}^2\psi = L^2\psi$  with  $\hat{L}^2$  as in (3.5) yields an ODE (ordinary differential equation) for  $\Theta_l^m(\theta)$ :

$$-\frac{\hbar^2}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta_l^m}{\partial \theta} \right) + \frac{\hbar^2 m^2}{\sin^2 \theta} \Theta_l^m = L^2 \Theta_l^m$$

We will define a scaled square angular momentum by  $L^2 = \hbar^2 \lambda^2$  so that we can divide away the  $\hbar^2$  from the ODE.

More importantly, let's recognize that the solutions will likely be in terms of cosines and sines of  $\theta$ , because they should be periodic if  $\theta$  changes by  $2\pi$ . If we again want to use power-series solution procedures, these transcendental functions are bad news, so we switch to a new variable  $x = \cos \theta$ . At the very least, that will reduce things to algebraic functions, since  $\sin \theta$  is in terms of  $x = \cos \theta$  equal to  $\sqrt{1 - x^2}$ . Converting the ODE to the new variable  $x$ , we get

$$-(1 - x^2) \frac{d^2 \Theta_l^m}{dx^2} + 2x \frac{d \Theta_l^m}{dx} + \frac{m^2}{1 - x^2} \Theta_l^m = \lambda^2 \Theta_l^m$$

As you may guess from looking at this ODE, the solutions  $\Theta_l^m$  are likely to be problematic near  $x = \pm 1$ , (physically, near the  $z$ -axis where  $\sin \theta$  is zero.) If you examine the solution

near those points by defining a local coordinate  $\xi$  as in  $x = \pm(1 - \xi)$ , and then deduce the leading term in the power series solutions with respect to  $\xi$ , you find that it is either  $\xi^{m/2}$  or  $\xi^{-m/2}$ , (in the special case that  $m = 0$ , that second solution turns out to be  $\ln \xi$ .) Either way, the second possibility is not acceptable, since it physically would have infinite derivatives at the  $z$ -axis and a resulting expectation value of square momentum, as defined in section 3.3.3, that is infinite. We need to have that  $\Theta_l^m$  behaves as  $\xi^{m/2}$  at each end, so in terms of  $x$  it must have a factor  $(1 - x)^{m/2}$  near  $x = 1$  and  $(1 + x)^{m/2}$  near  $x = -1$ . The two factors multiply to  $(1 - x^2)^{m/2}$  and so  $\Theta_l^m$  can be written as  $(1 - x^2)^{m/2} f_l^m$  where  $f_l^m$  must have finite values at  $x = 1$  and  $x = -1$ .

If we substitute  $\Theta_l^m = (1 - x^2)^{m/2} f_l^m$  into the ODE for  $\Theta_l^m$ , we get an ODE for  $f_l^m$ :

$$-(1 - x^2) \frac{d^2 f_l^m}{dx^2} + 2(1 + m)x \frac{df_l^m}{dx} + (m^2 + m)f_l^m = \lambda^2 f_l^m$$

We plug in a power series,  $f_l^m = \sum c_p x^p$ , to get, after clean up,

$$\sum p(p-1)c_p x^{p-2} = \sum [(p+m)(p+m+1) - \lambda^2] c_p x^p$$

Using similar arguments as for the harmonic oscillator, we see that the starting power will be zero or one, leading to basic solutions that are again odd or even. And just like for the harmonic oscillator, we must again have that the power series terminates; even in the least case that  $m = 0$ , the series for  $f_l^m$  at  $|x| = 1$  is like that of  $\ln(1 - x^2)$  and will not converge to the finite value we stipulated. (For rigor, use Gauss's test.)

To get the series to terminate at some final power  $p = n$ , we must have according to the above equation that  $\lambda^2 = (n+m)(n+m+1)$ , and if we decide to call  $n+m$  the azimuthal quantum number  $l$ , we have  $\lambda^2 = l(l+1)$  where  $l \geq m$  since  $l = n+m$  and  $n$ , like any power  $p$ , is greater or equal to zero.

The rest is just a matter of table books, because with  $\lambda^2 = l(l+1)$ , the ODE for  $f_l^m$  is just the  $m$ -th derivative of the differential equation for the  $L_l$  Legendre polynomial, [5, 28.1], so our  $f_l^m$  must be just the  $m$ -th derivative of those polynomials. In fact, we can now recognize that our ODE for the  $\Theta_l^m$  is just Legendre's associated differential equation [5, 28.49], and that the solutions that we need are the associated Legendre functions of the first kind [5, 28.50].

To normalize the eigenfunctions on the surface area of the unit sphere, find the corresponding integral in a table book, like [5, 28.63]. As mentioned at the start of this long and still very condensed story, to include negative values of  $m$ , just replace  $m$  by  $|m|$ . There is one additional issue, though, the sign pattern. In order to simplify some more advanced analysis, physicists like the sign pattern to vary with  $m$  according to the so-called "ladder operators." That requires, {38}, that starting from  $m = 0$ , the spherical harmonics for  $m > 0$  have the alternating sign pattern of the "ladder-up operator," and those for  $m < 0$  the unvarying sign of the "ladder-down operator." Physicists will still allow you to select your own sign for the  $m = 0$  state, bless them.

There is a more intuitive way to derive the spherical harmonics: they define the power series solutions to the Laplace equation. In particular, each  $r^l Y_l^m$  is a different power

series solution  $P$  of the Laplace equation  $\nabla^2 P = 0$  in Cartesian coordinates. Each takes the form

$$\sum_{\alpha+\beta+\gamma=l} c_{\alpha\beta\gamma} x^\alpha y^\beta z^\gamma$$

where the coefficients  $c_{\alpha\beta\gamma}$  are such as to make the Laplacian zero.

Even more specifically, the spherical harmonics are of the form

$$\sum_{2a+b=l-m} c_{ab} u^{a+m} v^a z^b \quad a, b, m \geq 0$$

$$\sum_{2a+b=l-|m|} c_{ab} u^a v^{a+|m|} z^b \quad a, b, -m \geq 0$$

where the coordinates  $u = x + iy$  and  $v = x - iy$  serve to simplify the Laplacian. That these are the basic power series solutions of the Laplace equation is readily checked.

To get from those power series solutions back to the equation for the spherical harmonics, one has to do an inverse separation of variables argument for the solution of the Laplace equation in a sphere in spherical coordinates (compare also the derivation of the hydrogen atom.) Also, one would have to accept on faith that the solution of the Laplace equation is just a power series, as it is in 2D, with no additional nonpower terms, to settle completeness. In other words, you must assume that the solution is analytic.

The simplest way of getting the spherical harmonics is probably the one given in {38}.

11. This will be child's play for us harmonic oscillator, {7}, and spherical harmonics, {10}, veterans. If we replace the angular terms in (3.16) by  $l(l+1)\hbar^2$ , and then divide the entire equation by  $\hbar^2$ , we get

$$-\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + l(l+1) - 2 \frac{m_e e^2}{4\pi\epsilon_0 \hbar^2} r = \frac{2m_e}{\hbar^2} r^2 E$$

Since  $l(l+1)$  is nondimensional, all terms in this equation must be. In particular, the ratio in the third term must be the inverse of a constant with the dimensions of length; we define the constant to be the Bohr radius  $a_0$ . We will also define a correspondingly nondimensionalized radial coordinate as  $\rho = r/a_0$ . The final term in the equation must be nondimensional too, and that means that the energy  $E$  must take the form  $(\hbar^2/2m_e a_0^2)\epsilon$ , where  $\epsilon$  is a nondimensional energy. In terms of these scaled coordinates we get

$$-\frac{1}{R} \frac{d}{d\rho} \left( \rho^2 \frac{dR}{d\rho} \right) + l(l+1) - 2\rho = \rho^2 \epsilon$$

or written out

$$-\rho^2 R'' - 2\rho R' + [l(l+1) - 2\rho - \epsilon\rho^2] R = 0$$

where the primes denote derivatives with respect to  $\rho$ .

Similar to the case of the harmonic oscillator, we must have solutions that become zero at large distances  $\rho$  from the nucleus:  $\int |\psi|^2 d^3\vec{r}$  gives the probability of finding the

particle integrated over all possible positions, and if  $\psi$  does not become zero sufficiently rapidly at large  $\rho$ , this integral would become infinite, rather than one (certainty) as it should. Now the ODE above becomes for large  $\rho$  approximately  $R'' + \epsilon R = 0$ , which has solutions of the rough form  $\cos(\sqrt{\epsilon}\rho + \phi)$  for positive  $\epsilon$  that do not have the required decay to zero. Zero scaled energy  $\epsilon$  is still too much, as can be checked by solving in terms of Bessel functions, so we must have that  $\epsilon$  is negative. In classical terms, the earth can only hold onto the moon since the moon's total energy is less than the potential energy far from the earth; if it was not, the moon would escape.

Anyway, for bound states, we must have the scaled energy  $\epsilon$  negative. In that case, the solution at large  $\rho$  takes the approximate form  $R \approx e^{\pm\sqrt{-\epsilon}\rho}$ . Only the negative sign is acceptable. We can make things a lot easier for ourselves if we peek at the final solution and rewrite  $\epsilon$  as being  $-1/n^2$  (that is not really cheating, since we are not at this time claiming that  $n$  is an integer, just a positive number.) In that case, the acceptable exponential behavior at large distance takes the form  $e^{-\frac{1}{2}\xi}$  where  $\xi = 2\rho/n$ . We split off this exponential part by writing  $R = e^{-\frac{1}{2}\xi}\bar{R}$  where  $\bar{R}(\xi)$  must remain bounded at large  $\xi$ . Substituting these new variables, the ODE becomes

$$-\xi^2\bar{R}'' + \xi(\xi - 2)\bar{R}' + [l(l+1) - (n-1)\xi]\bar{R} = 0$$

where the primes indicate derivatives with respect to  $\xi$ .

If we do a power series solution of this ODE, we see that it must start with either power  $\xi^l$  or with power  $\xi^{-l-1}$ . The latter is not acceptable, since it would correspond to an infinite expectation value of energy. We could now expand the solution further in powers of  $\xi$ , but the problem is that tabulated polynomials usually do not start with a power  $l$  but with power zero or one. So we would not easily recognize the polynomial we get. We will therefore try splitting off the leading power by defining  $\bar{R} = \xi^l\bar{\bar{R}}$ , which turns the ODE into

$$\xi\bar{\bar{R}}'' + [2(l+1) - \xi]\bar{\bar{R}}' + [n-l-1]\bar{\bar{R}} = 0$$

Substituting in a power series  $\bar{\bar{R}} = \sum c_p \xi^p$ , we get

$$\sum p[p+2l+1]c_p \xi^{p-1} = \sum [p+l+1-n]c_p \xi^p$$

The acceptable lowest power  $p$  of  $\xi$  is now zero. Again the series must terminate, otherwise the solution would behave as  $e^\xi$  at large distance, which is unacceptable. Termination at a highest power  $p = q$  requires that  $n$  equals  $q + l + 1$ . Since  $q$  and  $l$  are integers, so must be  $n$ , and since the final power  $q$  is at least zero,  $n$  is at least  $l + 1$ . We have obtained the correct scaled energy  $\epsilon = -1/n^2$  with  $n > l$ .

With  $n$  identified, we can identify our ODE as Laguerre's associated differential equation, e.g. [5, 30.26], the  $(2l+1)$ -th derivative of Laguerre's differential equation, e.g. [5, 30.1], and our polynomial solutions as the associated Laguerre polynomials  $L_{n+l}^{2l+1}$ , e.g. [5, 30.27], the  $(2l+1)$ -th derivatives of the Laguerre's polynomials  $L_{n+l}$ , e.g. [5, 30.2]. To normalize the wave function use an integral from a table book, e.g. [5, 30.46].

12. I am following the notations of [5, pp. 169-172], who define

$$L_n(x) = e^x \frac{d^n}{dx^n} (x^n e^{-x}), \quad L_n^m = \frac{d^m}{dx^m} L_n(x).$$

In other words,  $L_n^m$  is simply the  $m$ -th derivative of  $L_n$ , which certainly tends to simplify things. According to [3, p. 152], the “most nearly standard” notation defines

$$L_n^m = (-1)^m \frac{d^m}{dx^m} L_{n+m}(x).$$

13. To see that  $\langle \Psi | A | \Psi \rangle$  works for getting the expectation value, just write  $\Psi$  out in terms of the eigenfunctions  $\alpha_n$  of  $A$ :

$$\langle c_1\alpha_1 + c_2\alpha_2 + c_3\alpha_3 + \dots | A | c_1\alpha_1 + c_2\alpha_2 + c_3\alpha_3 + \dots \rangle$$

Now by the definition of eigenfunctions  $A\alpha_n = a_n\alpha_n$  for every  $n$ , so we get

$$\langle c_1\alpha_1 + c_2\alpha_2 + c_3\alpha_3 + \dots | c_1a_1\alpha_1 + c_2a_2\alpha_2 + c_3a_3\alpha_3 + \dots \rangle$$

Since eigenfunctions are orthonormal:

$$\langle \alpha_1 | \alpha_1 \rangle = 1 \quad \langle \alpha_2 | \alpha_2 \rangle = 1 \quad \langle \alpha_3 | \alpha_3 \rangle = 1 \quad \dots$$

$$\langle \alpha_1 | \alpha_2 \rangle = \langle \alpha_2 | \alpha_1 \rangle = \langle \alpha_1 | \alpha_3 \rangle = \langle \alpha_3 | \alpha_1 \rangle = \langle \alpha_2 | \alpha_3 \rangle = \langle \alpha_3 | \alpha_2 \rangle = \dots = 0$$

So, multiplying out produces the desired result:

$$\langle \Psi | A \Psi \rangle = |c_1|^2 a_1 + |c_2|^2 a_2 + |c_3|^2 a_3 + \dots \equiv \langle A \rangle$$

14. The reason that two operators that commute have a common set of eigenvectors can be seen as follows: assume that  $\vec{\alpha}$  is an eigenvector of  $A$  with eigenvalue  $a$ . Then since  $A$  and  $B$  commute,  $AB\vec{\alpha} = BA\vec{\alpha} = aB\vec{\alpha}$ , so, comparing start and end,  $B\vec{\alpha}$  must be an eigenvector of  $A$  with eigenvalue  $a$  too. If there is no degeneracy of the eigenvalue, that must mean that  $B\vec{\alpha}$  equals  $\vec{\alpha}$  or is at least proportional to it, which is the same as saying that  $\vec{\alpha}$  is an eigenvector of  $B$  too. (In the special case that  $B\vec{\alpha}$  is zero,  $\alpha$  is an eigenvector of  $B$  with eigenvalue zero.)

If there is degeneracy, the eigenvectors of  $A$  are not unique and you can mess with them until they all do become eigenvectors of  $B$  too. The following procedure will construct such a set of common eigenvectors in finite dimensional space. Consider each eigenvalue of  $A$  in turn. There will be more than one eigenvector corresponding to a degenerate eigenvalue  $a$ . Now by completeness, any eigenvector  $\beta$  can be written as a combination of the eigenvectors of  $A$ , and more particularly as  $\beta = \beta_n + \beta_a$  where  $\beta_a$  is a combination of the eigenvectors of  $A$  with eigenvalue  $a$  and  $\beta_n$  a combination of the eigenvectors of  $A$  with other eigenvalues. The vectors  $\beta_n$  and  $\beta_a$  separately are still eigenvectors of  $B$  if nonzero, since as noted above,  $B$  converts eigenvectors of  $A$  into eigenvectors with the same eigenvalue or zero. (For example, if  $B\beta_a$  was not  $\beta\beta_a$ ,  $B\beta_n$  would have to make up the difference, and  $B\beta_n$  can only produce combinations of eigenvectors of

$A$  that do *not* have eigenvalue  $a$ .) Now replace the eigenvector  $\beta$  by either  $\beta_a$  or  $\beta_n$ , whichever is independent of the other eigenvectors of  $B$ . Doing this for all eigenvectors of  $B$  we achieve that the replacement eigenvectors of  $B$  are either combinations of the eigenvectors of  $A$  with eigenvalue  $a$  or of the other eigenvectors of  $A$ . The set of new eigenvectors of  $B$  that are combinations of the eigenvectors of  $A$  with eigenvalue  $a$  can now be taken as the replacement eigenvectors of  $A$  with eigenvalue  $a$ . They are also eigenvectors of  $B$ . Repeat for all eigenvalues of  $A$ .

The operators do not really have to be Hermitian, just “diagonalizable”: they must have a complete set of eigenfunctions.

In the infinite dimensional case the mathematical justification gets much trickier. However, as the hydrogen atom and harmonic oscillator eigenfunction examples indicate, it continues to be relevant in nature.

15. For brevity, define  $A' = A - \langle A \rangle$  and  $B' = B - \langle B \rangle$ , then the general expression for standard deviation says

$$\sigma_A^2 \sigma_B^2 = \langle A'^2 \rangle \langle B'^2 \rangle = \langle \Psi | A'^2 \Psi \rangle \langle \Psi | B'^2 \Psi \rangle$$

Hermitian operators can be taken to the other side of inner products, so

$$\sigma_A^2 \sigma_B^2 = \langle A' \Psi | A' \Psi \rangle \langle B' \Psi | B' \Psi \rangle$$

Now the Cauchy-Schwartz inequality says that for any  $f$  and  $g$ ,

$$|\langle f | g \rangle| \leq \sqrt{\langle f | f \rangle} \sqrt{\langle g | g \rangle}$$

(For example, if  $f$  and  $g$  are real vectors, the inner products become dot products and we have  $|f \cdot g| = |f||g||\cos \theta| = \sqrt{f \cdot f} \sqrt{g \cdot g} |\cos(\theta)|$ , and a cosine is less than one in magnitude.) Using the Cauchy-Schwartz inequality in reversed order, we get

$$\sigma_A^2 \sigma_B^2 \geq |\langle A' \Psi | B' \Psi \rangle|^2 = |\langle A' B' \rangle|^2$$

Now by the definition of the inner product, the complex conjugate of  $\langle A' \Psi | B' \Psi \rangle$  is  $\langle B' \Psi | A' \Psi \rangle$ , so the complex conjugate of  $\langle A' B' \rangle$  is  $\langle B' A' \rangle$ , and averaging a complex number with minus its complex conjugate reduces its size, since the real part averages away, so

$$\sigma_A^2 \sigma_B^2 \geq \left| \frac{\langle A' B' \rangle - \langle B' A' \rangle}{2} \right|^2$$

The quantity in the top is the expectation value of the commutator  $[A', B']$ , and writing out it out shows that  $[A', B'] = [A, B]$ .

16. This note explains where the formulae of section 3.4.4 come from.

The general assertions are readily checked by simply writing out both sides of the equation and comparing. And some are just rewrites of earlier ones.

Position and potential energy operators commute since they are just ordinary numerical multiplications, and these commute.

The linear momentum operators commute because the order in which differentiation is done is irrelevant. Similarly, commutators between angular momentum in one direction and position in another direction commute since the other directions are not affected by the differentiation.

The commutator between  $x$ -position and  $p_x$ -linear momentum was worked out in the previous subsection to figure out Heisenberg's uncertainty principle. Of course, three-dimensional space has no preferred direction, so the result we got applies the same in any direction, including the  $y$ - and  $z$ -directions.

The angular momentum commutators are simplest obtained by just grinding out

$$[\hat{L}_x, \hat{L}_y] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z]$$

using the linear combination and product manipulation rules and the commutators for linear angular momentum. To generalize the result you get, you cannot just arbitrarily swap  $x$ ,  $y$ , and  $z$ , since, as every mechanic knows, a right-handed screw is not the same as a left-handed one, and some axes swaps would turn one into the other. But you can swap axes according to the “ $xyzxyz\dots$ ” “cyclic permutation” scheme, as in:

$$x \rightarrow y, \quad y \rightarrow z, \quad z \rightarrow x$$

which produces the other two commutators if you do it twice:

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \quad \longrightarrow \quad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \quad \longrightarrow \quad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

For the commutators with square angular momentum, work out

$$[\hat{L}_x, \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2]$$

using the manipulation rules and the commutators between angular momentum components.

17. Take the origin of a spherical coordinate system at the left proton, and the axis towards the right one. Then integrate the angular coordinates first. Do not forget that  $\sqrt{x^2} = |x|$ , not  $x$ , for any real quantity  $x$ , e.g.  $\sqrt{(-3)^2} = 3$ , not  $-3$ . More details and the results are in [3, pp. 305-307].
18. Of course “best” is a subjective term. If you are looking for the wave function within a definite set that has the most accurate expectation value of energy, then minimizing the expectation value of energy will do it. This function will also approximate the true eigenfunction shape the best, in some technical sense. (It will not have the smallest maximum deviation from the exact wave function, say.)

But given a set of approximate wave functions like those used in finite element methods, it may well be possible to get much better results using additional mathematical techniques like Richardson extrapolation. In effect you are then deducing what happens for wave functions that are beyond the approximate ones you are using.

19. The approximate ground state solution  $\psi$  may always be written as a sum of the eigenfunctions  $\psi_1, \psi_2, \dots$  as:

$$\psi = c_1\psi_1 + \varepsilon_2\psi_2 + \varepsilon_3\psi_3 + \dots$$

where, if the approximation is any good at all,  $c_1$  is close to one, while  $\varepsilon_2, \varepsilon_3, \dots$  are small. The condition that  $\psi$  is normalized,  $\langle \psi | \psi \rangle = 1$ , works out to be

$$1 = \langle c_1\psi_1 + \varepsilon_2\psi_2 + \dots | c_1\psi_1 + \varepsilon_2\psi_2 + \dots \rangle = c_1^2 + \varepsilon_2^2 + \dots$$

since the eigenfunctions  $\psi_1, \psi_2, \dots$  are orthonormal. Similarly, the energy  $E = \langle \psi | H\psi \rangle = 1$  works out to be

$$E = \langle c_1\psi_1 + \varepsilon_2\psi_2 + \dots | E_1c_1\psi_1 + E_2\varepsilon_2\psi_2 + \dots \rangle = c_1^2E_1 + \varepsilon_2^2E_2 + \dots$$

Eliminating  $c_1^2$  between the two gives

$$E = E_1 + \varepsilon_2^2(E_2 - E_1) + \varepsilon_3^2(E_3 - E_1) + \dots$$

So, while the deviations of the wave function from the exact ground state  $\psi_1$  are proportional to the coefficients  $\varepsilon_2, \varepsilon_3, \dots$ , the errors in energy are proportional to the *squares* of those coefficients. And the square of any reasonably small quantity is much smaller than the quantity itself. So the ground state energy is much more accurate than would be expected from the wave function errors.

Also note from the final expression above that the expectation energy of *all* wave functions is greater or equal to the ground state; not just those of pure eigenfunctions. The text glossed over that distinction.

20. If the Hamiltonian is real, taking real and imaginary parts of the eigenvalue problem,  $H\psi = E\psi$  shows that the real and imaginary parts of  $\psi$  each separately are eigenfunctions with the same eigenvalue, and both are real. So we can take  $\psi$  to be real without losing anything.

The expectation value of the energy of  $|\psi|$  is the same as that for  $\psi$ , (assuming that an integration by parts has been done on the kinetic energy part), so  $|\psi|$  must be the same function as  $\psi$ , assuming the ground state is unique. That means that  $\psi$  cannot change sign and can be taken to be positive. (Regrettably this argument stops working for more than two electrons due to the antisymmetrization requirement of section 4.7.)

21. Let  $z$  be the horizontal coordinate measured from the symmetry plane. Let  $M$  be the “mirror operator” that changes the sign of  $z$ , in other words,

$$M\Psi(x, y, z) = \Psi(x, y, -z)$$

This operator commutes with the Hamiltonian  $H$  since the energy evaluates the same way at positive and negative  $z$ . This means that operators  $H$  and  $M$  must have a complete set of common eigenfunctions. That set must include the ground state of lowest energy: so the ground state must be an eigenfunction of  $M$  too. Now the eigenvalues of  $M$  are either  $+1$  or  $-1$ : if  $M$  is applied twice, it gives back the same wave function,

i.e.  $1\Psi$ , so the square of the eigenvalue is 1, so that the eigenvalue itself can only be 1 and -1. Eigenfunctions with eigenvalue 1 are called “symmetric”, eigenfunctions with eigenvalue -1 are called “antisymmetric”. Since we already know that the ground state must be everywhere positive, it can only be a symmetric one.

Similarly, let  $R$  be the operator that rotates  $\Psi$  over a small angle  $\phi$  around the axis of symmetry. The magnitude of the eigenvalues of  $R$  must be 1, since  $\Psi$  must stay normalized to 1 after the rotation. Complex numbers of magnitude 1 can be written as  $e^{ia}$  where  $a$  is a real number. Number  $a$  must be proportional to  $\phi$ , since rotating  $\Psi$  twice is equivalent to rotating it once over twice the angle, so the eigenvalues are  $e^{in\phi}$ , where  $n$  is a constant independent of  $\phi$ . (In addition,  $n$  must be integer since rotating over 360 degrees must give back the original wave function.) In any case, the only way that  $\Psi$  can be real and positive at all angular positions is if  $n = 0$ , so the eigenvalue is 1, implying that  $\Psi$  does not change when rotated; it must be the same at all angles.

22. The example given in section 4.5 is not quite the one of Bell. Bell really used the inequality:

$$|2(f_3 + f_4 + f_5 + f_6) - 2(f_2 + f_4 + f_5 + f_7)| \leq 2(f_2 + f_3 + f_6 + f_7)$$

So I cheated. And of course, Bell allowed general directions of measurement. See [3, pp. 423-426].

23. The expectation value of the energy is  $\langle E \rangle = \langle \Psi | H\Psi \rangle$ . The first term in  $H\Psi$  takes the form

$$(H\Psi_{++} \uparrow\uparrow) = H(\Psi_{++}(\vec{r}_1, \vec{r}_2)\chi_+(S_{z1})\chi_+(S_{z2})) = (H\Psi_{++}) \uparrow\uparrow$$

since the Hamiltonian that we wrote down does not involve the spin at all. The other three terms in  $H\Psi$  can be written similarly. So the inner product  $\langle \Psi | H\Psi \rangle$  becomes

$$\begin{aligned} & \langle \Psi_{++} \uparrow\uparrow + \Psi_{+-} \uparrow\downarrow + \Psi_{-+} \downarrow\uparrow + \Psi_{--} \downarrow\downarrow \\ & | (H\Psi_{++}) \uparrow\uparrow + (H\Psi_{+-}) \uparrow\downarrow + (H\Psi_{-+}) \downarrow\uparrow + (H\Psi_{--}) \downarrow\downarrow \rangle \end{aligned}$$

Because of the orthonormality of the spin states, this simplifies to

$$\langle E \rangle = \langle \Psi_{++} | H\Psi_{++} \rangle + \langle \Psi_{+-} | H\Psi_{+-} \rangle + \langle \Psi_{-+} | H\Psi_{-+} \rangle + \langle \Psi_{--} | H\Psi_{--} \rangle$$

In addition, the wave function must be normalized,  $\langle \Psi | \Psi \rangle = 1$ , or

$$1 = \langle \Psi_{++} | \Psi_{++} \rangle + \langle \Psi_{+-} | \Psi_{+-} \rangle + \langle \Psi_{-+} | \Psi_{-+} \rangle + \langle \Psi_{--} | \Psi_{--} \rangle$$

Now when the component states are proportional to the spatial ground state  $\psi_{gs} = a(\psi_L\psi_R + \psi_R\psi_L)$  with the lowest energy  $E_{gs}$ , their individual contributions to the energy will be  $\langle \Psi_{\pm\pm} | H\Psi_{\pm\pm} \rangle = E_{gs}\langle \Psi_{\pm\pm} | \Psi_{\pm\pm} \rangle$ , the lowest possible. Then the total energy  $\langle \Psi | H\Psi \rangle$  will be  $E_{gs}$ . Anything else will have more energy and cannot be the ground state.

24. If we drop the shielding approximation for the remaining electron in the ionized state, as common sense would suggest, the ionization energy would become negative! This illustrates the dangers of mixing models at random. This problem might also be why the discussion in [3] is based on the zero shielding approximation, rather than the full shielding approximation used here.

But zero shielding does make the base energy levels of the critical outer electrons of heavy atoms very large, proportional to the square of the atom number. And that might then suggest the question: if the energy levels explode like that, why doesn't the ionization energy or the electronegativity? And it makes the explanation why helium would not want another electron more difficult. Full shielding puts you in the obviously more desirable starting position of the additional electron not being attracted, and the already present electrons being shielded from the nucleus by the new electron. And how about the size of the atoms imploding in zero shielding?

Overall, I think I prefer the full shielding approach. Zero shielding would predict the helium ionization energy to be 54.4 eV, which really seems worse than our 13.6 eV when compared to the exact value of 24.6 eV. On the other hand, zero shielding does give a fair approximation of the actual total energy of the atom; 109 eV instead of an exact value of 79. Full shielding produces a poor value of 27 eV for the total energy; the total energy is proportional to the *square* of the effective nucleus strength, so a lack of full shielding will increase the total energy very strongly. But also importantly, full shielding avoids the reader's distraction of having to rescale the wave functions to account for the non-unit nuclear strength.

If I eventually find I need to cover X-ray diffraction, I think a description of "hot" relativistic inner electrons would fix any problem well.

25. This claim can be formally justified by examining the power series expansion of the wave function around the origin. The wave function  $\psi_{nlm}$ , (3.20), starts with power  $r^l$ , so the higher  $l$ , the smaller  $|\psi_{nlm}|^2$  is for small enough r.
26. The probability of measuring an eigenvalue  $a_i$  for any arbitrary physical quantity  $a$  is according to the orthodox interpretation the square magnitude of the coefficient of the corresponding eigenfunction  $\alpha_i$ . This coefficient can be found as the inner product  $\langle \alpha_i | \Psi \rangle$ , which for a stationary state is  $\langle \alpha_i | c_n(0) e^{-iE_n t/\hbar} \psi_n \rangle$  and taking the square magnitude kills off the time-dependent exponential. So the probability of measuring any value for any physical quantity remains the same however long you wait if it is a stationary state.

It is of course assumed that the operator  $A$  does not explicitly depend on time. Otherwise its time variation would be automatic. (The eigenfunctions would depend on time.)

27. The states of lowest and highest energy are approximate energy eigenfunctions. They can be made exact energy eigenfunctions by defining  $(\psi_1 + \psi_2)/\sqrt{2}$  and  $(\psi_1 - \psi_2)/\sqrt{2}$  to be the exact symmetric ground state and the exact antisymmetric state of second lowest energy, and then reconstruct the corresponding  $\psi_1$  and  $\psi_2$  from that.

Note that  $\psi_1$  and  $\psi_2$  themselves are not energy eigenstates, though they might be so by approximation. The errors in this approximation, even if small, will produce the wrong result for the time evolution. (It are the small differences in energy that drive the *nontrivial* part of the unsteady evolution.)

28. Just write the definition of expectation value,  $\langle \Psi | A \Psi \rangle$ , differentiate to get

$$\langle \Psi_t | A \Psi \rangle + \langle \Psi | A \Psi_t \rangle + \langle \Psi | A_t \Psi \rangle$$

and replace  $\Psi_t$  by  $H\Psi/\text{i}\hbar$  on account of the Schrödinger equation. Note that in the first inner product, the  $\text{i}$  appears in the left part, hence comes out as its complex conjugate  $-\text{i}$ .

29. The virial theorem says that the expectation value of the kinetic energy of stationary states is given by

$$\langle T \rangle = \frac{1}{2} \langle \vec{r} \cdot \nabla V \rangle.$$

Note that according to the calculus rule for directional derivatives,  $\vec{r} \cdot \nabla V = r \partial V / \partial r$ .

For the  $V = \frac{1}{2}c_x x^2 + \frac{1}{2}c_y y^2 + \frac{1}{2}c_z z^2$  potential of a harmonic oscillator,  $x \partial V / \partial x + y \partial V / \partial y + z \partial V / \partial z$  produces  $2V$ . So for energy eigenstates of the harmonic oscillator, the expectation value of kinetic energy equals the one of the potential energy. And since their sum is the total energy  $E_{n_x n_y n_z}$ , each must be  $\frac{1}{2}E_{n_x n_y n_z}$ .

For the  $V = \text{constant}/r$  potential of the hydrogen atom,  $r \partial V / \partial r$  produces  $-V$ . So the expectation value of kinetic energy equals minus one half the one of the potential energy. And since their sum is the total energy  $E_n$ ,  $\langle T \rangle = -E_n$  and  $\langle V \rangle = 2E_n$ . Note that  $E_n$  is negative, so that the kinetic energy is positive as it should be.

To prove the virial theorem, work out the commutator in

$$\frac{d\langle \vec{r} \cdot \vec{p} \rangle}{dt} = \frac{\text{i}}{\hbar} \langle [H, \vec{r} \cdot \vec{p}] \rangle$$

using the formulae in chapter 3.4.4,

$$\frac{d\langle \vec{r} \cdot \vec{p} \rangle}{dt} = 2\langle T \rangle - \langle \vec{r} \cdot \nabla V \rangle,$$

and then note that the left hand side above is zero for stationary states, (in other words, states with a definite total energy).

30. Assume that the variable of real interest in a given problem has a time-invariant operator  $A$ . The generalized relationship between the uncertainties in energy and  $A$  is:

$$\sigma_E \sigma_A \geq \frac{1}{2} |\langle [H, A] \rangle|.$$

But  $|\langle [H, A] \rangle|$  is just  $\hbar |d\langle A \rangle/dt|$ . So just *define* the uncertainty in time to be

$$\sigma_t = \sigma_A \left/ \left| \frac{d\langle A \rangle}{dt} \right| \right..$$

That corresponds to the typical time in which the expectation value of  $A$  changes by one standard deviation. In other words, to the time it takes for  $A$  to change to a value sufficiently different that it will clearly show up in measurements.

31. Of course, a hydrogen atom is really an infinite state system, not a two state system, and we should write  $\Psi$  as a combination of all infinitely many eigenfunctions. But if we assume that the perturbation is small, and that only the coefficients  $a$  and  $b$  of  $\psi_L$  and  $\psi_H$  have non-negligible initial values, then we can ignore the effects of the other infinitely many coefficients as quadratically small: the small perturbation level insures that the other coefficients remain correspondingly small, and in addition their effect on  $a$  and  $b$  is much smaller still since the states hardly affect each other when the perturbation is small. (When the perturbation level is zero, they are energy eigenstates that evolve completely independently.)

While the other coefficients do therefore not have a noticeable effect on  $a$  and  $b$ , still if we start from the ground state  $|a| = 1$ , then  $b$  will remain small and the other coefficients will typically be comparably small. So, to find out what really happens to the complete system, usually you need to separately evaluate all possible transitions as two state systems, and then sum all the effects you get together.

32. The fact that there is a frequency *range* that can be absorbed may seem to violate the postulate of quantum mechanics that only the eigenvalues are observable. But actually an atom perturbed by an electromagnetic field is a slightly different system than an unperturbed atom, and will have slightly different energy eigenvalues. Indeed, the frequency range  $\omega_1$  is proportional to the strength of the perturbation, and in the limit of the perturbation strength becoming zero, only the exact unperturbed frequency will be absorbed.

For some reason, this spectral line broadening due to the strength of the transmitted light is not mentioned in the references I have seen. I assume it is included in what is called Stark broadening.

The “natural broadening” due to the always present ground state electromagnetic field perturbation is mentioned, but usually ascribed to the energy-time uncertainty  $\Delta E \Delta t \geq \frac{1}{2}\hbar$  where  $\Delta E$  is the uncertainty in energy and  $\Delta t$  some sort of uncertainty in time that in this case is claimed to be the typical life time of the excited state. And of course, a  $\geq$  sign is readily changed into an  $\approx$  sign; they are both mathematical symbols, not? Anyway, considered as a dimensional argument rather than a law of physics, it does seem to work; if there was no ground state electromagnetic field perturbing the atom, Schrödinger’s equation would have the excited state surviving forever;  $\Delta t$  would then be infinite, and the energy values would be the exact unperturbed ones. And transitions like the 21 cm line of astronomy that has a life time of 10 million years do indeed have a very small natural width.

Of course, broadening affects both the absorption spectra (frequencies removed from light that passes through the gas on its way towards us) and the emission spectra (spontaneously emitted radiation, like the “scattered” radiation re-emitted from absorbed light that passes through the gas not headed in our direction.)

An important other effect that causes spectral line deviations is atom motion, either thermal motion or global gas motion; it produces a Doppler shift in the radiation. This is not necessarily bad news; line broadening can provide an hint about the temperature of the gas you are looking at, while line displacement can provide a hint of its motion away from you. Line deviations can also be caused by surrounding atoms and other perturbations.

33. Since  $R_\varphi$  and  $H$  commute, they have a common set of eigenfunctions. Hence, if  $\rho$  is an eigenfunction of  $R_\varphi$  with eigenvalue  $r$ , it can always be written as a linear combination of eigenfunctions  $\rho_1, \rho_2, \dots$  with the same eigenvalue that are also eigenfunctions of  $H$ . So the wave function is

$$c_1 e^{-iE_1 t/\hbar} \rho_1 + c_2 e^{-iE_2 t/\hbar} \rho_2 + \dots$$

which is a linear combination of eigenfunctions with eigenvalue  $r$ , hence an eigenfunction with eigenvalue  $r$ . (Note that  $R_\varphi$  is diagonalizable since it is unitary.)

34. A more precise analysis of the start and the end of the wave packet shows that it will disperse out a distance of order  $\sqrt{t}$  beyond those limits, but  $\sqrt{t}$  is negligible compared to  $t$  if  $t$  is sufficiently large.
35. This postulate is not as unphysical as it may seem. If you read the background section 6.3, you saw that the angular momentum operators correspond to small rotations of the axis system through space. So, the commutator  $[\hat{L}_x, \hat{L}_y]$  really corresponds to the difference between a small rotation around the  $y$ -axis followed by a small rotation around the  $x$  axis, versus a small rotation around the  $x$ -axis followed by a small rotation around the  $y$  axis. And it works out that this difference is equivalent to a small rotation about the  $z$ -axis. (If you know a bit of linear algebra, you can verify this by writing down the matrices that describe the effects that rotations around each of the axes have on an arbitrary radius vector  $\vec{r}$ .) So, the fundamental commutator relations do have physical meaning; they say that this basic relationship between rotations around different axes continues to apply in the presence of spin.
36. Suppose that an eigenstate, call it  $|m\rangle$ , of  $\hat{L}_z$  is also an eigenstate of  $\hat{L}_x$ . Then  $[\hat{L}_z, \hat{L}_x]|m\rangle$  must be zero, and the commutator relations say that this is equivalent to  $\hat{L}_y|m\rangle = 0$ , which makes  $|m\rangle$  also an eigenvector of  $\hat{L}_y$ , and with the eigenvalue zero to boot. So the angular momentum in the  $y$  direction must be zero. Repeating the same argument using the  $[\hat{L}_x, \hat{L}_y]$  and  $[\hat{L}_y, \hat{L}_z]$  commutator pairs shows that the angular momentum in the other two directions is zero too. So there is no angular momentum at all,  $|m\rangle$  is an  $|0\ 0\rangle$  state.

I think I should point out that another assumption will be implicit in our use of the fundamental commutation relations, namely that they can be taken at face value. It is certainly possible to imagine that say  $\hat{L}_x$  would turn an eigenfunction of say  $\hat{L}_z$  into some singular object for which angular momentum would be ill-defined. That would of course make application of the fundamental commutation relations improper. It will be assumed that our operators are free of such pathological nastiness.

37. You might wonder whether this statement from classical vectors still applies in the quantum case. It does: just evaluate it using expectation values. Since states  $|l m\rangle$  are eigenstates, the expectation values of square angular momentum and square angular momentum in the  $z$ -direction only equal the actual values. And while the  $|l m\rangle$  states are not eigenstates of  $\hat{L}_x$  and  $\hat{L}_y$ , the expectation values of square Hermitian operators such as  $\hat{L}_x^2$  and  $\hat{L}_y^2$  is always positive anyway (as can be seen from writing it out in terms of the eigenstates of them.)
38. One application is to find the spherical harmonics, which as noted in chapter 3.1.3 is not an easy problem. To do it with ladder operators, show that

$$\hat{L}_x = \frac{\hbar}{i} \left( -\sin \phi \frac{\partial}{\partial \theta} - \frac{\cos \theta \cos \phi}{\sin \theta} \frac{\partial}{\partial \phi} \right) \quad \hat{L}_y = \frac{\hbar}{i} \left( \cos \phi \frac{\partial}{\partial \theta} - \frac{\cos \theta \sin \phi}{\sin \theta} \frac{\partial}{\partial \phi} \right)$$

then that

$$L^+ = \hbar e^{i\phi} \left( \frac{\partial}{\partial \theta} + i \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \phi} \right) \quad L^- = \hbar e^{-i\phi} \left( -\frac{\partial}{\partial \theta} + i \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \phi} \right)$$

Note that the spherical harmonics are of the form  $Y_l^m = e^{im\phi} \Theta_l^m(\theta)$ , so

$$L^+ Y_l^m = \hbar e^{i(m+1)\phi} \sin^m \theta \frac{d(\Theta_l^m / \sin^m \theta)}{d\theta} \quad L^- Y_l^m = -\hbar e^{i(m-1)\phi} \frac{1}{\sin^m \theta} \frac{d(\Theta_l^m \sin^m \theta)}{d\theta}$$

Find the  $Y_l^l$  harmonic from  $\hat{L}^+ Y_l^l = 0$ , then apply  $\hat{L}^-$  to find the rest of the ladder.

Interestingly enough, the solution of the one-dimensional harmonic oscillator problem can also be found using ladder operators. It turns out that, in the notation of that problem,

$$H^+ = -i\hat{p} + m\omega\hat{x} \quad H^- = i\hat{p} + m\omega\hat{x}$$

are commutator eigenoperators of the harmonic oscillator Hamiltonian, with eigenvalues  $\pm\hbar\omega$ . So, we can play the same games of constructing ladders. Easier, really, since there is no equivalent to square angular momentum to worry about in that problem: there is only one ladder. See [3, pp. 42-47] for details.

39. That is clearly following the Newtonian analogy: in classical physics each particle has its own independent angular momentum, and we just add them up,
40. The fact that you can do that is due to the orthonormality of the states involved. In terms of the real vectors of physics, it is simply that the component of one unit vector in the direction of another unit vector is the same as the component of the second unit vector in the direction of the first.
41. The procedure is exactly the same as for the two electron spin ladders, so it is simple enough to program. To further simplify things, it turns out that the coefficients are all square roots of rational numbers (rational numbers are ratios of integers such as 102/38.) The step-up and step-down operators by themselves produce square roots of rational numbers, so at first glance it would appear that the individual Clebsch-Gordan

coefficients would be sums of square roots. But the square roots of a given coefficient are all compatible and can be summed into one. To see why, consider the coefficients that result from applying the combined step down ladder  $\hat{L}_{ab}^-$  a few times on the top of the ladder  $|l l\rangle_a |l l\rangle_b$ . Every contribution to the coefficient of a state  $|l m\rangle_a |l m\rangle_b$  comes from applying  $\hat{L}_a^-$  for  $l_a - m_a$  times and  $\hat{L}_b^-$  for  $l_b - m_b$  times, so all contributions have compatible square roots.  $\hat{L}_{ab}^-$  merely adds an  $m_{ab}$  dependent normalization factor. You might think this pattern is broken when you start defining the tops of lower ladders, since that process uses the step up operators. But because  $\hat{L}^+ \hat{L}^-$  and  $\hat{L}^- \hat{L}^+$  are rational numbers (not square roots), applying the up operators is within a rational number the same as applying the down ones, and the pattern turns out to remain.

42. The more familiar machine language form leaves out the  $a$ ,  $b$ , and  $ab$  identifiers, the  $l_a =$  and  $l_b =$  clarifications from the header, and all square root signs, the  $l$  values of particles  $a$  and  $b$  from the kets, and all ket terminator bars and brackets, but combines the two  $m$ -values with missing  $l$  values together in a frame to resemble an  $lm$  ket as well as possible, and then puts it all in a font that is easy to read with a magnifying glass or microscope.
43. The normal triangle inequality continues to apply for expectation values in quantum mechanics. The way to show that is, like other triangle inequality proofs, rather curious: examine the combination of  $\hat{L}_a$ , not with  $\hat{L}_b$ , but with an arbitrary multiple  $\lambda$  of  $\hat{L}_b$ :

$$\langle (\vec{L}_a + \lambda \vec{L}_b)^2 \rangle = \langle (L_{x,a} + \lambda L_{x,b})^2 \rangle + \langle (L_{y,a} + \lambda L_{y,b})^2 \rangle + \langle (L_{z,a} + \lambda L_{z,b})^2 \rangle$$

For  $\lambda = 1$  this produces the expectation value of  $(\vec{L}_a + \vec{L}_b)^2$ , for  $\lambda = -1$ , the one for  $(\vec{L}_a - \vec{L}_b)^2$ . In addition, it is positive for all values of  $\lambda$ , since it consists of expectation values of square Hermitian operators. (Just examine each term in terms of its own eigenstates.) If we multiply out, we get

$$\langle (\vec{L}_a + \lambda \vec{L}_b)^2 \rangle = L_a^2 + 2M\lambda + L_b^2\lambda^2$$

where  $L_a \equiv \sqrt{\langle L_{xa}^2 + L_{ya}^2 + L_{za}^2 \rangle}$ ,  $L_b \equiv \sqrt{\langle L_{xb}^2 + L_{yb}^2 + L_{zb}^2 \rangle}$ , and  $M$  represents mixed terms that I am not going to write out. In order for this quadratic form in  $\lambda$  to always be positive, the discriminant must be negative:

$$M^2 - L_a^2 L_b^2 \leq 0$$

which means, taking square roots,

$$-L_a L_b \leq M \leq L_a L_b$$

and so

$$L_a^2 - 2L_a L_b + L_b^2 \leq \langle (\vec{L}_a + \vec{L}_b)^2 \rangle \leq L_a^2 + 2L_a L_b + L_b^2$$

or

$$|L_a - L_b|^2 \leq \langle (\vec{L}_a + \vec{L}_b) \rangle^2 \leq |L_a + L_b|^2$$

and taking square roots gives the triangle inequality. Note that this derivation does not use any properties specific to angular momentum and does not require the simultaneous existence of the components. With a bit of messing around, the azimuthal quantum number relation  $|l_a - l_b| \leq l_{ab} \leq l_a + l_b$  can be derived from it if a unique value for  $l_{ab}$  exists; the key is to recognize that  $L = l + \delta$  where  $\delta$  is an increasing function of  $l$  that stays below  $\frac{1}{2}$ , and the  $l$  values must be half integers. This derivation is not as elegant as using the ladder operators, but the result is the same.

44. Now of course you ask: how do we know how the mathematical expressions for spin states change when the coordinate system is rotated around some axis? Darn. If you did a basic course in linear algebra, they will have told you how the components of normal vectors change when the coordinate system is rotated, but not spin vectors, or spinors, which are two-dimensional vectors in three-dimensional space.

We need to go back to the fundamental meaning of angular momentum. The effect of rotations of the coordinate system around the  $z$ -axis was discussed in chapter 6.3. The expressions given there can be straightforwardly generalized to rotations around a line in the direction of an arbitrary unit vector  $(n_x, n_y, n_z)$ . Rotation by an angle  $\varphi$  multiplies the  $n$ -direction angular momentum eigenstates by  $e^{im\varphi}$  if  $m\hbar$  is the angular momentum in the  $n$ -direction. For electron spin, the values for  $m$  are  $\pm\frac{1}{2}$ , so, using the Euler identity (1.5) for the exponential, the eigenstates change by a factor

$$\cos\left(\frac{1}{2}\varphi\right) \pm i \sin\left(\frac{1}{2}\varphi\right)$$

For arbitrary combinations of the eigenstates, the first of the two terms above still represents multiplication by the number  $\cos\left(\frac{1}{2}\varphi\right)$ . The second term may be compared to the effect of the  $n$ -direction angular momentum operator  $\hat{L}_n$ , which multiplies the angular momentum eigenstates by  $\pm\frac{1}{2}\hbar$ ; it is seen to be  $2i \sin\left(\frac{1}{2}\varphi\right) \hat{L}_n/\hbar$ . So the operator that describes rotation of the coordinate system over an angle  $\varphi$  around the  $n$ -axis is

$$R_{n,\varphi} = \cos\left(\frac{1}{2}\varphi\right) + i \sin\left(\frac{1}{2}\varphi\right) \frac{2}{\hbar} \hat{L}_n$$

Further, in terms of the  $x$ ,  $y$ , and  $z$  angular momentum operators, the angular momentum in the  $n$ -direction is

$$\hat{L}_n = n_x \hat{L}_x + n_y \hat{L}_y + n_z \hat{L}_z$$

If we put it in terms of the Pauli spin matrices,  $\hbar$  drops out:

$$R_{n,\varphi} = \cos\left(\frac{1}{2}\varphi\right) + i \sin\left(\frac{1}{2}\varphi\right) (n_x \sigma_x + n_y \sigma_y + n_z \sigma_z)$$

Using this operator, we can find out how the spin-up and spin-down states are described in terms of correspondingly defined basis states along the  $x$ - or  $y$ -axis, and then deduce these correspondingly defined basis states in terms of the  $z$ -ones.

Note however that the very idea of defining the positive  $x$  and  $y$  angular momentum states from the  $z$ -ones by rotating the coordinate system over  $90^\circ$  is somewhat specious.

If we rotate the coordinate system over  $450^\circ$  instead, we get a different answer! Off by a factor  $-1$ , to be precise. But that is as bad as the indeterminacy gets; whatever way you rotate the axis system to the new position, the basis vectors you get will either be the same or only a factor  $-1$  different {45}.

More awkwardly, the negative momentum states obtained by rotation do not lead to real positive numerical factors for the corresponding ladder operators. Presumably, this reflects the fact that at the wave function level, nature does not have the rotational symmetry that it has for observable quantities. If you have a better explanation, tell me. Anyway, if nature does not bother to obey such symmetry, then I am not going to bother pretending it does. Especially since the nonpositive ladder factors would mess up various formulae. The negative spin states found by rotation go out of the window. Bye, bye.

45. How about that? A note on a note. Why can you only change the spin states you find in a given direction by a factor  $-1$  by rotating your point of view? Why not by  $i$ , say? With a bit of knowledge of linear algebra and some thought, you can see that this question is really: how can we change the spin states if we perform an arbitrary number of coordinate system rotations that end up in the same orientation as they started? I am not aware of a simple way to answer this, so what I did was to show that the effect of any two rotations of the coordinate system can be achieved by a single rotation over a suitably chosen net angle around a suitably chosen net axis. Applied repeatedly, any set of rotations of the starting axis system back to where it was becomes a single rotation around a single axis, and then it is easy to check that at most a change of sign is possible. (To show that any two rotations are equivalent to one, I just crunched out the multiplication of two rotations, which showed that it takes the algebraic form of a single rotation, though with a unit vector  $\vec{n}$  not immediately evident to be of length one. By noting that the determinant of the rotation matrix must be one, it follows that the length is in fact one.) Maybe I am overlooking something obvious here; let me know.
46. In particular, for the  $i$ -th component of the triple product  $\hat{\vec{p}} \times (\nabla \times \vec{A})$ ,

$$[\hat{\vec{p}} \times (\nabla \times \vec{A})]_i = \sum_{j=1}^3 \hat{p}_j \left( \frac{\partial A_j}{\partial x_i} - \frac{\partial A_i}{\partial x_j} \right)$$

and of  $(\nabla \times \vec{A}) \times \hat{\vec{p}}$ ,

$$[(\nabla \times \vec{A}) \times \hat{\vec{p}}]_i = \sum_{j=1}^3 \left( \frac{\partial A_i}{\partial x_j} - \frac{\partial A_j}{\partial x_i} \right) \hat{p}_j$$

Similar expressions apply when  $\hat{\vec{p}}$  is replaced by  $\vec{A}$ .

47. Since the voltage is minus the integral of the electric field, it might seem that I have my plus and minus mixed up in the figure. But actually, it is a bit more complex. The initial effect of the induced magnetic field is to drive the electrons towards the pole marked as negative. (Recall that the charge of electrons is negative, so the force on the electrons

is in the direction opposite to the electric field.) The accumulation of electrons at the negative pole sets up a counter-acting electric field that stops further motion of the electrons. Since the leads to the load will be stranded together rather than laid out in a circle, they are not affected by the induced electric field, but only by the counter-acting one. If you want, just forget about voltages and consider that the induced electric field will force the electrons out of the negative terminal and through the load.

One obvious improvement is to take a longer wire and wrap it around a few more times, giving a spool. Another is to stick in a piece of iron to enhance the magnetic field.

48. Some sources claim the spin is under an angle with the magnetic field; this is impossible since, as pointed out in chapter 3.1.4, the angular momentum vector does not exist. However, the angular momentum component along the magnetic field does have measurable values, and these component values, being one-dimensional, can only be aligned or anti-aligned with the magnetic field.
49. First get rid of the time dependence of the right-hand-side matrix by defining new variables  $A$  and  $B$  by

$$a = Ae^{i\omega t/2}, \quad b = Be^{-i\omega t/2}.$$

Then find the eigenvalues and eigenvectors of the now constant matrix. The eigenvalues can be written as  $\pm i\omega_1/f$ , where  $f$  is the resonance factor given in the main text. The solution is then

$$\begin{pmatrix} A \\ B \end{pmatrix} = C_1 \vec{v}_1 e^{i\omega_1 t/f} + C_2 \vec{v}_2 e^{-i\omega_1 t/f}$$

where  $\vec{v}_1$  and  $\vec{v}_2$  are the eigenvectors. To find the constants  $C_1$  and  $C_2$ , apply the initial conditions  $A(0) = a(0) = a_0$  and  $B(0) = b(0) = b_0$  and clean up as well as possible, using the definition of the resonance factor and the Euler identity. It's a mess.

50. There is an oft-cited story going around that the many worlds interpretation implies the existence of  $10^{99}$  worlds, and this number apparently comes from Everett, III himself. It is often used to argue that the many-worlds interpretation is just not credible. However, the truth is that the existence of infinitely many worlds, (or practically speaking infinitely many of them, maybe, if space and time would turn out to be discrete), is a basic requirement of quantum mechanics itself, regardless of interpretation. Everett, III cannot be blamed for that, just for coming up with the ludicrous number of  $10^{99}$  to describe infinity.

# Bibliography

- [1] Hugh Everett, III. The theory of the universal wave function. In Bryce S. DeWitt and Neill Graham, editors, *The Many-Worlds Interpretation of Quantum Mechanics*, pages 3–140. Princeton University Press, 1973.
- [2] R.P. Feynman, R.B. Leighton, and M. Sands. *The Feynman Lectures on Physics*, volume III. Addison-Wesley, 1965.
- [3] David J. Griffiths. *Introduction to Quantum Mechanics*. Pearson Prentice-Hall, second edition, 2005.
- [4] C. Kittel. *Introduction to Solid State Physics*. Wiley, 7th edition, 1996.
- [5] M.R. Spiegel and J. Liu. *Mathematical Handbook of Formulas and Tables*. Schaum’s Outline Series. McGraw-Hill, second edition, 1999.
- [6] A. Yariv. *Theory and Applications of Quantum Mechanics*. Wiley & Sons, 1982.



# Web Pages

Below is a list of relevant web pages. Some of the discussions were based on them.

1. Amber Schilling's page<sup>1</sup> One of the info sources for chemical bonds, with lots of good pictures.
2. Hyperphysics<sup>2</sup> An extensive source of info on chemical bonds and the periodic table.
3. Middlebury College Modern Physics Laboratory Manual<sup>3</sup> Gives a very understandable introduction to NMR with actual examples (item XIX.)
4. Purdue chemistry review<sup>4</sup> My source for the electronegativity values.
5. The Quantum Exchange<sup>5</sup> Lots of stuff.
6. University of Michigan<sup>6</sup> Invaluable source on the hydrogen molecule and chemical bonds. Have a look at the animated periodic table for actual atom energy levels.
7. Wikipedia<sup>7</sup> Probably my primary source of information on about everything, though somewhat uneven. Some great, some confusing, some overly technical.

---

<sup>1</sup>[http://wulfenite.fandm.edu/Intro\\_to\\_Chem/table\\_of\\_contents.htm](http://wulfenite.fandm.edu/Intro_to_Chem/table_of_contents.htm)

<sup>2</sup><http://hyperphysics.phy-astr.gsu.edu/hbase/hph.html>

<sup>3</sup><http://cat.middlebury.edu/~PHManual/>

<sup>4</sup><http://chemed.chem.purdue.edu/genchem/topicreview/index.html>

<sup>5</sup><http://www.compadre.org/quantum/>

<sup>6</sup><http://www.umich.edu/~chem461/>

<sup>7</sup><http://wikipedia.org>



# Notations

The below are the simplest possible descriptions of various symbols, just to help you keep reading if you do not remember/know what they stand for. Don't cite them on a math test and then blame me for your grade.

Watch it. I may have forgotten some usages of symbols. Always use common sense first in guessing what a symbol means in a given context.

· A dot might indicate

- A dot product between vectors, if in between them.
- A time derivative of a quantity, if on top of it.

And also many more prosaic things (punctuation signs, decimal points, ...).

× Multiplication symbol. May indicate

- An emphatic multiplication.
- A vectorial product between vectors.

! Might be used to indicate a factorial. Example:  $5! = 1 \times 2 \times 3 \times 4 \times 5 = 120$ .

| May indicate:

- The magnitude or absolute value of the number or vector, if enclosed between a pair of them.
- The determinant of a matrix, if enclosed between a pair of them.
- The norm of the function, if enclosed between two pairs of them.
- The end of a bra or start of a ket.
- A visual separator in inner products.

↑ Indicates the “spin up” state. Mathematically, equals the function  $\chi_+(S_z)$  which is by definition equal to 1 at  $S_z = \frac{1}{2}\hbar$  and equal to 0 at  $S_z = -\frac{1}{2}\hbar$ . A spatial wave function multiplied by ↑ is a particle in that spatial state with its spin up. For multiple particles, the spins are listed with particle 1 first.

$\downarrow$  Indicates the “spin down” state. Mathematically, equals the function  $\chi_-(S_z)$  which is by definition equal to 0 at  $S_z = \frac{1}{2}\hbar$  and equal to 1 at  $S_z = -\frac{1}{2}\hbar$ . A spatial wave function multiplied by  $\downarrow$  is a particle in that spatial state with its spin down. For multiple particles, the spins are listed with particle 1 first.

$\Sigma$  Summation symbol. Example: if in three dimensional space a vector  $\vec{f}$  has components  $f_1 = 2, f_2 = 1, f_3 = 4$ , then  $\sum_{\text{all } i} f_i$  stands for  $2 + 1 + 4 = 7$ .

$\int$  Integration symbol, the continuous version of the summation symbol. For example,

$$\int_{\text{all } x} f(x) dx$$

is the summation of  $f(x) dx$  over all little fragments  $dx$  that make up the entire  $x$ -range.

$\rightarrow$  May indicate:

- An approaching process.  $\lim_{\varepsilon \rightarrow 0}$  indicates for practical purposes the value of the expression following the  $\lim$  when  $\varepsilon$  is extremely small,  $\lim_{r \rightarrow \infty}$  the value of the following expression when  $r$  is extremely large.
- The fact that the left side leads to, or implies, the right-hand side.

$\vec{\cdot}$  Vector symbol. An arrow above a letter indicates it is a vector. A vector is a quantity that requires more than one number to be characterized. Typical vectors in physics include position  $\vec{r}$ , velocity  $\vec{v}$ , linear momentum  $\vec{p}$ , acceleration  $\vec{a}$ , force  $\vec{F}$ , angular momentum  $\vec{L}$ , etcetera.

$\hat{\cdot}$  A hat over a letter in this document indicates that it is the operator, turning functions into other functions, instead of the numerical value associated with it.

$'$  May indicate

- A derivative of a function. Examples:  $1' = 0, x' = 1, \sin'(x) = \cos(x), \cos'(x) = -\sin(x), (e^x)' = e^x$ .
- A small or modified quantity.

$\nabla$  The spatial differentiation operator nabla. In Cartesian coordinates:

$$\nabla \equiv \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) = \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z}$$

Nabla can be applied to a scalar function  $f$  in which case it gives a vector of partial derivatives called the gradient of the function:

$$\text{grad } f = \nabla f = \hat{i} \frac{\partial f}{\partial x} + \hat{j} \frac{\partial f}{\partial y} + \hat{k} \frac{\partial f}{\partial z}.$$

Nabla can be applied to a vector in a dot product multiplication, in which case it gives a scalar function called the divergence of the vector:

$$\operatorname{div} \vec{v} = \nabla \cdot \vec{v} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}$$

or in index notation

$$\operatorname{div} \vec{v} = \nabla \cdot \vec{v} = \sum_{i=1}^3 \frac{\partial v_i}{\partial x_i}$$

Nabla can also be applied to a vector in a vectorial product multiplication, in which case it gives a vector function called the curl or rot of the vector. In index notation, the  $i$ -th component of this vector is

$$(\operatorname{curl} \vec{v})_i = (\operatorname{rot} \vec{v})_i = (\nabla \times \vec{v})_i = \frac{\partial v_{\bar{i}}}{\partial x_i} - \frac{\partial v_i}{\partial x_{\bar{i}}}$$

where  $\bar{i}$  is the index following  $i$  in the sequence 123123..., and  $\bar{i}$  the one preceding it.

The operator  $\nabla^2$  is called the Laplacian. In Cartesian coordinates:

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In non Cartesian coordinates, don't guess; look these operators up in a table book.

\* A superscript star normally indicates a complex conjugate. In the complex conjugate of a number, every  $i$  is changed into a  $-i$ .

< Less than.

$\langle \dots \rangle$  May indicate:

- An inner product.
- An expectation value.

> Greater than.

[...] May indicate:

- A grouping of terms in a formula.
- A commutator. For example,  $[A, B] = AB - BA$ .

$\equiv$  Emphatic equals sign. Typically means "by definition equal" or "everywhere equal."

$\sim$  Indicates approximately equal when something is small or large. I suggest you read it as "is approximately equal to."

$\alpha$  May indicate:

- The fine structure constant,  $e^2/4\pi\epsilon_0\hbar c$ , about 1/137 in value.
- A Dirac equation matrix.
- Some constant.
- Some angle.
- An eigenfunction of a generic operator  $A$ .
- A summation index.

$\beta$  May indicate:

- Some constant.
- Some angle.
- An eigenfunction of a generic operator  $B$ .
- A summation index.

$\gamma$  May indicate:

- Gyromagnetic ratio.
- Summation index.

$\Delta$  May indicate:

- An increment in the quantity following it.
- A delta particle.
- Often used to indicate the Laplacian  $\nabla^2$ .

$\delta$  May indicate:

- With two subscripts, the “Kronecker delta”, which by definition is equal to one if its two subscripts are equal, and zero in all other cases.
- Without two subscripts, the “Dirac delta function”, which is infinite when its argument is zero, and zero if it is not. In addition the infinity is such that the integral of the delta function is unity. The delta function is not a normal function, but a distribution. It is best to think of it as the approximate function shown in the right hand side of figure 6.2 for a very, very, small positive value of  $\varepsilon$ .
- Often used to indicate a small amount of the following quantity, or of a small change in the following quantity. There are nuanced differences in the usage of  $\delta$ ,  $\partial$  and  $d$  that are too much to go in here.
- Often used to indicate a second small quantity in addition to  $\varepsilon$ .

$\partial$  Indicates a vanishingly small change or interval of the following variable. For example,  $\partial f/\partial x$  is the ratio of a vanishingly small change in function  $f$  divided by the vanishingly small change in variable  $x$  that causes this change in  $f$ . Such ratios define derivatives, in this case the partial derivative of  $f$  with respect to  $x$ .

$\epsilon$  May indicate:

- Energy level.
- Scaled energy.
- A small quantity, if symbol  $\varepsilon$  is not available.

$\epsilon_0$  Permittivity of space. Equal to  $8.85419 \cdot 10^{-12} \text{ C}^2/\text{J m}$

$\varepsilon$  The Greek symbol that is conventionally used to indicate very small quantities.

$\eta$   $y$ -position of a particle.

$\Theta$  Used in this document to indicate some function of  $\theta$  to be determined.

$\theta$  May indicate:

- In spherical coordinates, the angle from the chosen  $z$  axis, with apex at the origin.
- $z$ -position of a particle.
- A generic angle, like the one between the vectors in a cross or dot product.

$\vartheta$  An alternate symbol for  $\theta$ .

$\kappa$  A constant that physically corresponds to some wave number.

$\lambda$  May indicate:

- Some multiple of something.
- Summation index.
- Wave length.
- Scaled square momentum.
- Second azimuthal quantum number.

$\mu$  May indicate:

- Magnetic dipole moment.
- Chemical potential.
- Second magnetic quantum number.

$\xi$  May indicate:

- Scaled argument of the one-dimensional harmonic oscillator eigenfunctions.
- $x$ -position of a particle.

$\pi$  May indicate:

- The area of a circle of unit radius. Value 3.141592...
- Half the perimeter of a circle of unit radius. Value 3.141592...
- A  $180^\circ$  angle expressed in radians. Note that  $e^{\pm i\pi} = -1$ . Value 3.141592...
- A bond that looks from the side like a p state.
- A particle involved in the forces keeping the nuclei of atoms together ( $\pi$ -meson).

$\rho$  May indicate

- Electric charge per unit volume.
- Scaled radial coordinate.
- Radial coordinate.
- Eigenfunction of a rotation operator  $R$ .

$\sigma$  May indicate:

- A standard deviation of a value.
- A chemical bond that looks like an s state when seen from the side.
- Pauli spin matrix.

$\tau$  Some coefficient.

$\Phi$  May indicate:

- Some function of  $\phi$  to be determined.
- The momentum-space wave function.

$\phi$  May indicate:

- In spherical coordinates, the angle around the chosen  $z$  axis. Increasing  $\phi$  by  $2\pi$  encircles the  $z$ -axis exactly once.
- A state of a particle in a quantum system.
- An electric potential.
- A phase angle.
- Something equivalent to an angle.

$\varphi$  May indicate:

- A change in angle  $\phi$ .
- An alternate symbol for  $\phi$ .

$\chi$  May indicate:

- Spin basis function.
- Spinor component.

$\Psi$  Upper case psi is used for the wave function.

$\psi$  Lower case psi is typically used to indicate an energy eigenfunction. Depending on the system, indices may be added to distinguish different ones. In some cases  $\psi$  might be used instead of  $\Psi$  to indicate a system in an energy eigenstate. Let me know and I will change it. A system in an energy eigenstate should be written as  $\Psi = c\psi$ , not  $\psi$ , with  $c$  a constant of magnitude 1.

$\omega$  May indicate:

- Natural frequency of the classical harmonic oscillator. Equal to  $\sqrt{c/m}$  where  $c$  is the spring constant and  $m$  the mass.
- Natural frequency of a system.
- Natural frequency of light waves.
- Perturbation frequency,
- Any quantity having units of frequency, 1/s.

$A$  May indicate:

- Repeatedly used to indicate the operator for a generic physical quantity  $a$ , with eigenfunctions  $\alpha$ .
- Electromagnetic vector potential.
- Some generic matrix.
- Some constant.

$\text{\AA}$  \text{\AA}ngstrom. Equal to  $10^{-10}$  m.

$a$  May indicate:

- Repeatedly used to indicate the value of a generic physical quantity.
- Repeatedly used to indicate the amplitude of the spin-up state
- Repeatedly used to indicate the amplitude of the first state in a two-state system.
- Acceleration.
- Start point of an integration interval.
- The first of a pair of particles.
- Some coefficient.
- Some constant.

$a_0$  May indicate

- Bohr radius. Equal to 0.529177 Å. Comparable in size to atoms, and a good size to use to simplify various formulae.
- The initial value of a coefficient  $a$ .

*B* May indicate:

- Repeatedly used to indicate a generic second operator or matrix.
- Magnetic field strength.
- Some constant.

*b* May indicate:

- Repeatedly used to indicate the amplitude of the spin-down state
- Repeatedly used to indicate the amplitude of the second state in a two-state system.
- End point of an integration interval.
- The second of a pair of particles.
- Some coefficient.
- Some constant.

*C* May indicate:

- A third operator.
- A variety of different constants.

*c* May indicate:

- The speed of light, about  $2.99792 \times 10^8$  m/s.
- A variety of different constants.

**Classical** Can mean any older theory. In this work, most of the time it either means “non-quantum,” or “nonrelativistic.”

**cos** The cosine function, a periodic function oscillating between 1 and -1 as shown in [5, pp. 40-...].

*d* May indicate a variety of different constants. For example,  $d$  is used for the distance between the protons of a hydrogen molecule.

**d** Indicates a vanishingly small change or interval of the following variable. For example,  $dx$  can be thought of as a small segment of the  $x$ -axis.

**derivative** A derivative of a function is the ratio of a vanishingly small change in a function divided by the vanishingly small change in the independent variable that causes the change in the function. The derivative of  $f(x)$  with respect to  $x$  is written as  $df/dx$ , or also simply as  $f'$ . Note that the derivative of function  $f(x)$  is again a function of  $x$ : a ratio  $f'$  can be found at every point  $x$ . The derivative of a function  $f(x, y, z)$  with respect to  $x$  is written as  $\partial f/\partial x$  to indicate that there are other variables,  $y$  and  $z$ , that do not vary.

**determinant** The determinant of a square matrix  $A$  is a single number indicated by  $|A|$ . If this number is nonzero,  $A\vec{v}$  can be any vector  $\vec{w}$  for the right choice of  $\vec{v}$ . Conversely, if the determinant is zero,  $A\vec{v}$  can only produce a very limited set of vectors, though if it can produce a vector  $w$ , it can do so for multiple vectors  $\vec{v}$ .

There is a recursive algorithm that allows you to compute determinants from increasingly bigger matrices in terms of determinants of smaller matrices. For a  $1 \times 1$  matrix consisting of a single number, the determinant is simply that number:

$$|a_{11}| = a_{11}$$

(This determinant should not be confused with the absolute value of the number, which is written the same way. Since we normally do not deal with  $1 \times 1$  matrices, there is normally no confusion.) For  $2 \times 2$  matrices, the determinant can be written in terms of  $1 \times 1$  determinants:

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = +a_{11} \begin{vmatrix} a_{22} \end{vmatrix} - a_{12} \begin{vmatrix} a_{21} \end{vmatrix}$$

so the determinant is  $a_{11}a_{22} - a_{12}a_{21}$  in short. For  $3 \times 3$  matrices, we have

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = +a_{11} \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12} \begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13} \begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}$$

and we already know how to work out those  $2 \times 2$  determinants, so we now know how to do  $3 \times 3$  determinants. Written out fully:

$$a_{11}(a_{22}a_{33} - a_{23}a_{32}) - a_{12}(a_{21}a_{33} - a_{23}a_{31}) + a_{13}(a_{21}a_{32} - a_{22}a_{31})$$

For  $4 \times 4$  determinants,

$$\begin{aligned} \begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{vmatrix} &= +a_{11} \begin{vmatrix} a_{22} & a_{23} & a_{24} \\ a_{32} & a_{33} & a_{34} \\ a_{42} & a_{43} & a_{44} \end{vmatrix} - a_{12} \begin{vmatrix} a_{21} & a_{23} & a_{24} \\ a_{31} & a_{33} & a_{34} \\ a_{41} & a_{43} & a_{44} \end{vmatrix} \\ &\quad + a_{13} \begin{vmatrix} a_{21} & a_{22} & a_{24} \\ a_{31} & a_{32} & a_{34} \\ a_{41} & a_{42} & a_{44} \end{vmatrix} - a_{14} \begin{vmatrix} a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \\ a_{41} & a_{42} & a_{43} \end{vmatrix} \end{aligned}$$

Etcetera. Note the alternating sign pattern of the terms.

As you might infer from the above, computing a good size determinant takes a large amount of work. Fortunately, it is possible to simplify the matrix to put zeros in suitable locations, and that can cut down the work of finding the determinant greatly. We are allowed to use the following manipulations without seriously affecting the computed determinant:

1. We may “transpose” the matrix, i.e. change its columns into its rows.
2. We can create zeros in a row by subtracting a suitable multiple of another row.
3. We may also swap rows, as long as we remember that each time that we swap two rows, it will flip over the sign of the computed determinant.
4. We can also multiply an entire row by a constant, but that will multiply the computed determinant by the same constant.

Applying these tricks in a systematic way, called “Gaussian elimination” or “reduction to lower triangular form”, we can eliminate all matrix coefficients  $a_{ij}$  for which  $j$  is greater than  $i$ , and that makes evaluating the determinant pretty much trivial.

*E* May indicate:

- The total energy. Possible values are the eigenvalues of the Hamiltonian.
- Electric field strength.

*e* May indicate:

- The basis for the natural logarithms. Equal to 2.718281828459... This number produces the “exponential function”  $e^x$ , or  $\exp(x)$ , or in words “ $e$  to the power  $x$ ”, whose derivative with respect to  $x$  is again  $e^x$ . If  $a$  is a constant, then the derivative of  $e^{ax}$  is  $ae^{ax}$ . Also, if  $a$  is an ordinary real number, then  $e^{ia}$  is a complex number with magnitude 1.
- The magnitude of the charge of an electron or proton, equal to  $1.60218 \cdot 10^{-19}$  C.
- Often used to indicate a unit vector.

$e^{iax}$  Assuming that  $a$  is an ordinary real number, and  $x$  a real variable,  $e^{iax}$  is a complex function of magnitude one. The derivative of  $e^{iax}$  with respect to  $x$  is  $iae^{iax}$

**eV** The electron volt, a commonly used unit of energy equal to  $1.60218 \cdot 10^{-19}$  J.

**exponential function** A function of the form  $e^{\dots}$ , also written as  $\exp(\dots)$ . See function and *e*.

*F* May indicate:

- The force in Newtonian mechanics. Equal to the negative gradient of the potential. Quantum mechanics is formulated in terms of potentials, not forces.

- The anti-derivative of some function  $f$ .
- Some function.

$f$  May indicate:

- A generic function.
- A generic vector.
- A fraction.
- The resonance factor.

**function** A mathematical object that associates values with other values. A function  $f(x)$  associates every value of  $x$  with a value  $f$ . For example, the function  $f(x) = x^2$  associates  $x = 0$  with  $f = 0$ ,  $x = \frac{1}{2}$  with  $f = \frac{1}{4}$ ,  $x = 1$  with  $f = 1$ ,  $x = 2$  with  $f = 4$ ,  $x = 3$  with  $f = 9$ , and more generally, any arbitrary value of  $x$  with the square of that value  $x^2$ . Similarly, function  $f(x) = x^3$  associates any arbitrary  $x$  with its cube  $x^3$ ,  $f(x) = \sin(x)$  associates any arbitrary  $x$  with the sine of that value, etcetera. A wave function  $\Psi(x, y, z)$  associates each spatial position  $(x, y, z)$  with a wave function value.

$g$  May indicate:

- A second generic function or a second generic vector.
- The strength of gravity,  $9.81 \text{ m/s}^2$  under standard conditions on the surface of the earth.
- The g-factor, a nondimensional constant that indicates the gyromagnetic ratio relative to charge and mass.

**Gauss' Theorem** This theorem, also called divergence theorem or Gauss-Ostrogradsky theorem, says that for a continuously differentiable vector  $\vec{v}$ ,

$$\int_V \nabla \cdot \vec{v} dV = \int_S \vec{v} \cdot \vec{n} dS$$

where the first integral is over the volume of an arbitrary region and the second integral is over all the surface of that region;  $\vec{n}$  is at each point found as the unit vector that is normal to the surface at that point.

$H$  May indicate:

- The Hamiltonian, or total energy, operator. Its eigenvalues are indicated by  $E$ .
- $H_n$  stands for the  $n$ -th order Hermite polynomial.

$h$  May indicate:

- Planck's unscaled constant  $h = 2\pi\hbar$ .
- $h_n$  is a one-dimensional harmonic oscillator eigenfunction.

$\hbar$  Planck's constant, scaled, equal to  $1.05457 \cdot 10^{-34}$  Js. A measure of the uncertainty of nature in quantum mechanics. Multiply by  $2\pi$  to get his original constant.

*I* May indicate:

- Electrical current.
- Unit matrix.

*i* Typically used as a summation or generic index. Not to be confused with  $i$ .

$i$  The standard square root of minus one:  $i = \sqrt{-1}$ ,  $i^2 = -1$ ,  $1/i = -i$ ,  $i^* = -i$ .

**index notation** A more concise and powerful way of writing vector and matrix components by using a numerical index to indicate the components. For Cartesian coordinates, we might number the coordinates  $x$  as 1,  $y$  as 2, and  $z$  as 3. In that case, a sum like  $v_x + v_y + v_z$  can be more concisely written as  $\sum_i v_i$ . And a statement like  $v_x \neq 0, v_y \neq 0, v_z \neq 0$  can be more compactly written as  $v_i \neq 0$ . To really see how it simplifies the notations, have a look at the matrix entry. (And that one shows only 2 by 2 matrices. Just imagine 100 by 100 matrices.)

**iff** Emphatic “if.” Should be read as “if and only if.”

**integer** Integer numbers are the whole numbers:  $\dots, -2, -1, 0, 1, 2, 3, 4, \dots$

*J* May indicate:

- Electrical current density.
- Total angular momentum.

*j* Typically used as a summation index.

**K** The atomic states or orbitals with theoretical energy  $E_1$

*k* May indicate:

- A wave number. A wave number is a measure for how fast a periodic function oscillates with variations in spatial position.
- A summation index.

$k_B$  Boltzmann constant. Equal to  $1.38065 \cdot 10^{-23}$  J/K. Relates absolute temperature to a typical unit of heat motion energy.

**L** The atomic states or orbitals with theoretical energy  $E_2$

*L* Angular momentum.

*l* May indicate:

- The azimuthal quantum number.

- A generic summation index.

$\ell$  May indicate:

- The typical length in the harmonic oscillator problem.
- The dimensions of a solid block (with subscripts).
- A length.

**lim** Indicates the final result of an approaching process.  $\lim_{\varepsilon \rightarrow 0}$  indicates for practical purposes the value of the following expression when  $\varepsilon$  is extremely small.

**M** The atomic states or orbitals with theoretical energy  $E_3$

**M** Mirror operator.

**m** May indicate:

- Mass.
  - $m_e$  Electron mass. Equal to  $9.10938 \cdot 10^{-31}$  kg.
  - $m_p$  Proton mass. Equal to  $1.67262 \cdot 10^{-27}$  kg.
- The magnetic quantum number.
- A generic summation index or generic integer.

**matrix** A table of numbers.

As a simple example, a two-dimensional matrix  $A$  is a table of four numbers called  $a_{11}$ ,  $a_{12}$ ,  $a_{21}$ , and  $a_{22}$ :

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$$

unlike a two-dimensional (ket) vector  $\vec{v}$ , which would consist of only two numbers  $v_1$  and  $v_2$  arranged in a column:

$$\begin{pmatrix} v_1 \\ v_2 \end{pmatrix}$$

(Such a vector can be seen as a “rectangular matrix” of size  $2 \times 1$ , but let’s not get into that.)

In index notation, a matrix  $A$  is a set of numbers  $\{a_{ij}\}$  indexed by two indices. The first index  $i$  is the row number, the second index  $j$  is the column number. A matrix turns a vector  $\vec{v}$  into another vector  $\vec{w}$  according to the recipe

$$w_i = \sum_{\text{all } j} a_{ij} v_j \quad \text{for all } i$$

where  $v_j$  stands for “the  $j$ -th component of vector  $\vec{v}$ ,” and  $w_i$  for “the  $i$ -th component of vector  $\vec{w}$ .”

As an example, the product of  $A$  and  $\vec{v}$  above is by definition

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = \begin{pmatrix} a_{11}v_1 + a_{12}v_2 \\ a_{21}v_1 + a_{22}v_2 \end{pmatrix}$$

which is another two-dimensional ket vector.

Note that in matrix multiplications like the example above, in geometric terms we take dot products between the rows of the first factor and the column of the second factor.

To multiply two matrices together, just think of the columns of the second matrix as separate vectors. For example:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} = \begin{pmatrix} a_{11}b_{11} + a_{12}b_{21} & a_{11}b_{12} + a_{12}b_{22} \\ a_{21}b_{11} + a_{22}b_{21} & a_{21}b_{12} + a_{22}b_{22} \end{pmatrix}$$

which is another two-dimensional matrix. In index notation, the  $ij$  component of the product matrix has value  $\sum_k a_{ik}b_{kj}$ .

The zero matrix is like the number zero; it does not change a matrix it is added to and turns whatever it is multiplied with into zero. A zero matrix is zero everywhere. In two dimensions:

$$\begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

A unit matrix is the equivalent of the number one for matrices; it does not change the quantity it is multiplied with. A unit matrix is one on its “main diagonal” and zero elsewhere. The 2 by 2 unit matrix is:

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

More generally the coefficients,  $\{\delta_{ij}\}$ , of a unit matrix are one if  $i = j$  and zero otherwise.

**N** May indicate:

- Number of states.
- Counter for the harmonic oscillator energy levels.

**N** The atomic states or orbitals with theoretical energy  $E_4$

**n** May indicate:

- The principal quantum number for hydrogen atom energy eigenfunctions.
- A quantum number for harmonic oscillator energy eigenfunctions.
- Generic summation index over energy eigenfunctions.
- Generic summation index over other eigenfunctions.
- A generic index.

- A natural number.

and maybe some other stuff.

**natural** Natural numbers are the numbers: 1, 2, 3, 4, . . .

*P* May indicate:

- The linear momentum eigenfunction.
- A power series solution.

*p* May indicate:

- Linear momentum.
- Linear momentum in the  $x$ -direction.
- Integration variable with units of linear momentum.

**p** Energy state with orbital azimuthal quantum number  $l = 1$ .

**photon** Unit of electromagnetic radiation (which includes light, x-rays, microwaves, etcetera).

A photon has a energy  $\hbar\omega$ , where  $\omega$  is its natural frequency, and a wave length  $2\pi c/\omega$  where  $c$  is the speed of light.

$p_x$  Linear momentum in the  $x$ -direction. (In the one-dimensional cases at the end of the unsteady evolution chapter, the  $x$  subscript is omitted.) Components in the  $y$ - and  $z$ -directions are  $p_y$  and  $p_z$ . Classical Newtonian physics has  $p_x = mu$  where  $m$  is the mass and  $u$  the velocity in the  $x$ -direction. In quantum mechanics, the possible values of  $p_x$  are the eigenvalues of the operator  $\hat{p}_x$  which equals  $\hbar\partial/\partial x$ . (But which becomes canonical momentum in a magnetic field.)

*q* Charge.

*R* May indicate:

- Some function of  $r$  to be determined.
- Some function of  $(x, y, z)$  to be determined.
- $R_{nl}$  is a hydrogen radial wave function.
- Rotation operator.

*r* May be radial distance from the chosen origin of the coordinate system.

$\vec{r}$  The position vector. In Cartesian coordinates  $(x, y, z)$  or  $x\hat{i} + y\hat{j} + z\hat{k}$ . In spherical coordinates  $r\hat{r}$ .

*S* May indicate:

- Number of states per unit volume.

- Number of states at a given energy level.
- Spin angular momentum (as an alternative to using  $L$  for generic angular momentum.)

**s** Energy state with orbital azimuthal quantum number  $l = 0$ . Spherically symmetric.

**s** Spin value of a particle. Equals  $\frac{1}{2}$  for electrons, protons, and neutrons, is also half an odd natural number for other fermions, and is a nonnegative integer for bosons. It is the azimuthal quantum number  $l$  due to spin.

**sin** The sine function, a periodic function oscillating between 1 and -1 as shown in [5, pp. 40-]. Good to remember:  $\cos^2 \alpha + \sin^2 \alpha = 1$ .

**Stokes' Theorem** This theorem, first derived by Kelvin and first published by someone else I cannot recall, says that for any reasonably smoothly varying vector  $\vec{v}$ ,

$$\int_S (\nabla \times \vec{v}) \cdot d\vec{S} = \oint \vec{v} \cdot d\vec{r}$$

where the first integral is over any smooth surface  $S$  and the second integral is over the edge of that surface. How did Stokes get his name on it? He tortured his students with it, that's why!

**symmetry** Symmetries are operations under which an object does not change. For example, a human face is almost, but not completely, mirror symmetric: it looks almost the same in a mirror as when seen directly. The electrical field of a single point charge is spherically symmetric; it looks the same from whatever angle you look at it, just like a sphere does. A simple smooth glass (like a glass of water) is cylindrically symmetric; it looks the same whatever way you rotate it around its vertical axis.

**T** May indicate:

- Kinetic energy. A hat indicates the associated operator. The operator is given by the Laplacian times  $-\hbar^2/2m$ .
- Temperature.

**t** The time.

**temperature** A measure of the heat motion of the particles making up macroscopic objects. At absolute zero temperature, the particles are in the “ground state” of lowest possible energy.

**u** May indicate:

- The first velocity component in a Cartesian coordinate system.
- A complex coordinate in the derivation of spherical harmonics.

$V$  The potential energy.  $V$  is used interchangeably for the numerical values of the potential energy and for the operator that corresponds to multiplying by  $V$ . In other words,  $\hat{V}$  is simply written as  $V$ .

$v$  May indicate:

- The second velocity component in a Cartesian coordinate system.
- A complex coordinate in the derivation of spherical harmonics.

$\vec{v}$  May indicate:

- Velocity vector.
- Generic vector.
- Summation index of a lattice potential.

**vector** A list of numbers. A vector  $\vec{v}$  in index notation is a set of numbers  $\{v_i\}$  indexed by an index  $i$ . In normal three-dimensional Cartesian space,  $i$  takes the values 1, 2, and 3, making the vector a list of three numbers,  $v_1$ ,  $v_2$ , and  $v_3$ . These numbers are called the three components of  $\vec{v}$ . The list of numbers can be visualized as a column, and is then called a ket vector, or as a row, in which case it is called a bra vector. This convention indicates how multiplication should be conducted with them. A bra times a ket produces a single number, the dot product or inner product of the vectors:

$$(1, 3, 5) \begin{pmatrix} 7 \\ 11 \\ 13 \end{pmatrix} = 1 \cdot 7 + 3 \cdot 11 + 5 \cdot 13 = 105$$

To turn a ket into a bra for purposes of taking inner products, write the complex conjugates of its components as a row.

**vectorial product** An vectorial product, or cross product is a product of vectors that produces another vector. If

$$\vec{c} = \vec{a} \times \vec{b},$$

it means in index notation that the  $i$ -th component of vector  $\vec{c}$  is

$$c_i = a_{\bar{i}} b_{\bar{i}} - a_{\bar{i}} b_{\bar{i}}$$

where  $\bar{i}$  is the index following  $i$  in the sequence 123123..., and  $\bar{i}$  the one preceding it. For example,  $c_1$  will equal  $a_2 b_3 - a_3 b_2$ .

$w$  May indicate the third velocity component in a Cartesian coordinate system.

$\vec{w}$  Generic vector.

$X$  Used in this document to indicate a function of  $x$  to be determined.

$x$  May indicate:

- First coordinate in a Cartesian coordinate system.
- A generic argument of a function.
- An unknown value.

*Y* Used in this document to indicate a function of *y* to be determined.

$Y_l^m$  Spherical harmonic. Eigenfunction of both angular momentum in the *z*-direction and of total square angular momentum.

*y* May indicate:

- Second coordinate in a Cartesian coordinate system.
- A generic argument of a function.

*Z* May indicate:

- Number of particles.
- Atomic number (number of protons in the nucleus).
- Used in this document to indicate a function of *z* to be determined.

*z* May indicate:

- Third coordinate in a Cartesian coordinate system.
- A generic argument of a function.

# Index

- $F$ , 286  
 $N$ , 290  
 $T$ , 292  
 $\cdot$ , 277  
 $\times$ , 277  
 $!$ , 277  
 $|$ , 277  
 $\uparrow$ , 277  
 $\downarrow$ , 277  
 $\Sigma$ , 6  
 $\sum$ , 278  
 $\int$ , 278  
 $\rightarrow$ , 278  
 $\neg$ , 278  
 $\hat{}$ , 278  
 $'$ , 278  
 $\nabla$ , 278  
 $*$ , 279  
 $<$ , 279  
 $\langle \dots \rangle$ , 279  
 $>$ , 279  
 $[ \dots ]$ , 279  
 $\equiv$ , 279  
 $\sim$ , 279  
 $\alpha$ , 279  
 $\beta$ , 280  
 $\gamma$ , 280  
 $\Delta$ , 280  
 $\delta$ , 280  
 $\partial$ , 280  
 $\epsilon$ , 280  
 $\epsilon_0$ , 281  
 $\varepsilon$ , 281  
 $\eta$ , 281  
 $\Theta$ , 281  
 $\theta$ , 281  
 $\vartheta$ , 281  
 $\kappa$ , 281  
 $\lambda$ , 281  
 $\mu$ , 281  
 $\xi$ , 281  
 $\pi$ , 281  
 $\rho$ , 282  
 $\sigma$ , 282  
 $\tau$ , 282  
 $\Phi$ , 282  
 $\phi$ , 282  
 $\varphi$ , 282  
 $\chi$ , 282  
 $\Psi$ , 283  
 $\psi$ , 283  
 $\omega$ , 283  
 $A$ , 283  
 $\text{\AA}$ , 283  
 $a$ , 283  
 $a_0$ , 283  
absolute value, 2  
absolute zero  
    nonzero energy, 46  
acceleration  
    in quantum mechanics, 169  
Aharonov-Bohm effect, 220  
angular momentum, 55  
    definition, 55  
    eigenstate normalization factors, 203  
    ladder operators, 199  
    ladders, 199  
    possible values, 202  
    uncertainty, 61  
angular momentum commutation relations, 198  
angular momentum components, 56  
antisymmetrization for fermions, 115  
atomic number, 123

atoms  
     eigenfunctions, 124  
     eigenvalues, 124  
     ground state, 125  
     Hamiltonian, 123  
 azimuthal quantum number, 60  
  
 $B$ , 284  
 $b$ , 284  
 Balmer transitions, 68  
 band gap, 148  
 band structure  
     solids, 148  
 Bell, 107  
 binding energy  
     definition, 94  
 Bohm, 107  
 Bohr radius, 70  
 bond length  
     definition, 94  
 Born's statistical interpretation, 16  
 Born-Oppenheimer approximation, 88  
 Bose-Einstein distribution, 159  
 bosons, 106  
     statistics, 160  
 bra, 7  
  
 $C$ , 284  
 $c$ , 284  
 canonical commutation relation, 85  
 cat, Schrödinger's, 24  
 chemical bonds, 131  
     covalent pi bonds, 132  
     covalent sigma bonds, 131  
     hybridization, 134  
     ionic bonds, 136  
     polar covalent bonds, 133  
     promotion, 134  
     sp<sup>n</sup> hybridization, 134  
 classical, 284  
 Clebsch-Gordan coefficients, 207  
 coefficients of eigenfunctions  
     evaluating, 52  
     give probabilities, 23  
 collapse of the wave function, 21  
  
 commutation relation  
     canonical, 85  
 commutation relations  
     fundamental, 198  
 commutator, 82  
     definition, 84  
 commutator eigenvalue problems, 200  
 commuting operators, 82  
     common eigenfunctions, 82  
 complete set, 12  
 complex conjugate, 2  
 complex numbers, 1  
 component waves, 184  
 components of a vector, 4  
 conduction band, 148  
 conduction of electricity, 148  
 confined electrons, 137  
 confinement, 38  
     density of states, 142  
 conservation laws, 175  
 Copenhagen Interpretation, 21  
 cos, 284  
 Coulomb potential, 62  
 covalent bond  
     hydrogen molecular ion, 88  
 cross product, 293  
 curl, 279  
  
 $d$ , 284  
 $d$ , 284  
 degeneracy, 50  
 degeneracy pressure, 137  
 delta function, 180  
 density of states, 142  
 derivative, 284  
 determinant, 285  
 Dirac delta function, 180  
 Dirac equation, 213  
 Dirac notation, 14  
 div, 279  
 divergence, 279  
 divergence theorem, 287  
 dot product, 6  
  
 $E$ , 286

$e$ , [286](#)  
 effective mass  
     hydrogen atom electron, [63](#)  
 Ehrenfest's theorem, [169](#)  
 $e^{i\alpha x}$ , [286](#)  
 eigenfunction, [10](#)  
 eigenfunctions  
     angular momentum components, [56](#)  
     atoms, [124](#)  
     free electron gas, [140](#)  
     harmonic oscillator, [47](#)  
     hydrogen atom, [70](#)  
     linear momentum, [181](#)  
     position, [179](#)  
     solids, [148](#)  
     square angular momentum, [58](#)  
 eigenvalue, [10](#)  
 eigenvalue problems  
     commutator type, [200](#)  
     ladder operators, [200](#)  
 eigenvalues  
     angular momentum components, [56](#)  
     atoms, [124](#)  
     free electron gas, [140](#)  
     harmonic oscillator, [44](#)  
     hydrogen atom, [67](#)  
     linear momentum, [181](#)  
     position, [179](#)  
     solids, [148](#)  
     square angular momentum, [58](#)  
 eigenvector, [10](#)  
 Einstein  
     dice, [23](#)  
 Einstein Podolski Rosen, [108](#)  
 electric charge  
     electron and proton, [62](#)  
 electric dipole approximation, [173](#)  
 electricity  
     conduction, [148](#)  
 electromagnetic field  
     Hamiltonian, [218](#)  
     Maxwell's equations, [220](#)  
 electron  
     in magnetic field, [227](#)  
 electronegativity, [130](#)  
     atoms, [127](#)  
     energy conservation, [164](#)  
     energy spectrum  
         banded, [148](#)  
         free electron gas, [140](#)  
         harmonic oscillator, [45](#)  
         hydrogen atom, [67](#)  
         solids, [148](#)  
     energy-time uncertainty principle, [167](#)  
     EPR, [108](#)  
     Euler identity, [2](#)  
     eV, [286](#)  
     Everett, III, [242](#)  
     every possible combination, [97](#)  
     expectation value, [74](#)  
         definition, [77](#)  
         simplified expression, [78](#)  
 exponential function, [286](#)  
  
 $f$ , [287](#)  
 Fermi-Dirac distribution, [159](#)  
 fermions, [106](#)  
     statistics, [160](#)  
 Fine structure, [237](#)  
 fine structure constant, [237](#)  
 flopping frequency, [234](#)  
 forbidden transitions, [173](#)  
 force  
     in quantum mechanics, [169](#)  
 free electron gas, [137](#)  
     eigenfunctions, [140](#)  
     eigenvalues, [140](#)  
     energy spectrum, [140](#)  
     ground state, [141](#)  
     Hamiltonian, [138](#)  
 function, [4](#), [5](#), [287](#)  
 fundamental commutation relations, [198](#)  
  
 $g$ , [287](#)  
 g-factor, [227](#)  
 Gauss' theorem, [287](#)  
 generalized uncertainty relationship, [84](#)  
 grad, [278](#)  
 gradient, [278](#)  
 ground state

atoms, 125  
 free electron gas, 141  
 harmonic oscillator, 47  
 hydrogen atom, 68, 70  
 hydrogen molecular ion, 95  
 hydrogen molecule, 102, 114, 116  
 nonzero energy, 46  
 group velocity, 186  
 gyromagnetic ratio, 227

$H$ , 287  
 $h$ , 287  
 Hamiltonian, 20  
     and physical symmetry, 176  
     atoms, 123  
     electromagnetic field, 218  
     free electron gas, 138  
     gives time variation, 163  
     harmonic oscillator, 41  
         partial, 42  
     hydrogen atom, 62  
     hydrogen molecular ion, 88  
     hydrogen molecule, 98  
     in matrix form, 120  
     numbering of eigenfunctions, 20  
     one-dimensional free space, 183  
     solids, 151

harmonic oscillator  
     classical frequency, 40

harmonic oscillator, 40  
     eigenfunctions, 47  
     eigenvalues, 44  
     energy spectrum, 45  
     ground state, 47  
     Hamiltonian, 41  
     partial Hamiltonian, 42  
     particle motion, 191

$\hbar$ , 287  
 Heisenberg uncertainty principle, 17  
 Heisenberg uncertainty relationship, 85  
 Hermitian operators, 11  
 hidden variables, 23, 108  
 hidden versus nonexisting, 61  
 hybridization, 134  
 hydrogen atom, 62

    eigenfunctions, 70  
     eigenvalues, 67  
     energy spectrum, 67  
     ground state, 68, 70  
     Hamiltonian, 62  
 hydrogen bonds, 133  
 hydrogen molecular ion, 88  
     bond length, 95  
     experimental binding energy, 95  
     ground state, 95  
     Hamiltonian, 88  
     shared states, 91  
 hydrogen molecule, 98  
     binding energy, 102  
     bond length, 102  
     ground state, 102, 114, 116  
     Hamiltonian, 98

$I$ , 288  
 $i$ , 1, 288  
     inverse, 2  
 $i$  index, 4  
 $i$ , 288  
 identical particles, 115  
 iff, 8, 288  
 imaginary part, 1  
 index notation, 288  
 inner product  
     multiple variables, 14  
 inner product of functions, 7  
 inner product of vectors, 6  
 integer, 288  
 interpretation  
     interpretations, 22  
     many worlds, 242  
     orthodox, 21  
     relative state, 242  
     statistical, 21  
 ionic bonds, 136  
 ionization, 68  
 ionization energy  
     atoms, 127  
     hydrogen atom, 68

$J$ , 288

$j$ , 288  
 $K$ , 288  
 $k$ , 288  
 $k_B$ , 288  
ket, 7  
ket notation  
    spherical harmonics, 59  
    spin states, 106  
kinetic energy  
    operator, 19  
kinetic energy operator  
    in spherical coordinates, 62  
L, 288  
 $L$ , 288  
 $l$ , 288  
 $\ell$ , 289  
ladder operators  
    angular momentum, 199  
Laplacian, 279  
Larmor frequency  
    definition, 231  
Larmor precession, 233  
laser, 171  
length of a vector, 7  
light waves  
    classical, 226  
lim, 289  
linear momentum  
    classical, 17  
    eigenfunctions, 181  
    eigenvalues, 181  
    operator, 19  
localization  
    absence of, 184  
Lyman transitions, 68  
M, 289  
 $M$ , 289  
 $m$ , 289  
 $m_e$ , 289  
 $m_p$ , 289  
magnetic dipole moment, 227  
magnetic quantum number, 57  
magnitude, 2  
matrix, 9, 289  
Maxwell's equations, 220  
Maxwell-Boltzmann distribution, 159  
measurable values, 21  
measurement, 22  
momentum space wave function, 182  
N, 290  
 $n$ , 290  
nabla, 278  
natural, 291  
Newton's second law  
    in quantum mechanics, 169  
Newtonian analogy, 19  
Newtonian mechanics, 15  
    in quantum mechanics, 167  
noble gas, 126  
nonexisting versus hidden, 61  
norm of a function, 7  
normalized, 7  
normalized wave functions, 16  
nuclear magnetic resonance, 229  
observable values, 21  
one-dimensional free space  
    Hamiltonian, 183  
operators, 9  
    angular momentum components, 56  
    Hamiltonian, 20  
    kinetic energy, 19  
        in spherical coordinates, 62  
    linear momentum, 19  
    position, 19  
    potential energy, 20  
    quantum mechanics, 19  
    square angular momentum, 58  
    total energy, 20  
orthodox interpretation, 21  
orthogonal, 8  
orthonormal, 8  
 $P$ , 291  
p states, 71  
 $p$ , 291  
p-state, 291  
Paschen transitions, 68

Pauli exclusion principle, 119  
     atoms, 127  
     common phrasing, 128  
     free electron gas, 137  
 Pauli spin matrices, 211  
 permittivity of space, 62  
 photon, 291  
 physical symmetry  
     commutes with Hamiltonian, 176  
 pi bonds, 132  
 Planck formula, 69  
 Planck's constant, 19  
 pointer states, 72  
 polar bonds, 133  
 population inversion, 172  
 position  
     eigenfunctions, 179  
     eigenvalues, 179  
     operator, 19  
 possible values, 21  
 potential energy  
     operator, 20  
 principal quantum number, 65  
 probabilities  
     evaluating, 52  
     from coefficients, 23  
 probability density, 99  
 probability to find the particle, 16  
 promotion, 134  
 $p_x$ , 291  
 $q$ , 291  
 quantum dot, 39  
 quantum mechanics  
     acceleration, 169  
     force, 169  
     Newton's second law, 169  
     Newtonian mechanics, 167  
     velocity, 168  
     wave packet velocity, 186  
 quantum well, 39  
 quantum wire, 39  
 $R$ , 291  
 $r$ , 291  
      $\vec{r}$ , 291  
 Rabi flopping frequency, 234  
 random number generator, 23  
 real part, 1  
 relative state formulation, 244  
 relative state interpretation, 242  
 Relativistic effects  
     Dirac equation, 213  
 resonance factor, 234  
 rot, 279  
 $S$ , 291  
 s state, 292  
 s states, 71  
 scattering, 193  
 Schrödinger equation, 163  
     failure?, 240  
 Schrödinger's cat, 24  
 separation of variables, 41  
     for atoms, 124  
     for free electron gas, 138  
     linear momentum, 181  
     position, 179  
 shielding approximation, 124  
 sigma bonds, 131  
 sin, 292  
 singlet state, 114  
     derivation, 204  
 Slater determinants, 118  
 small perturbation theory, 149, 151  
 solids  
     band structure, 148  
     eigenfunctions, 148  
     eigenvalues, 148  
     energy spectrum, 148  
     Hamiltonian, 151  
     sp<sup>n</sup> hybridization, 134  
     spectral line broadening, 175  
     spectrum  
         hydrogen, 69  
     spherical coordinates, 56  
     spherical harmonics  
         derivation, 268  
     spin, 105  
         value, 106

$x$ - and  $y$ -eigenstates, 212  
 spin down, 106  
 spin states  
     ambiguity in sign, 271  
     axis rotation, 270  
 spin up, 106  
 spinor, 112  
 square angular momentum, 58  
     eigenfunctions, 58  
     eigenvalues, 58  
 standard deviation, 74  
     definition, 76  
     simplified expression, 78  
 states, 116  
 stationary states, 165  
 statistical interpretation, 21  
 statistical mechanics, 159  
 statistics  
     bosons, 160  
     fermions, 160  
 Stokes' theorem, 292  
 superluminal interactions, 106  
 symmetrization requirement  
     identical bosons, 115  
     identical fermions, 115  
 symmetry, 292  
  
 $t$ , 292  
 temperature, 292  
 temperatures above absolute zero, 159  
 throw the dice, 23  
 time variation  
     Hamiltonian, 163  
 total energy  
     operator, 20  
 transitions  
     hydrogen atom, 68  
 transpose of a matrix, 286  
 triplet states, 114  
     derivation, 204  
 tunneling, 194  
 two state systems  
     ground state energy, 103  
     time variation, 166  
     unsteady perturbations, 169  
  
 $u$ , 292  
 uncertainty principle  
     angular momentum, 61  
     energy, 49, 165  
     Heisenberg, 17  
     position and linear momentum, 17  
 uncertainty relationship  
     generalized, 84  
     Heisenberg, 85  
 unit matrix, 290  
  
 $V$ , 292  
 $v$ , 293  
 $\vec{v}$ , 293  
 valence band, 148  
 values  
     measurable, 21  
     observable, 21  
     possible, 21  
 variational method, 93  
 vector, 4, 293  
 vectorial product, 293  
 velocity  
     in quantum mechanics, 168  
     wave packet, 186  
 virial theorem, 167  
  
 $w$ , 293  
 $\vec{w}$ , 293  
 wave function, 15  
     multiple particles, 97  
     multiple particles with spin, 113  
     with spin, 111  
 wave packet  
     accelerated motion, 190  
     definition, 185  
     free space, 182, 190  
     harmonic oscillator, 191  
     partial reflection, 193  
     physical interpretation, 185  
     reflection, 190  
  
 $X$ , 293  
 $x$ , 293  
  
 $Y$ , 294

$y$ , 294  
 $Y_l^m$ , 294

$Z$ , 294  
 $z$ , 294  
zero matrix, 290