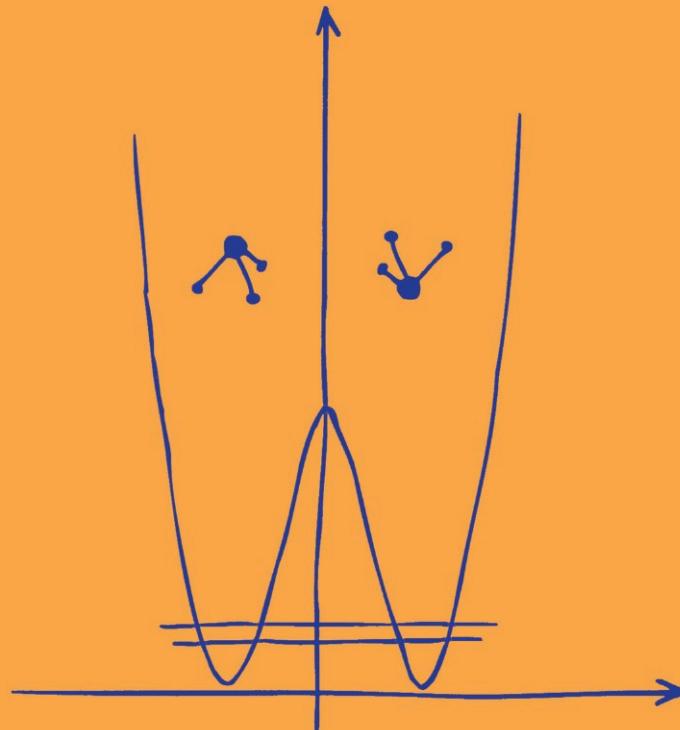


K.T. Hecht

Quantum Mechanics



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Preface

This book is an outgrowth of lectures given at the University of Michigan at various times from 1966–1996 in a first-year graduate course on quantum mechanics. It is meant to be at a fairly high level. On the one hand, it should provide future research workers with the tools required to solve real problems in the field. On the other hand, the beginning graduate courses at the University of Michigan should be self-contained. Although most of the students will have had an undergraduate course in quantum mechanics, the lectures are intended to be such that a student with no previous background in quantum mechanics (perhaps an undergraduate mathematics or engineering major) can follow the course from beginning to end.

Part I of the course, Introduction to Quantum Mechanics, thus begins with a brief background chapter on the duality of nature, which hopefully will stimulate students to take a closer look at the two references given there. These references are recommended for every serious student of quantum mechanics. Chapter 1 is followed by a review of Fourier analysis before we meet the Schrödinger equation and its interpretation. The dual purpose of the course can be seen in Chapters 4 and 5, where an introduction to simple square well problems and a first solution of the one-dimensional harmonic oscillator by Fuchsian differential equation techniques are followed by an introduction to the Bargmann transform, which gives us an elegant tool to show the completeness of the harmonic oscillator eigenfunctions and enables us to solve some challenging harmonic oscillator problems, (e.g., the case of general n for problem 11). Early chapters (7 through 12) on the eigenvalue problem are based on the coordinate representation and include detailed solutions of the spherical harmonics and radial functions of the hydrogen atom, as well as many of the soluble, one-dimensional potential problems. These chapters are based on the factorization method. It is hoped the ladder step-up and step-down

operator approach of this method will help to lead the student naturally from the Schrödinger equation approach to the more modern algebraic techniques of quantum mechanics, which are introduced in Chapters 13 to 19. The full Dirac bra, ket notation is introduced in Chapter 13. These chapters also give the full algebraic approach to the general angular momentum problem, $\text{SO}(3)$ or $\text{SU}(2)$, the harmonic oscillator algebra, and the $\text{SO}(2,1)$ algebra. The solution for the latter is given in problem 23, which is used in considerable detail in later chapters. The problems often amplify the material of the course.

Part II of the course, Chapters 20 to 26, on time-independent perturbation theory, is based on Fermi's view that most of the important problems of quantum mechanics can be solved by perturbative techniques. This part of the course shows how various types of degeneracies can be handled in perturbation theory, particularly the case in which a degeneracy is not removed in lowest order of perturbation theory so that the lowest order perturbations do not lead naturally to the symmetry-adapted basis; a case ignored in many books on quantum mechanics and perhaps particularly important in the case of accidental near-degeneracies. Chapters 25 and 26 deal with magnetic-field perturbations, including a short section on the Aharonov–Bohm effect, and a treatment on fine structure and Zeeman perturbations in one-electron atoms.

Part III of the course, Chapters 27 to 35, then gives a detailed treatment of angular momentum and angular momentum coupling theory, including a derivation of the matrix elements of the general rotation operator, Chapter 29; spherical tensor operators, Chapter 31; the Wigner–Eckart theorem, Chapter 32; angular momentum recoupling coefficients and their use in matrix elements of coupled tensor operators in an angular-momentum-coupled basis, Chapter 34; as well as the use of an $\text{SO}(2,1)$ algebra and the stretched Coulombic basis and its power in hydrogenic perturbation theory without the use of the infinite sum and continuum integral contributions of the conventional hydrogenic basis, Chapter 35.

Since the full set of chapters is perhaps too much for a one-year course, some chapters or sections, and, in particular, some mathematical appendices, are marked in the table of contents with an asterisk (*). This symbol designates that the chapter can be skipped in a first reading without loss of continuity for the reader. Chapters 34 and 35 are such chapters with asterisks. Because of their importance, however, an alternative is to skip Chapters 36 and 37 on the WKB approximation. These chapters are therefore placed at this point in the book, although they might well have been placed in Part II on perturbation theory.

Part IV of the lectures, Chapters 38 to 40, gives a first introduction to systems of identical particles, with the emphasis on the two-electron atom and a chapter on variational techniques.

Parts I through IV of the course deal with bound-state problems. Part V on scattering theory, which might constitute the beginning of a second semester, begins the treatment of continuum problems with Chapters 41 through 56 on scattering theory, including a treatment of inelastic scattering processes and rearrangement collisions, and the spin dependence of scattering cross sections. The polarization

of particle beams and the scattering of particles with spin are used to introduce density matrices and statistical distributions of states.

Part VI of the course gives a conventional introduction to time-dependent perturbation theory, including a chapter on magnetic resonance and an application of the sudden and adiabatic approximations in the reversal of magnetic fields.

Part VII on atom-photon interactions includes an expansion of the quantized radiation field in terms of the full set of vector spherical harmonics, leading to a detailed derivation of the general electric and magnetic multipole-transition matrix elements needed in applications to nuclear transitions, in particular.

Parts V through IX may again be too much material for the second semester of a one-year course. At the University of Michigan, curriculum committees have at various times insisted that the first-year graduate course include *either* an introduction to Dirac theory of relativistic spin $\frac{1}{2}$ -particles *or* an introduction to many-body theory. Part VIII of the course on relativistic quantum mechanics, Chapters 69 through 77, and Part IX, an introduction to many-body theory, Chapters 78 and 79, are therefore written so that a lecturer could choose *either* Part VIII *or* Part IX to complete the course.

The problems are meant to be an integral part of the course. They are often meant to build on the material of the lectures and to be real problems (rather than small exercises, perhaps to derive specific equations). They are, therefore, meant to take considerable time and often to be somewhat of a challenge. In the actual course, they are meant to be discussed in detail in problem sessions. For this reason, detailed solutions for a few key problems, particularly in the first part of the course, are given in the text as part of the course (e.g., the results of problem 23 are very much used in later chapters, and problem 34, actually a very simple problem in perturbation theory is used to illustrate how various types of degeneracies can be handled properly in perturbation theory in a case in which the underlying symmetry leading to the degeneracy *might not* be easy to recognize). In the case of problem 34, the underlying symmetry *is* easy to recognize. The solution therefore also shows how this symmetry should be exploited.

The problems are not assigned to specific chapters, but numbered 1 through 55 for Parts I through IV of the course, and, again, 1 through 51 for Parts V through IX, the second semester of the course. They are placed at the point in the course where the student should be ready for a particular set of problems.

The applications and assigned problems of these lectures are taken largely from the fields of atomic and molecular physics and from nuclear physics, with a few examples from other fields. This selection, of course, shows my own research interests, but I believe, is also because these fields are fertile for the applications of nonrelativistic quantum mechanics.

I first of all want to acknowledge my own teachers. I consider myself extremely fortunate to have learned the subject from David M. Dennison and George E. Uhlenbeck. Among the older textbooks used in the development of these lectures, I acknowledge the books by Leonard I. Schiff, *Quantum Mechanics*, McGraw-Hill, 1949; Albert Messiah, *Quantum Mechanics, Vol. I and II*, John Wiley and Sons, 1965; Eugene Merzbacher, *Quantum Mechanics*, John Wiley and Sons, 1961; Kurt

Gottfried, *Quantum Mechanics*, W. A. Benjamin, Inc., 1966; and L. D. Landau and E. M. Lifshitz, *Quantum Mechanics. Nonrelativistic Theory. Vol. 3. Course of Theoretical Physics*, Pergamon Press 1958. Hopefully, the good features of these books have found their way into my lectures.

References to specific books, chapters of books, or research articles are given throughout the lectures wherever they seemed to be particularly useful or relevant. Certainly, no attempt is made to give a complete referencing. Each lecturer in a course on quantum mechanics must give the student his own list of the many textbooks a student should consult. The serious student of the subject, however, must become familiar with the two classics: P. A. M. Dirac, *The Principles of Quantum Mechanics*, Oxford University Press, first ed. 1930; and Wolfgang Pauli, *General Principles of Quantum Mechanics*, Springer-Verlag, 1980, (an English translation of the 1933 Handbuch der Physik article in Vol. 24 of the Handbuch).

Finally, I want to thank the many students at the University of Michigan who have contributed to these lectures with their questions. In fact, it was the encouragement of former students of this course that has led to the idea these lectures should be converted into book form. I also thank Prof. Yasuyuki Suzuki for his many suggestions after a careful reading of an early version of the manuscript. Particular thanks are due to Dr. Sudha Swaminathan and Dr. Frank Lamelas for their great efforts in making all of the figures.

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Introduction to Quantum Mechanics

1

Background: The Duality of Nature

(Good references for this chapter on the historical background are the article by Niels Bohr, entitled “Discussions with Einstein. Epistemological Problems in Atomic Physics.” In *Albert Einstein. Philosopher-Scientist*. Vol. VII of Library of Living Philosophers, Paul A. Schilpp, ed., Evanston, Illinois, 1949; and the little book by Werner Heisenberg, *The Physical Principles of the Quantum Theory*, Dover Publications, 1949.)

The results of the experimental developments of the late nineteenth and early twentieth century led us to a picture of nature that showed the *duality* of nature on the atomic scale. *Both* material particles and electromagnetic radiation show *both* particle-like and wave-like aspects. However, particles can be localized in space-time. In classical physics, x, y, z, t for a particle can be specified exactly. Particles are also indivisible. Half an electron, or a fractional part of an electron, does not exist. On the other hand, waves *cannot* be localized. They must be somewhat extended in space-time to give a meaning to wavelength, λ , and frequency, ν . Waves are always divisible. Partial reflection and transmission of a wave at an interface between two media can exist.

This duality poses a real dilemma: The particle picture seems incompatible with that of waves, in particular, the interference effects. Yet, it is precisely the interference effects that determine λ and ν , which via the deBroglie relation, $p = h/\lambda$, and the Bohr relation, $E = \hbar\nu$, determine the dynamical attributes of the particle.

A The Young Double Slit Experiment

To illustrate the paradoxical situation, consider the classical interference experiment of the Young double slit. We could think either of light waves, electromagnetic radiation, or of matter waves, electron deBroglie waves, going through the double slit arrangement.

The incident beam can be made so weak that, on average, only one photon (or electron) at a time will pass through the apparatus and be incident on the photographic plate. Because only one photon at a time goes through the apparatus, the possibility of interference between different photons is eliminated. An interference pattern will still be on the photographic plate, however. Clearly, a photon that has reached the photographic plate must have passed through *either* slit 1 *or* slit 2. Imagine it was slit 1; then, if slit 2 had been closed, no interference pattern would have occurred. Hence, the seemingly terrible paradox that the behavior of the photon is influenced by the presence of a slit, through which it cannot have passed.

The resolution of the paradox rests on the fact that the classical causal space-time description of nature which rests on the “clear-cut separability between the phenomena and the means of observing these phenomena,” does not apply. On the atomic scale, an “uncontrollable interaction between the object and the measuring instrument” exists. (The words in quotation marks are those of Niels Bohr.) As a result, the above experiment can be set up in either of two “complementary” ways; as above, and as shown in Fig. 1.1, to exhibit the interference fringes but in a setup that makes it impossible to answer experimentally the question: “Through which slit did the photon pass?”. Alternatively, we could alter the experimental setup to answer experimentally the question: “Through which slit did the photon pass?” In setting up the experiment in this second way, however, we have lost the possibility of a precise wavelength measurement through the interference pattern. The interference pattern will have been wiped out.

Because our knowledge of phenomena on the atomic scale is restricted, a wave-field must be associated with the particle motion. For any wavefield, an uncertainty relation exists connecting position and wavelength; $\Delta k \Delta x \approx 2\pi$, where $k = 2\pi/\lambda$. This relation follows from straightforward Fourier analysis of a wave packet of finite extent in space. Now, with the deBroglie relation, $p = h/\lambda$, this leads to $\Delta p \Delta x \approx h$, the Heisenberg uncertainty relation.

B More Detailed Analysis of the Double Slit Experiment

In region I, to the left of the single slit (see Fig. 1.1), we assume we have a plane wave effectively of infinite extent in the y direction and proceeding in the x direction. Then, in region I, $p_y = 0$; i. e., p_y is known precisely, so $\Delta p_y = 0$;

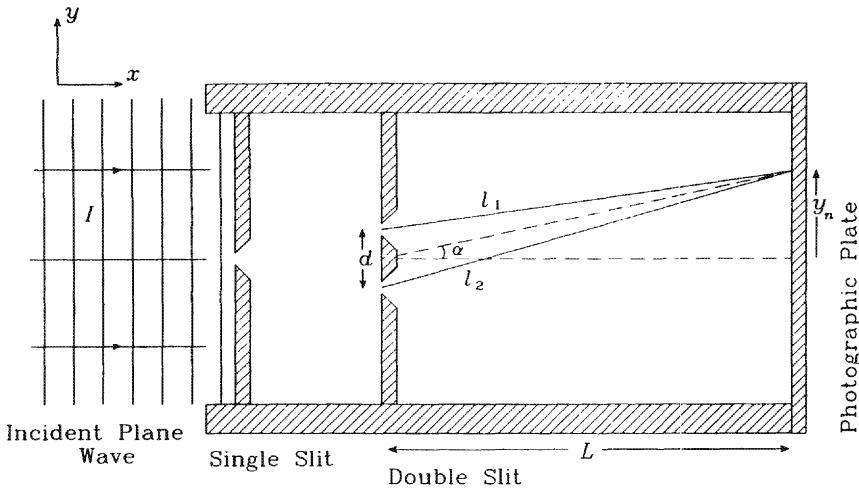


FIGURE 1.1. Conventional double slit experimental setup. Rigidly fixed slits.

now, we have no knowledge of where the photon is located in space, $\Delta y = \infty$. The y position of the particle is completely uncertain.

At the position of the double slit (with massive, rigidly fixed slits bolted to massive apparatus; see the figures in the article by Bohr), no experimental means of determining through which slit the photon is passing exist. It must go through either of the two slits. Hence, at this x -position, $\Delta y \approx d$. In its passage through one of the slits, the photon will interact with the slit jaw, which is massive, bolted firmly to a huge apparatus, and it can absorb recoil momentum without moving. Most of the photons end up within the first few bright fringes near the central maximum. We cannot predict which fringe, however. Let us assume the photon ends up in the n^{th} bright fringe, where n is a small integer. Then, the change in p_y at the double slit position is

$$\Delta p_y \approx p\alpha = \frac{h}{\lambda}\alpha \approx \frac{h}{\lambda} \frac{y_n}{L}. \quad (1)$$

Note

$$\begin{aligned} l_1^2 &= (\frac{1}{2}d - y_n)^2 + L^2 \\ l_2^2 &= (\frac{1}{2}d + y_n)^2 + L^2, \end{aligned} \quad (2)$$

so

$$l_2^2 - l_1^2 = 2y_n d \approx (l_2 - l_1)2L, \quad (3)$$

and

$$\frac{y_n}{L} = \frac{(l_2 - l_1)}{d} = \frac{n\lambda}{d}. \quad (4)$$

Therefore, at the x-position of the double slit, with $\Delta y \approx d$,

$$\Delta y \Delta p_y \approx d \frac{h}{\lambda} \frac{y_n}{L} = d \frac{h n \lambda}{\lambda d} = nh, \quad (5)$$

where the uncertainty in the y-component of the momentum at the position of the double slit must be of the same order of magnitude as the change of y-component of momentum of a photon that ends up at the interference maximum given by a relatively small integer, n . Thus, at the double slit,

$$\Delta p_y \Delta y \approx nh, \quad (6)$$

where n is a relatively small number.

C Complementary Experimental Setup

The question now arises: Could we have modified the experimental setup at the x-position of the double slit to narrow the uncertainty in y at this x-position? In particular, could we have modified the experimental setup to answer experimentally the question: Through which slit did the photon pass? We could do this by making the slit jaws movable, so the momentum exchange between photon and slit jaw could be detected. Bohr imagines the very light slit jaws being suspended from springs, so the photon will jiggle the slit as it goes through the slit opening. (See Fig. 1.2, drawn in the style of the Bohr article.) Imagine the photon ends up at the position where the central interference maximum would have occurred in the conventional double slit experiment, (with the apparatus of Fig. 1.1, that is, at the most likely final position of the photon for the experimental setup of Fig. 1.1). Then,

$$p_{y_{\text{final}}} - p_{y_{\text{initial}}} \approx p \times \theta = \frac{h}{\lambda} \times \frac{d}{2L} = \frac{h}{\lambda} \times \frac{\lambda}{2(y_1 - y_0)} = \frac{h}{2(y_1 - y_0)}, \quad (7)$$

where $(y_1 - y_0)$ is the distance between the first and zeroth (central) bright fringe in the interference pattern of the conventional experimental setup. This actual change in the photon's momentum at the position of the slits would now lead to a recoil in the slit jaws, which can be detected. An uncertainty will still exist in the y-position of the photon as it passes through the slit, because of this jiggling of the slit; even though our jiggle detectors can tell us through which slit the photon has passed (so $\Delta y \ll d$). Now, let us use the uncertainty relation to determine the best possible Δy caused by the jiggling of the slit,

$$\Delta y \approx \frac{h}{\Delta p_y} \approx \frac{h \times 2(y_1 - y_0)}{h} = 2(y_1 - y_0). \quad (8)$$

That is, Δy is of the order of the distance between bright fringes in the conventional double slit setup. This Δy , however, is now due to the jiggling of the slit. If the slit jiggles on average by an amount equal to the distance between interference fringes, the interference pattern on the photographic plate will surely be washed out

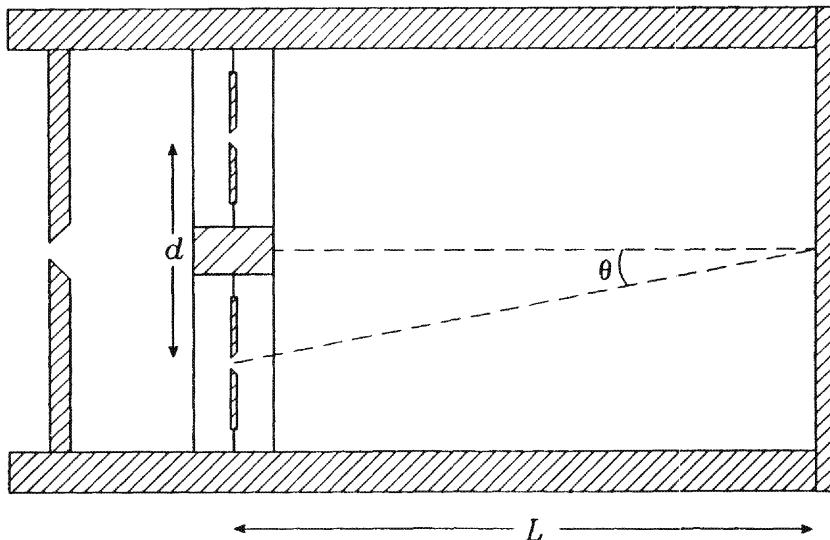


FIGURE 1.2. Complementary double slit experimental setup. Movable slits.

completely. In answering experimentally the question through which slit did the photon pass, we have by altering the experimental setup destroyed those features of the setup that previously made the precise wavelength measurement possible. This illustrates Bohr's complementarity principle. We can set up the double slit experiment to get very precise wavelength (hence, momentum) information about the photon. In this case, we cannot make a position measurement of the photon precise enough to tell us through which slit the photon passed. Alternatively, if we use the complementary experimental setup, which can answer this question about the position of the photon experimentally, we cannot determine the wavelength (hence, momentum) of the photon with sufficient accuracy.

Because we can have only partial position and partial momentum information about a photon or a material particle on the atomic scale, it becomes natural to associate a wave packet with the motion of the particle (either photon or material particle). A wave packet can give us partial position and wavelength (or wave-number k) information through the wave packet relation, $\Delta k_y \Delta y \approx 2\pi$, which follows from the Fourier analysis of the wave packet, the subject of the next chapter.

2

The Motion of Wave Packets: Fourier Analysis

Because we will need to work with wave packets of finite extent, it will be very useful to first give a brief review of Fourier analysis.

A Fourier Series

We shall start by studying periodic functions of infinite extent in space. First consider periodic functions $f(x)$ with a periodicity interval 2π , such that $f(x + 2\pi) = f(x)$. For real functions $f(x)$, we usually use Fourier expansions in cosine and sine functions. For the complex functions of quantum theory, it will be advantageous to use a Fourier expansion in exponential functions.

1. Fourier Expansion:

$$f(x) = \sum_{n=-\infty}^{\infty} a_n e^{inx}, \quad (1)$$

where we will exploit the orthogonality of the exponential functions.

2. Orthogonality:

$$\int_{-\pi}^{\pi} dx' e^{i(n-m)x'} = 2\pi \delta_{nm}, \quad (2)$$

which is expressed in terms of the usual Kronecker delta. With this orthogonality relation, the expansion coefficients, a_n , can be determined via the Fourier inversion theorem. If we multiply $f(x)$ by the complex conjugate of a specific exponential, say, e^{-imx} , with some specific, fixed m , and integrate both sides of the resultant

equation over the periodicity interval, say, from $-\pi$ to $+\pi$, the orthogonality property will pick out one specific a_m , with value given by the Fourier coefficients.

3. Fourier coefficients:

$$a_m = \frac{1}{2\pi} \int_{-\pi}^{\pi} dx' f(x') e^{-imx'}. \quad (3)$$

Substituting this coefficient back into the Fourier expansion, we get the

4. Fourier expression for $f(x)$:

$$f(x) = \sum_{n=-\infty}^{\infty} \frac{1}{2\pi} \int_{-\pi}^{\pi} dx' f(x') e^{in(x-x')}. \quad (4)$$

It will be convenient to introduce orthonormal functions, $\phi_n(x)$,

$$\phi_n(x) = \frac{1}{\sqrt{2\pi}} e^{inx}. \quad (5)$$

The four basic Fourier equations can then be rewritten as

$$f(x) = \sum_{n=-\infty}^{\infty} b_n \phi_n(x), \quad (6)$$

$$\int_{-\pi}^{\pi} dx' \phi_n^*(x') \phi_m(x') = \delta_{nm}, \quad (7)$$

$$b_n = \int_{-\pi}^{\pi} dx' f(x') \phi_n^*(x'), \quad (8)$$

$$f(x) = \sum_{n=-\infty}^{\infty} \int_{-\pi}^{\pi} dx' f(x') \phi_n(x) \phi_n^*(x'). \quad (9)$$

Finally, it will be convenient to use a periodicity interval of length $(2l)$, where l has the dimension of a length, where now $f(x + 2l) = f(x)$ and the orthonormal functions can be expressed as

$$\frac{1}{\sqrt{2l}} e^{\frac{inx}{l}}.$$

The four basic Fourier equations can then be rewritten as

$$f(x) = \sum_{n=-\infty}^{\infty} c_n \frac{1}{\sqrt{2l}} e^{\frac{inx}{l}}, \quad (10)$$

$$\frac{1}{2l} \int_{-l}^{+l} dx' e^{i(n-m)\frac{\pi x'}{l}} = \delta_{nm}, \quad (11)$$

$$c_n = \frac{1}{\sqrt{2l}} \int_{-l}^{+l} dx' f(x') e^{-i\frac{n\pi x'}{l}}, \quad (12)$$

$$f(x) = \frac{1}{2l} \sum_{n=-\infty}^{\infty} \int_{-l}^{+l} dx' f(x') e^{i \frac{n\pi}{l}(x-x')}.$$
 (13)

It will now be useful to introduce the wavenumber, k_n

$$k_n = \frac{n\pi}{l} = \frac{2\pi}{\lambda_n}; \quad \text{with} \quad \lambda_n = \frac{2l}{n},$$
 (14)

so $\phi_n(x) = \frac{1}{\sqrt{2l}} e^{ik_n x}$. This relation will be particularly useful in making the transition from the Fourier series to the Fourier integral for a wave packet of finite extent.

B Fourier Integrals

Now suppose the repeating function, with periodicity interval ($2l$), has the form of a wave packet of extent $\sim a$, with $a < l$, which repeats from $-\infty$ to $+\infty$, as shown in Fig. 2.1. Now, suppose we let $l \rightarrow \infty$, keeping the wave packet unchanged, with a fixed. Then, by taking the limit $l \rightarrow \infty$, provided $f(x) \rightarrow 0$ sufficiently rapidly as $x \rightarrow \pm\infty$, we can make the transition from a periodic function to a nonperiodic one, i.e., a transition from an infinite wave train to a wave packet of finite extent in space. As $l \rightarrow \infty$, the spectrum of possible k_n goes from a discrete spectrum to a continuous one, because

$$k_{n+1} - k_n = \frac{\pi}{l} \rightarrow 0 \quad \text{as} \quad l \rightarrow \infty.$$
 (15)

Because the number of spectral terms in a k -space interval dk is (see Fig. 2.2)

$$\frac{dk}{(\text{interval between successive } k_n)} = \frac{dk}{\pi/l},$$

the discrete sum over n in the Fourier series goes over to a continuous integral

$$\sum_{n=-\infty}^{\infty} \rightarrow \int_{-\infty}^{\infty} \frac{dk}{\pi/l}.$$

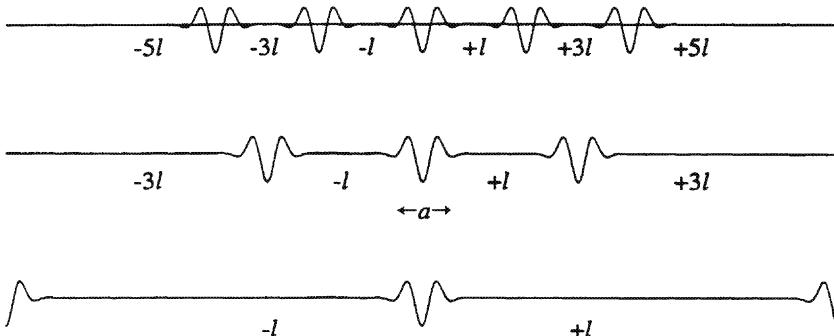


FIGURE 2.1. Periodic wave form, $l \rightarrow \infty$, a fixed.

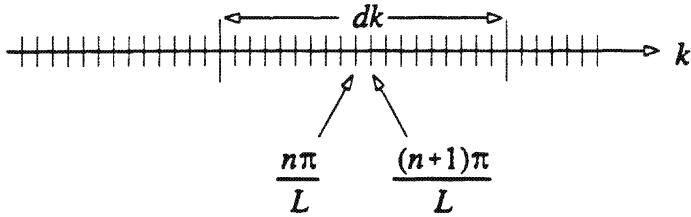


FIGURE 2.2. The spectrum of k values, $k_n = n\pi/L$. The number of spectral terms in the dk interval $= \left[dk/\frac{\pi}{L} \right]$.

Thus, the Fourier expression for $f(x)$ becomes

$$f(x) = \frac{1}{2l\pi} \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dx' f(x') e^{ik(x-x')}.$$
 (16)

We can then think of the Fourier development in terms of a Fourier amplitude function, $g(k)$, as

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk g(k) e^{ikx},$$
 (17)

with amplitude function $g(k)$, the so-called Fourier transform of $f(x)$, given by

$$g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx' f(x') e^{-ikx'}.$$
 (18)

Note, however, the orthonormality integral becomes divergent when $k = k'$,

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} dx' e^{ix'(k-k')} = \delta(k - k').$$
 (19)

The Kronecker delta becomes a Dirac delta function.

C The Dirac Delta Function

If we rewrite the Fourier series in terms of a limit of a sum over a finite number of terms,

$$f(x) = \lim_{N \rightarrow \infty} \int_{-\pi}^{\pi} dx' f(x') \sum_{n=-N}^{+N} \phi_n(x) \phi_n^*(x');$$
 (20)

or, similarly, if we rewrite the Fourier integral as

$$f(x) = \lim_{k_0 \rightarrow \infty} \int_{-\infty}^{\infty} dx' f(x') \frac{1}{2\pi} \int_{-k_0}^{k_0} dk e^{ik(x-x')},$$
 (21)

the function

$$K(x, x') = \sum_{n=-N}^{+N} \phi_n(x) \phi_n^*(x') \quad \text{or} \quad K(x, x') = \frac{1}{2\pi} \int_{-k_0}^{+k_0} dk e^{ik(x-x')} \quad (22)$$

becomes, in the limit of large N or large k_0 , a function strongly peaked at $x = x'$ with oscillations of very small amplitude for $x \neq x'$. Keeping in mind that the real limiting processes should be those expressed by eqs. (20) and (21), physicists blithely interchange the infinite sum or the infinite k -integral with the x' -integral, through the definition of the Dirac delta “function”

$$\begin{aligned} \sum_{n=-\infty}^{\infty} \phi_n(x) \phi_n^*(x') &= \delta(x - x') \\ \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{ik(x-x')} &= \delta(x - x'), \end{aligned} \quad (23)$$

where the Dirac delta “function” is not at all a function in the mathematician’s sense. It is what mathematicians call a “distribution” (see, e.g., an appendix in Vol. I of the books by Messiah). The Dirac delta function “picks out” the value $x' = x$ for the function being integrated. It has meaning only through the integrals. By itself, it diverges at the value $x' = x$. The Dirac delta function is defined through the following properties:

$$\delta(x - x') = 0 \quad \text{for} \quad x' \neq x. \quad (24)$$

For $x' = x$, the Dirac delta function becomes ∞ in such a way that

$$\int_a^b dx' \delta(x - x') = 1, \quad \text{if } x' = x \text{ is in the interval } (a, b), \quad (25)$$

and

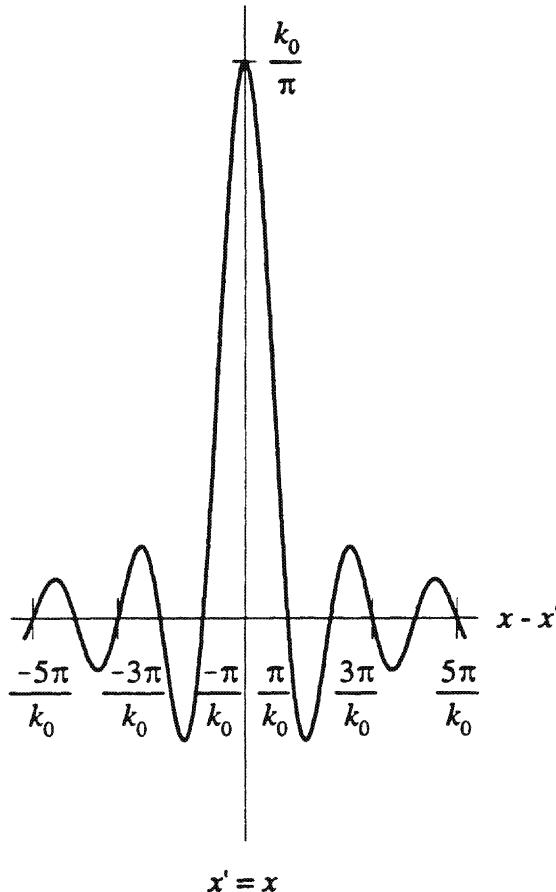
$$\int_{-\infty}^{\infty} dx' f(x') \delta(x - x') = f(x). \quad (26)$$

Our limiting process, given through eq. (21), e.g., would give

$$\delta(x - x') = \lim_{k_0 \rightarrow \infty} \frac{1}{2\pi} \int_{-k_0}^{k_0} dk e^{ik(x-x')} = \lim_{k_0 \rightarrow \infty} \frac{\sin k_0(x - x')}{\pi(x - x')}. \quad (27)$$

See Fig. 2.3 for a plot of this diffraction-like peaked function for finite k_0 . This representation of the Dirac delta function is not, however, unique. Another example (of the infinite number of possibilities) would be

$$\delta(x - x') = \frac{1}{\pi} \lim_{\epsilon \rightarrow 0} \frac{\epsilon}{[(x - x')^2 + \epsilon^2]}. \quad (28)$$

FIGURE 2.3. The function $\frac{\sin[k_0(x-x')]}{\pi(x-x')}$.

D Properties of the Dirac Delta Function

The Dirac delta function is an even function of its argument

$$\delta(-x) = \delta(x). \quad (29)$$

Other properties, such as

$$x \frac{d}{dx} \delta(x) = -\delta(x), \quad (30)$$

follow by integration by parts, because delta function relations have meaning only through their applications within integrals

$$\int_a^b dx x \delta'(x) = \left[x \delta(x) \right]_a^b - \int_a^b dx \delta(x) = - \int_a^b dx \delta(x). \quad (31)$$

If a is a real number,

$$\delta(ax) = \frac{1}{|a|} \delta(x). \quad (32)$$

Note the absolute value sign follows from

$$\int_{-\infty}^{\infty} dx \delta(ax) = \frac{1}{a} \int_{-\infty}^{\infty} d(ax) \delta(ax) = \pm \frac{1}{a} \int_{-\infty}^{\infty} dx' \delta(x'), \quad (33)$$

where the upper sign applies for $a > 0$ and the lower sign applies for $a < 0$, because the change of variable $ax = x'$ interchanges the limits in this latter case. If the variable in the delta function is itself a function of x ,

$$\delta(\phi(x)) = \sum_n \frac{1}{\left| \left(\frac{d\phi}{dx} \right)_{x_n} \right|} \delta(x - x_n), \quad (34)$$

where the x_n are the zeros of the function, $\phi(x)$, and the sum is a sum over all such zeros. As a very specific example,

$$\delta(x^2 - a^2) = \frac{1}{2|a|} [\delta(x - a) + \delta(x + a)]. \quad (35)$$

E Fourier Integrals in Three Dimensions

It is straightforward to generalize the Fourier series and Fourier integrals to functions in our three-dimensional (3-D) space, $f(x, y, z)$. For a 3-D wave packet,

$$f(x, y, z) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y \int_{-\infty}^{\infty} dk_z \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \\ \times \int_{-\infty}^{\infty} dz' f(x', y', z') e^{i[k_x(x-x') + k_y(y-y') + k_z(z-z')]} \quad (36)$$

It will be useful to introduce the following shorthand notation for this Fourier integral expression

$$f(\vec{r}) = \frac{1}{(2\pi)^3} \int d\vec{k} \int d\vec{r}' f(\vec{r}') e^{i\vec{k} \cdot (\vec{r} - \vec{r}')}, \quad (37)$$

where

$$f(\vec{r}) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int d\vec{k} g(\vec{k}) e^{i\vec{k} \cdot \vec{r}}, \quad (38)$$

$$g(\vec{k}) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int d\vec{r}' f(\vec{r}') e^{-i\vec{k} \cdot \vec{r}'} \quad (39)$$

(Note, in particular, the symbol, $d\vec{r}$, when it follows an integral sign, is merely a shorthand notation for $d\vec{r} \equiv dx dy dz$ and the single integral sign preceding $d\vec{r}$ is shorthand for a triple integral over all of 3-D space.)

F The Operation $\frac{1}{i} \frac{\partial}{\partial x}$

We note

$$\frac{1}{i} \frac{\partial}{\partial x} f(\vec{r}) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int d\vec{k} g(\vec{k}) k_x e^{i(\vec{k} \cdot \vec{r})}. \quad (40)$$

Thus, we see, if $g(\vec{k})$ is the Fourier transform of $f(\vec{r})$, $\vec{k}g(\vec{k})$ is the Fourier transform of $\frac{1}{i} \vec{\nabla} f(\vec{r})$, similarly, $-(\vec{k} \cdot \vec{k})g(\vec{k})$ is the Fourier transform of $\nabla^2 f(x, y, z)$, and so on.

G Wave Packets

A plane scalar wave propagating in the direction of the \vec{k} vector can be given by the scalar function

$$\psi(\vec{r}, t) = A e^{i(\vec{k} \cdot \vec{r} - \omega t)}, \quad (41)$$

with constant amplitude, A , where the circular frequency, ω , is in general related to \vec{k} through the dispersion law

$$\omega = f(\vec{k}), \quad \text{or} \quad \omega = f(k), \quad \text{with} \quad k = |\vec{k}|, \quad (42)$$

where the latter is valid for an isotropic medium. Moreover, in a nondispersive medium, in vacuum, e.g., $\omega = ck$.

To go from this infinite wave train to a wave packet of finite extent in space, we need to form the wave packet from a superposition of amplitudes with different \vec{k} -values. For a 3-D wave packet,

$$\psi(\vec{r}, t) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int d\vec{k} A(\vec{k}) e^{i(\vec{k} \cdot \vec{r} - \omega t)}. \quad (43)$$

To simplify the discussion, assume the wave packet proceeds in one dimension only, say, the x -direction. Then,

$$\psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk A(k) e^{i(kx - \omega t)}. \quad (44)$$

To use a very simple example, assume $A(k)$ is different from zero only in an interval, $k_0 - \frac{1}{2}\Delta k \leq k \leq k_0 + \frac{1}{2}\Delta k$, and moreover, assume $A(k)$ has the constant value, A , in this k -space interval. If the interval Δk is not too large, we can expand $\omega(k)$ about k_0 , and retain only the dominant terms,

$$\omega(k) = \omega(k_0) + (k - k_0) \left(\frac{d\omega}{dk} \right)_0 + \dots, \quad (45)$$

and the wave function can be written as

$$\psi(x, t) = \frac{A}{\sqrt{2\pi}} e^{i[k_0 x - \omega(k_0)t]} \int_{k_0 - \frac{1}{2}\Delta k}^{k_0 + \frac{1}{2}\Delta k} dk e^{i(k - k_0)[x - (\frac{d\omega}{dk})_0 t]}$$

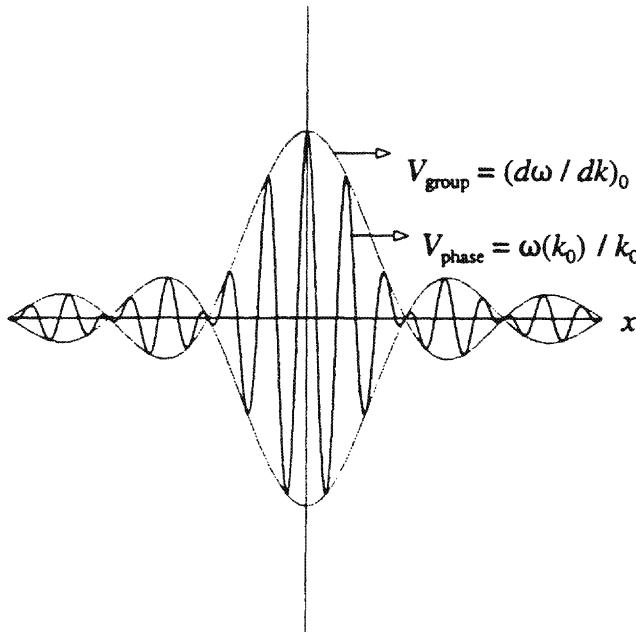


FIGURE 2.4. The wave packet of eq. (46).

$$= \sqrt{\frac{2}{\pi}} A e^{i[k_0 x - \omega(k_0)t]} \frac{\sin\left(\frac{\Delta k}{2} [x - (\frac{d\omega}{dk})_0 t]\right)}{[x - (\frac{d\omega}{dk})_0 t]}. \quad (46)$$

This wave packet is shown in Fig. 2.4. We note, in particular, the individual wavelets travel with the phase velocity

$$v_{\text{phase}} = \frac{\omega(k_0)}{k_0}. \quad (47)$$

The wave train itself, the envelope of the packet, however, travels with the group velocity

$$v_{\text{group}} = \left(\frac{d\omega}{dk} \right)_0. \quad (48)$$

If we assume most of the energy of the wave train lies in the large central peak of the wave envelope, we can take the extent of the wave packet to be $\Delta x \approx 2 \frac{2\pi}{\Delta k}$. Even for more sophisticated functions, $A(k)$, we will find the Fourier integral analysis always gives

$$\Delta x \Delta k \approx 2\pi, \quad (49)$$

neglecting factors of order 2 in this approximation. This is the uncertainty relation for a wave packet. Note, in particular, it follows for all wave packets, merely from the Fourier analysis.

H Propagation of Wave Packets: The Wave Equation

The wave equation, the propagation law for the wave, is intimately related to the dispersion law

$$\omega = f(k). \quad (50)$$

In one dimension, with

$$\psi(x, t) = \frac{1}{\sqrt{2\pi}} \int dk A(k) e^{i(kx - \omega t)}, \quad (51)$$

$$-\frac{1}{i} \frac{\partial}{\partial t} \psi = \frac{1}{\sqrt{2\pi}} \int dk \omega A(k) e^{i(kx - \omega t)}, \quad (52)$$

$$\left(\frac{1}{i}\right)^n \frac{\partial^n}{\partial x^n} \psi = \frac{1}{\sqrt{2\pi}} \int dk k^n A(k) e^{i(kx - \omega t)}. \quad (53)$$

For functions $f(k)$ that can be given by Taylor expansions,

$$f(k) = \sum_{n=0} \alpha_n k^n,$$

we then have

$$f\left(\frac{1}{i} \frac{\partial}{\partial x}\right) \psi = \frac{1}{\sqrt{2\pi}} \int dk f(k) A(k) e^{i(kx - \omega t)}. \quad (54)$$

Eqs. (52) and (54) then lead to

$$\left[-\frac{1}{i} \frac{\partial}{\partial t} - f\left(\frac{1}{i} \frac{\partial}{\partial x}\right)\right] \psi = \frac{1}{\sqrt{2\pi}} \int dk [\omega - f(k)] A(k) e^{i(kx - \omega t)} = 0, \quad (55)$$

so the dispersion law, $\omega = f(k)$, leads to the wave equation

$$\left[-\frac{1}{i} \frac{\partial}{\partial t} - f\left(\frac{1}{i} \frac{\partial}{\partial x}\right)\right] \psi = 0. \quad (56)$$

For the special case of a nondispersive medium, with $\omega = ck$, we would have

$$-\frac{1}{i} \frac{\partial \psi}{\partial t} - \frac{c}{i} \frac{\partial \psi}{\partial x} = \int dk [\omega - ck] A(k) e^{i(kx - \omega t)} = 0. \quad (57)$$

So that, seemingly, the wave equation in this simple case of a nondispersive medium becomes

$$\frac{1}{c} \frac{\partial \psi}{\partial t} + \frac{\partial \psi}{\partial x} = 0. \quad (58)$$

This equation looks like a strange wave equation, however. Its solutions would be $\psi(x, t) = F(x - ct)$, where F is any arbitrary function. That is, this wave equation would permit wave propagation only in the positive x -direction and, hence, would correspond to a nonisotropic medium. The difficulty here is not with our method of arriving at the wave equation, but that we have written the dispersion law in a

way that builds in this anisotropy. For a nondispersive, isotropic medium, we have to express the dispersion law in the form

$$\omega^2 - c^2 k^2 = 0, \quad (59)$$

or in three dimensions

$$\omega^2 - c^2(k_x^2 + k_y^2 + k_z^2) = 0. \quad (60)$$

The technique we have used to arrive at the wave equation would then give us

$$\frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2} - \frac{\partial^2 \psi}{\partial x^2} = 0 \quad (61)$$

in one dimension, and

$$\frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2} - \nabla^2 \psi = 0 \quad (62)$$

in three dimensions.

Note, finally, our method of arriving at the wave equation from the dispersion law is not a derivation of the wave equation. Our method may also not give a unique expression for the wave equation.

3

The Schrödinger Wave Equation and Probability Interpretation

A The Wave Equation

With the Bohr relation for the energy, $E = \hbar\omega$, and the deBroglie relation for the momentum vector, $\vec{p} = \hbar\vec{k}$, we see the dispersion relation for waves, $\omega = f(\vec{k})$, goes over to a relation between energy and momentum. For a conservative system, this relation can be expressed through $E = H(\vec{p}, \vec{r})$, where H is the Hamiltonian function. In particular, for a free, nonrelativistic particle, of mass m , this “dispersion relation” becomes

$$E = \frac{(\vec{p} \cdot \vec{p})}{2m}. \quad (1)$$

Now, convert our wave packet expansion from an expansion in \vec{k} to one in \vec{p}

$$\Psi(\vec{r}, t) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int d\vec{p} A(\vec{p}) e^{\frac{i}{\hbar}(\vec{p} \cdot \vec{r} - Et)}, \quad (2)$$

so

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int d\vec{p} E A(\vec{p}) e^{\frac{i}{\hbar}(\vec{p} \cdot \vec{r} - Et)}, \quad (3)$$

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int d\vec{p} \frac{(\vec{p} \cdot \vec{p})}{2m} A(\vec{p}) e^{\frac{i}{\hbar}(\vec{p} \cdot \vec{r} - Et)}. \quad (4)$$

As a result, we get

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} + \frac{\hbar^2}{2m} \nabla^2 \Psi = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int d\vec{p} \left[E - \frac{(\vec{p} \cdot \vec{p})}{2m} \right] e^{\frac{i}{\hbar}(\vec{p} \cdot \vec{r} - Et)} = 0, \quad (5)$$

and the relation between E and \vec{p} leads us to the wave equation for a free particle, the Schrödinger equation for a free particle,

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t). \quad (6)$$

The group velocity of a wave packet now becomes

$$\vec{v}_{\text{group}} = \frac{d\omega}{dk} = \frac{dE}{d\vec{p}} = \frac{\vec{p}}{m} = \vec{v}_{\text{particle}}. \quad (7)$$

The uncertainty relations for waves go over to the Heisenberg uncertainty relations

$$\begin{aligned} \Delta k_x \Delta x &\approx 2\pi & \rightarrow & \Delta p_x \Delta x \approx \hbar \\ \Delta k_y \Delta y &\approx 2\pi & \rightarrow & \Delta p_y \Delta y \approx \hbar \\ \Delta k_z \Delta z &\approx 2\pi & \rightarrow & \Delta p_z \Delta z \approx \hbar. \end{aligned} \quad (8)$$

For a particle subject to a conservative force derivable from a potential $V(x, y, z)$, with

$$E = H(\vec{p}, \vec{r}) = \frac{(\vec{p} \cdot \vec{p})}{2m} + V(x, y, z), \quad (9)$$

this relation between E and \vec{p} gives the wave equation

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V(x, y, z) \Psi. \quad (10)$$

Finally, we end with a remark about relativistic wave equations. The relation between energy and momentum for a relativistic particle, of rest mass m_0 ,

$$\frac{E^2}{c^2} - p^2 = m_0^2 c^2, \quad (11)$$

would lead us to a wave equation both second order in time and space derivatives, and again involving a single wave function $\Psi(\vec{r}, t)$. (See Problem 2). This equation leads to the so-called Klein–Gordon equation. An alternative solution for the relativistic wave equation was given by Dirac, whose wave equation is first order in both time and space derivatives. Essentially, it comes from the square root of the above dispersion relation and, therefore, leads to both positive and negative energy solutions. It is based not on a single Ψ , but on a number of ψ_α , actually, with $\alpha = 1, \dots, 4$. We shall come back to the Dirac equation near the end of the book.

B The Probability Axioms

To use the Schrödinger wave equation, we need to understand the physical meaning of the wave function, Ψ . We begin with a few remarks:

1. The particle and the wavefield are equally real. (The wavefield is not a ghost field guiding the particle.) Both are pictures in the human mind to account for physical reality; both, however, have their limitations.

2. In practice, the wavefield is used in the following way: The result of a certain experiment lets us represent the particle motion by a wave packet at a certain time. The wave equation is then used to predict how the experiment evolves in time.

3. Because of the uncontrollable interaction of object and measuring instrument, we are led to a probability description.

The probability of finding a particle within a volume element $dxdydz$ about a point x, y, z at a time t , will be given by

$$W(x, y, z; t) dxdydz,$$

where $W(x, y, z; t)$ is a probability density. This probability density must satisfy certain sensibility restrictions; i.e., $W(x, y, z; t)$ must be a sensible probability density:

$$W \geq 0. \quad (12)$$

A negative probability density makes no sense. To make W patently positive, it makes sense to let the probability density be given by

$$W(\vec{r}; t) = \Psi^* \Psi. \quad (13)$$

Note, in optics or electromagnetism, physically measurable quantities, such as energy or intensity, are proportional to the square of the amplitude of the wave, or if the amplitude can be complex to the absolute value squared. Also,

$$\frac{d}{dt} \int_{\text{all space}} d\vec{r} W(\vec{r}, t) = 0. \quad (14)$$

The probability of finding the particle somewhere is independent of time. In non-relativistic quantum mechanics, we are building a theory of indestructible particles. Also,

$$\int_{\text{all space}} d\vec{r} W \text{ is Galilean invariant.} \quad (15)$$

All observers agree one particle exists somewhere.

The conservation of probability leads to a continuity equation. Because Ψ can be complex, the Schrödinger equation is really two equations

$$\begin{aligned} -\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} &= -\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi \\ + \frac{\hbar}{i} \frac{\partial \Psi^*}{\partial t} &= -\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V \Psi^*. \end{aligned} \quad (16)$$

Multiplying the first of these equations by $-\Psi^*$, the second equation by Ψ , and adding the two resultant equations, assuming also the potential function is real, we get

$$\frac{\hbar}{i} \frac{\partial}{\partial t} (\Psi^* \Psi) = \frac{\hbar^2}{2m} \operatorname{div}(\Psi^* \vec{\nabla} \Psi - \Psi \vec{\nabla} \Psi^*). \quad (17)$$

This relation has the form of a continuity equation

$$\frac{\partial W}{\partial t} + \operatorname{div} \vec{S} = 0, \quad (18)$$

if we choose

$$\vec{S} = \frac{\hbar}{2mi} (\Psi^* \vec{\nabla} \Psi - \Psi \vec{\nabla} \Psi^*), \quad (19)$$

where this equation must be interpreted as a probability density current; i.e., as the probability per second per unit area normal to the direction of \vec{S} that the particle be streaming in the direction of \vec{S} . The integral form of the continuity equation could be written as

$$\frac{d}{dt} \int_{\text{Vol.}} d\vec{r} \Psi^* \Psi + \int_{\text{Surf.}} dA (\vec{S} \cdot \vec{n}) = 0, \quad (20)$$

where the volume integral is over a finite volume and the surface integral is over the surface surrounding this finite volume, dA being an element of surface area and \vec{n} being the outward normal to the surface. In integral form, this equation says: The time rate of change of probability of finding the particle within the finite volume must be the negative of the probability of the net outflow of the particle. If we let the volume grow to include all of our 3-D space and if we assume Ψ and $\Psi^* \rightarrow 0$ sufficiently fast as a function of r as the surface recedes to infinity, the surface integral will go to zero and our second probability restriction is satisfied.

Finally, examine the Galilean invariance. Suppose observers in a primed reference frame are moving with velocity, v , parallel to the x -direction. Then,

$$x = x' + vt', \quad y = y', \quad z = z', \quad t = t', \quad (21)$$

with

$$\frac{\partial}{\partial t'} = 1 \frac{\partial}{\partial t} + v \frac{\partial}{\partial x}, \quad \frac{\partial}{\partial x'} = 1 \frac{\partial}{\partial x} + 0 \frac{\partial}{\partial t}, \quad \frac{\partial}{\partial y'} = \frac{\partial}{\partial y}, \quad \frac{\partial}{\partial z'} = \frac{\partial}{\partial z}. \quad (22)$$

In addition, the wave function must also change under the Galilean transformation, according to

$$\Psi'(x', y', z'; t') = \Psi(x, y, z; t) e^{-\frac{i}{\hbar}(mvx - \frac{1}{2}mv^2t)}. \quad (23)$$

Comparing the Schrödinger equations in the primed and unprimed frames, we are led to

$$W' = W; \quad \vec{S}' = \vec{S} - \vec{v} \Psi^* \Psi. \quad (24)$$

If observers in the unprimed frame see no streaming of probability to right or left, $(\vec{S}) = 0$, observers in the primed frame will see a streaming to the left, as they should because a particle in a region with $W \neq 0$ will appear to be moving in the direction of $-\vec{v}$ to an observer in the primed frame.

A final remark: If Ψ is real everywhere, \vec{S} is zero everywhere; then, no transport of probability exists. A probability density with a real Ψ corresponds to a situation in which particles will stream in the $+x$ and $-x$ directions with equal probability.

Note, we need complex Ψ 's to describe beams of particles streaming toward or away from a target.

C The Calculation of Average Values of Dynamical Quantities

On the atomic scale, we cannot give an exact orbit description, e.g., $x(t)$, for the motion of a particle. We can, however, give the probability theory average value of dynamical variables, such as x , as functions of the time. Define this average or expectation value of x through

$$\langle x \rangle = \int d\vec{r} x \Psi^*(\vec{r}, t)\Psi(\vec{r}, t); \quad (25)$$

or, similarly,

$$\langle x^n \rangle = \int d\vec{r} x^n \Psi^*(\vec{r}, t)\Psi(\vec{r}, t). \quad (26)$$

The question then arises, how do we define the corresponding expectation value of a momentum component, $\langle p_x \rangle$? It will be convenient to define a momentum space probability density, so the probability of finding a particle in the momentum range $dp_x dp_y dp_z$ about some value p_x, p_y, p_z is given by

$$\phi^*(\vec{p}, t)\phi(\vec{p}, t)dp_x dp_y dp_z,$$

so

$$\langle p_x \rangle = \int d\vec{p} p_x \phi^*(\vec{p}, t)\phi(\vec{p}, t), \quad (27)$$

where $\phi(\vec{p}, t)$ is the Fourier transform of $\Psi(\vec{r}, t)$. Comparing with eq. (2), and letting $\phi(\vec{p}, t) = A(\vec{p})e^{-\frac{i}{\hbar}E't}$,

$$\phi(\vec{p}, t) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int d\vec{r}' \Psi(\vec{r}', t) e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}'}, \quad (28)$$

$$\Psi(\vec{r}, t) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int d\vec{p} \phi(\vec{p}, t) e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}, \quad (29)$$

$$\Psi(\vec{r}, t) = \frac{1}{(2\pi\hbar)^3} \int d\vec{p} \int d\vec{r}' \Psi(\vec{r}', t) e^{\frac{i}{\hbar}\vec{p}\cdot(\vec{r}-\vec{r}')}. \quad (30)$$

Note

$$\begin{aligned} \int d\vec{p} \phi^*(\vec{p}, t)\phi(\vec{p}, t) &= \frac{1}{(2\pi\hbar)^3} \int d\vec{p} \int d\vec{r} \Psi^*(\vec{r}, t) \int d\vec{r}' \Psi(\vec{r}', t) e^{\frac{i}{\hbar}\vec{p}\cdot(\vec{r}-\vec{r}')} \\ &= \int d\vec{r} \Psi^*(\vec{r}, t) \underline{\Psi(\vec{r}, t)}, \end{aligned} \quad (31)$$

where the underlined quantities in the first line of this equation give $\Psi(\vec{r}, t)$ via the use of eq. (30). This relation between $\Psi(\vec{r}, t)$ and its Fourier transform $\phi(\vec{p}, t)$ is known as Parseval's theorem. Note, the probability of finding the particle *somewhere*, with *some* momentum, is equal to 1 for a theory of one particle.

The same type of Fourier transformation can also be used to express the expectation value $\langle p_x \rangle$ in terms of a space rather than a momentum integral

$$\begin{aligned}\langle p_x \rangle &= \int d\vec{p} p_x \phi^*(\vec{p}, t) \phi(\vec{p}, t) \\ &= \frac{1}{(2\pi\hbar)^3} \int d\vec{p} \int d\vec{r} \Psi^*(\vec{r}, t) p_x \int d\vec{r}' \Psi(\vec{r}', t) e^{\frac{i}{\hbar} \vec{p} \cdot (\vec{r} - \vec{r}')} \\ &= \frac{1}{(2\pi\hbar)^3} \int d\vec{p} \int d\vec{r} \Psi^*(\vec{r}, t) \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \int d\vec{r}' \Psi(\vec{r}', t) e^{\frac{i}{\hbar} \vec{p} \cdot (\vec{r} - \vec{r}')} \right) \\ &= \int d\vec{r} \Psi^*(\vec{r}, t) \frac{\hbar}{i} \frac{\partial}{\partial x} \underline{\Psi(\vec{r}, t)},\end{aligned}\quad (32)$$

so $\langle p_x \rangle$ can also be evaluated through

$$\langle p_x \rangle = \int d\vec{r} \Psi^*(\vec{r}, t) \frac{\hbar}{i} \left(\frac{\partial}{\partial x} \Psi(\vec{r}, t) \right). \quad (33)$$

Similarly,

$$\langle p_x^2 \rangle = \int d\vec{r} \Psi^*(\vec{r}, t) \left(-\hbar^2 \frac{\partial^2}{\partial x^2} \Psi(\vec{r}, t) \right). \quad (34)$$

Finally, by the same technique, we could express $\langle x \rangle$ in terms of momentum rather than space integrals

$$\langle x \rangle = \int d\vec{p} \phi^*(\vec{p}, t) i\hbar \left(\frac{\partial}{\partial p_x} \phi(\vec{p}, t) \right). \quad (35)$$

D Precise Statement of the Uncertainty Principle

Now that we have defined $\langle x \rangle$, $\langle x^2 \rangle$, and so on precisely in terms of the probability densities, we can formulate the Heisenberg uncertainty principle more precisely. Taking the usual statistical definition of the uncertainty, Δx ,

$$\begin{aligned}(\Delta x)^2 &= \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - 2\langle x \rangle \langle x \rangle + \langle x \rangle^2 \\ &= \langle x^2 \rangle - \langle x \rangle^2,\end{aligned}\quad (36)$$

and, similarly, for Δp_x . The precise statement of the Heisenberg uncertainty principle is then

$$\begin{aligned}\Delta p_x \Delta x &\geq \frac{1}{2}\hbar \\ \Delta p_y \Delta y &\geq \frac{1}{2}\hbar \\ \Delta p_z \Delta z &\geq \frac{1}{2}\hbar.\end{aligned}\quad (37)$$

For simplicity, give a derivation only for one-dimensional (1-D) motion and consider the motion to be in the x-direction. To prove the uncertainty relation, consider

the following integral, a function of a real parameter λ ,

$$I(\lambda) \equiv \int_{-\infty}^{\infty} dx \left| (x - \langle x \rangle)\Psi + i\lambda \left(\frac{\hbar}{i} \frac{\partial \Psi}{\partial x} - \langle p_x \rangle \Psi \right) \right|^2. \quad (38)$$

Note, through its definition, $I(\lambda) \geq 0$. Writing out all of the terms

$$\begin{aligned} I(\lambda) = & \int_{-\infty}^{\infty} dx \Psi^* (x - \langle x \rangle)^2 \Psi \\ & + \lambda \hbar \int_{-\infty}^{\infty} dx (\Psi^* \frac{\partial \Psi}{\partial x} + \Psi \frac{\partial \Psi^*}{\partial x}) (x - \langle x \rangle) \\ & + \lambda^2 \hbar^2 \int_{-\infty}^{\infty} dx \frac{\partial \Psi^*}{\partial x} \frac{\partial \Psi}{\partial x} \\ & + \lambda^2 \langle p_x \rangle \frac{\hbar}{i} \int_{-\infty}^{\infty} dx \left[\Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x} \right] \\ & + \lambda^2 \langle p_x \rangle^2 \int_{-\infty}^{\infty} dx \Psi^* \Psi. \end{aligned} \quad (39)$$

Now, note term (2) (in the second line) can be rewritten

$$\int_{-\infty}^{\infty} dx \frac{\partial(\Psi^* \Psi)}{\partial x} (x - \langle x \rangle) = \left[(x - \langle x \rangle) \Psi^* \Psi \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} dx \Psi^* \Psi = -1, \quad (40)$$

where we have assumed $\Psi \rightarrow 0$ sufficiently fast as $x \rightarrow \pm\infty$, so the integrated term is zero. Similarly, term (3) can be rewritten as

$$\hbar^2 \int_{-\infty}^{\infty} dx \frac{\partial \Psi^*}{\partial x} \frac{\partial \Psi}{\partial x} = \hbar^2 \left[\Psi^* \frac{\partial \Psi}{\partial x} \right]_{-\infty}^{\infty} + \int_{-\infty}^{\infty} dx \Psi^* \left(-\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} \right) = \langle p_x^2 \rangle. \quad (41)$$

Finally, in term (4), rewrite

$$\frac{\hbar}{i} \int_{-\infty}^{\infty} dx \frac{\partial \Psi^*}{\partial x} \Psi = \frac{\hbar}{i} \left[\Psi^* \Psi \right]_{-\infty}^{\infty} - \int dx \Psi^* \frac{\hbar}{i} \frac{\partial \Psi}{\partial x} = -\langle p_x \rangle, \quad (42)$$

so the full expression of term (4) can be rewritten as $-2\langle p_x \rangle^2$. Putting together all of the terms, we then get

$$I(\lambda) = (\Delta x)^2 - \hbar \lambda + (\Delta p_x)^2 \lambda^2 \geq 0. \quad (43)$$

With $I(\lambda) = a\lambda^2 + b\lambda + c$, the requirement, $I(\lambda) \geq 0$, is met if $b^2 - 4ac \leq 0$. Thus, $\hbar^2 - 4(\Delta x)^2(\Delta p_x)^2 \leq 0$, and, therefore,

$$\Delta p_x \Delta x \geq \frac{1}{2}\hbar. \quad (44)$$

Thus, in the most favorable wave packet, the so-called minimum wave packet, we can have the minimum uncertainty, $\frac{1}{2}\hbar$. We shall see later this is true for a Gaussian wave packet.

E Ehrenfest's Theorem: Equations of Motion

Classically, the Hamiltonian for a single particle of mass m ,

$$H = \frac{\vec{p}^2}{2m} + V(x, y, z), \quad (45)$$

leads to the equations of motion

$$\frac{dx}{dt} = \frac{\partial H}{\partial p_x}; \quad \frac{dp_x}{dt} = -\frac{\partial H}{\partial x} = -\frac{\partial V}{\partial x}. \quad (46)$$

Quantum mechanically the velocity of the particle no longer has a precise meaning, but we can ask: How does the expectation value of x change with time? Calculate $\frac{d\langle x \rangle}{dt}$:

$$\frac{d\langle x \rangle}{dt} = \int d\vec{r} x \frac{\partial}{\partial t} (\Psi^*(\vec{r}, t)\Psi(\vec{r}, t)). \quad (47)$$

(Note, in particular, the quantity x in the integrand is not a function of the time. It is merely the dummy integration variable, which weights the time-dependent function $\Psi^*\Psi$. It says we must weight all values of x from $-\infty$ to $+\infty$ with x and the probability density function to obtain $\langle x \rangle$.) Using the continuity equation, we can rewrite this as

$$\begin{aligned} \frac{d\langle x \rangle}{dt} &= - \int d\vec{r} x \operatorname{div} \vec{S} = - \int d\vec{r} x \left(\frac{\partial S_x}{\partial x} + \frac{\partial S_y}{\partial y} + \frac{\partial S_z}{\partial z} \right) \\ &= - \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz [x S_x]_{x=-\infty}^{\infty} - \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dz [x S_y]_{y=-\infty}^{\infty} \\ &\quad - \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy [x S_z]_{z=-\infty}^{\infty} + \int d\vec{r} S_x \\ &= \frac{\hbar}{2mi} \int d\vec{r} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right) \\ &= \frac{1}{m} \int d\vec{r} \Psi^* \left(\frac{\hbar}{i} \frac{\partial \Psi}{\partial x} \right) = \frac{1}{m} \langle p_x \rangle, \end{aligned} \quad (48)$$

where all integrated terms disappear, and we have done one more integration by parts on the $\Psi^* \frac{\partial \Psi}{\partial x}$ term in the last step. Therefore, we see

$$\frac{d\langle x \rangle}{dt} = \frac{1}{m} \langle p_x \rangle, \quad (49)$$

which is the first equation of motion, provided we replace x and p_x by their expectation values $\langle x \rangle$ and $\langle p_x \rangle$. In exactly the same fashion,

$$\begin{aligned} \frac{d\langle p_x \rangle}{dt} &= \frac{d}{dt} \int d\vec{r} \Psi^* \frac{\hbar}{i} \frac{\partial \Psi}{\partial x} \\ &= \int d\vec{r} \left(\frac{\hbar}{i} \frac{\partial \Psi^*}{\partial t} \right) \left(\frac{\partial \Psi}{\partial x} \right) + \int d\vec{r} \Psi^* \frac{\hbar}{i} \left(\frac{\partial^2 \Psi}{\partial t \partial x} \right) \\ &= \int d\vec{r} \left(\frac{\hbar}{i} \frac{\partial \Psi^*}{\partial t} \right) \left(\frac{\partial \Psi}{\partial x} \right) + \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{\hbar}{i} \Psi^* \frac{\partial \Psi}{\partial t} \Big|_{x=-\infty}^{\infty} \end{aligned}$$

$$\begin{aligned}
& + \int d\vec{r} \frac{\partial \Psi^*}{\partial x} \left(-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} \right) \\
& = -\frac{\hbar^2}{2m} \int d\vec{r} \left[\nabla^2 \Psi^* \frac{\partial \Psi}{\partial x} + \frac{\partial \Psi^*}{\partial x} \nabla^2 \Psi \right] + \int d\vec{r} \left[\Psi^* V \frac{\partial \Psi}{\partial x} + \frac{\partial \Psi^*}{\partial x} V \Psi \right] \\
& = -\frac{\hbar^2}{2m} [0] + \int d\vec{r} V \frac{\partial(\Psi^* \Psi)}{\partial x} \\
& = \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \Psi^* \Psi V \Big|_{x=-\infty}^{\infty} - \int d\vec{r} \Psi^* \Psi \left(\frac{\partial V}{\partial x} \right), \tag{50}
\end{aligned}$$

where the term with ∇^2 operators disappears via integrations by parts, similarly to the integrated terms shown explicitly. Thus,

$$\frac{d\langle p_x \rangle}{dt} = - < \left(\frac{\partial V}{\partial x} \right) >, \tag{51}$$

which is the quantum-mechanical analogue of the second classical equation of motion, where again the classical quantities, p_x , and, $\frac{\partial V}{\partial x}$, have been replaced with their quantum-mechanical expectation values.

F Operational Calculus, The Linear Operators of Quantum Mechanics, Hilbert Space

In the last few sections, we have met many operators acting on the Schrödinger Ψ . In this section, we want to make a more systematic study of the linear operators of quantum theory. The operator, O , is a command. Acting on a function, it produces another function, $(O\Psi(x))$. Examples include $O = f(x)$. Acting on the function $\Psi(x)$, it produces the new function, $f(x)\Psi(x)$. The command is: Multiply the old function by $f(x)$. The second common example is the operator $\frac{d}{dx}$. When acting on the function Ψ , it produces the new function

$$\frac{d\Psi(x)}{dx}.$$

The operators of quantum theory are linear operators. When acting on functions $\Psi(x)$, which are linear combinations of functions, $\Psi(x) = \lambda_1\Psi_1(x) + \lambda_2\Psi_2(x)$, where λ_1 and λ_2 are arbitrary complex numbers, the linear operator O yields

$$(O\Psi(x)) = \lambda_1(O\Psi_1(x)) + \lambda_2(O\Psi_2(x)). \tag{52}$$

Another type of operator is the parity or space-inversion operator, P . It is the command: Change x to $-x$, y to $-y$, and z to $-z$ in the function on which it acts

$$P\Psi(x, y, z) = \Psi(-x, -y, -z).$$

Products of operators are operators acting in succession on our functions:

$$O_2 O_1 \Psi = O_2(O_1 \Psi).$$

Because we deal with wave functions and operators acting on wave functions, we need to define the function space on which the operators act. The wave functions of quantum mechanics are square-integrable in coordinate space.

$$\int d\vec{r} \Psi^* \Psi = \text{finite}. \quad (53)$$

The space of all square-integrable functions is known as a Hilbert space. It will be useful to define a Scalar Product of the functions Φ and Ψ by

$$\int d\vec{r} \Phi^* \Psi = \langle \Phi, \Psi \rangle. \quad (54)$$

The functions Φ and Ψ are said to be orthogonal to each other if $\langle \Phi, \Psi \rangle = 0$. Note, the scalar product has the property

$$\langle \Phi, \Psi \rangle = \langle \Psi, \Phi \rangle^*. \quad (55)$$

Note also, the scalar product is linear in Ψ ,

$$\langle \Phi, \lambda_1 \Psi_1 + \lambda_2 \Psi_2 \rangle = \lambda_1 \langle \Phi, \Psi_1 \rangle + \lambda_2 \langle \Phi, \Psi_2 \rangle, \quad (56)$$

but is antilinear in Φ ,

$$\langle \lambda_1 \Phi_1 + \lambda_2 \Phi_2, \Psi \rangle = \lambda_1^* \langle \Phi_1, \Psi \rangle + \lambda_2^* \langle \Phi_2, \Psi \rangle. \quad (57)$$

Eq. (56) follows from the linear character of the unit operator.

An important concept is the Adjoint of an Operator, written as O^\dagger .

$$\int d\vec{r} \Phi^* (O \Psi) = \int d\vec{r} (O^\dagger \Phi)^* \Psi \quad (58)$$

for any arbitrary pair of functions Φ and Ψ of our function space.

A Hermitian Operator, O , is a self-adjoint operator. If

$$O = O^\dagger, \quad \text{then } O \text{ is hermitian.} \quad (59)$$

Note, the operator

$$\frac{d}{dx} \quad \text{is not hermitian,}$$

but the operator

$$\frac{\hbar}{i} \frac{d}{dx} \quad \text{is hermitian,}$$

because

$$\begin{aligned} \int d\vec{r} \Psi^* \left(\frac{\hbar}{i} \frac{d\Phi}{dx} \right) &= \frac{\hbar}{i} \int \int dy dz \Psi^* \Phi \Big|_{x=-\infty}^{\infty} - \frac{\hbar}{i} \int d\vec{r} \frac{d\Psi^*}{dx} \Phi \\ &= \int d\vec{r} \left(\frac{\hbar}{i} \frac{d\Psi}{dx} \right)^* \Phi, \end{aligned} \quad (60)$$

where the integrated term must be zero for square-integrable functions, Ψ and Φ . Note also, the operator $\frac{\hbar}{i} \frac{\partial}{\partial x}$ is the momentum operator, p_x , when acting on a

function of the coordinates.

$$(p_x)_{\text{op.}} \Psi(\vec{r}, t) = \frac{\hbar}{i} \frac{\partial}{\partial x} \Psi(\vec{r}, t). \quad (61)$$

The product of two hermitian operators is in general not hermitian,

$$\int d\vec{r} \Psi^* O_2 O_1 \Phi = \int d\vec{r} (O_2^\dagger \Psi)^* O_1 \Phi = \int d\vec{r} (O_1^\dagger O_2^\dagger \Psi)^* \Phi, \quad (62)$$

so

$$(O_2 O_1)^\dagger = O_1^\dagger O_2^\dagger. \quad (63)$$

The product of the two hermitian operators is hermitian only if the operators commute. In the general case (for noncommuting operators), if O_1 and O_2 are both hermitian,

$$(O_1 O_2 + O_2 O_1) \quad \text{and} \quad i(O_1 O_2 - O_2 O_1)$$

are hermitian.

The commutator of two operators is very important in quantum mechanics. It is defined as

$$[O_1, O_2] = (O_1 O_2 - O_2 O_1). \quad (64)$$

G The Heisenberg Commutation Relations

The commutator

$$[p_x, x] = \frac{\hbar}{i}. \quad (65)$$

This commutator relation follows from

$$(p_x x - x p_x) \Psi = \frac{\hbar}{i} \frac{\partial}{\partial x} (x \Psi) - x \frac{\hbar}{i} \frac{\partial}{\partial x} (\Psi) = \frac{\hbar}{i} \Psi \quad (66)$$

for all Ψ of the Hilbert space. Eq. (65) is known as the Heisenberg commutation relation. Although we have demonstrated it here with the use of the wave function, it was introduced into quantum theory by Heisenberg without the concept of a wave function (see chapter 6D). Similarly, again using the technique of eq. (66),

$$[p_x, F(x, y, z)] = \frac{\hbar}{i} \frac{\partial F}{\partial x}. \quad (67)$$

On the other hand,

$$[p_x, G(p_x, p_y, p_z)] = 0, \quad (68)$$

but

$$[G(p_x, p_y, p_z), x] = \frac{\hbar}{i} \frac{\partial G}{\partial p_x}. \quad (69)$$

In particular, if H is a Hamiltonian, a function of the operators, p_x, p_y, p_z, x, y, z ,

$$[p_x, H] = \frac{\hbar}{i} \frac{\partial H}{\partial x}; \quad [x, H] = -\frac{\hbar}{i} \frac{\partial H}{\partial p_x}. \quad (70)$$

Expectation values of Hermitian operators are real. If $O = O^\dagger$,

$$\langle \Psi, O\Psi \rangle = \langle O^\dagger \Psi, \Psi \rangle = \langle O\Psi, \Psi \rangle = \langle \Psi, O\Psi \rangle^*, \quad (71)$$

so $\langle O \rangle = \langle O \rangle^*$.

If $O = O(\vec{p}, \vec{r}, t)$,

$$\frac{\hbar}{i} \frac{d}{dt} \langle O \rangle = \langle [H, O] \rangle + \frac{\hbar}{i} \langle \frac{\partial O}{\partial t} \rangle, \quad (72)$$

where H is the Hamiltonian of the system, a hermitian operator, $H = H^\dagger$.

$$\begin{aligned} \frac{d}{dt} \langle \Psi, O\Psi \rangle &= \left(\langle \frac{\partial \Psi}{\partial t}, O\Psi \rangle + \langle \Psi, O \frac{\partial \Psi}{\partial t} \rangle + \langle \Psi, \frac{\partial O}{\partial t} \Psi \rangle \right) \\ &= \frac{i}{\hbar} [\langle H\Psi, O\Psi \rangle + \langle \Psi, O(-H\Psi) \rangle] + \langle \frac{\partial O}{\partial t} \rangle \\ &= \frac{i}{\hbar} \langle \Psi, (H^\dagger O - OH)\Psi \rangle + \langle \frac{\partial O}{\partial t} \rangle \\ &= \frac{i}{\hbar} \langle \Psi, (HO - OH)\Psi \rangle + \langle \frac{\partial O}{\partial t} \rangle. \end{aligned} \quad (73)$$

H Generalized Ehrenfest Theorem

In the above relation, let $O = q_s$, where q_s is a generalized coordinate, and the Hamiltonian of the system is expressed in terms of generalized coordinates, q_s , and their canonically conjugate momenta, p_s . Then,

$$\begin{aligned} \frac{\hbar}{i} \frac{d}{dt} \langle q_s \rangle &= \langle [H, q_s] \rangle = \frac{\hbar}{i} \langle \frac{\partial H}{\partial p_s} \rangle \\ \frac{\hbar}{i} \frac{d}{dt} \langle p_s \rangle &= \langle [H, p_s] \rangle = -\frac{\hbar}{i} \langle \frac{\partial H}{\partial q_s} \rangle. \end{aligned} \quad (74)$$

These relations are the quantum analogues of the Hamiltonian form of the equations of motion.

$$\begin{aligned} \frac{d}{dt} \langle q_s \rangle &= \langle \frac{\partial H}{\partial p_s} \rangle \\ \frac{d}{dt} \langle p_s \rangle &= -\langle \frac{\partial H}{\partial q_s} \rangle. \end{aligned} \quad (75)$$

I Conservation Theorems: Angular Momentum, Runge–Lenz Vector, Parity

In the last section, we showed

$$\frac{d}{dt} \langle O \rangle = \frac{i}{\hbar} \langle [H, O] \rangle + \langle \frac{\partial O}{\partial t} \rangle. \quad (76)$$

Thus, if an operator, O , commutes with the Hamiltonian, H , and is not an explicit function of the time, the time derivative of its expectation value in any state, Ψ , is equal to zero. This operator is the quantum-mechanical analogue of a classical “integral” of the motion. The operator, O , is conserved.

The simplest example, as in classical physics, is the Hamiltonian operator itself, provided it is not an explicit function of the time. For such a Hamiltonian, the conserved value of H is the energy E , as in classical physics. As a second example, consider single-particle motion in a central force field, with

$$H = \frac{1}{2m}(\vec{p} \cdot \vec{p}) + V(r), \quad (77)$$

where the potential function is a function of the scalar r only, where $r^2 = x^2 + y^2 + z^2$. (Note, we could also have chosen the two-body system with a central interaction, provided we replace m by the reduced mass and \vec{r} stands for the relative vector, $\vec{r}_1 - \vec{r}_2$; see the next section). In this case, the three components of the orbital angular momentum vector,

$$\vec{L} = [\vec{r} \times \vec{p}], \quad (78)$$

are conserved quantities. For example,

$$\begin{aligned} [H, L_x] &= [H, (yp_z - zp_y)] = y[H, p_z] + [H, y]p_z - z[H, p_y] - [H, z]p_y \\ &= y[V, p_z] + \frac{1}{2m}[p_y^2, y]p_z - z[V, p_y] - \frac{1}{2m}[p_z^2, z]p_y \\ &= -\frac{\hbar}{i}y\frac{\partial V}{\partial z} + \frac{\hbar}{i}\frac{p_y}{m}p_z - z\left(-\frac{\hbar}{i}\frac{\partial V}{\partial y}\right) - \frac{\hbar}{i}\frac{p_z}{m}p_y \\ &= \frac{\hbar}{i}\left(-y\frac{dV}{dr}\frac{z}{r} + z\frac{dV}{dr}\frac{y}{r}\right) = 0. \end{aligned} \quad (79)$$

Similarly,

$$[H, L_y] = [H, L_z] = 0. \quad (80)$$

In the above calculation, we have made use of the trivial but useful commutator identities

$$[A, BC] = B[A, C] + [A, B]C; \quad \text{also} \quad [AB, C] = A[B, C] + [A, C]B. \quad (81)$$

From the commutators, $[H, L_k] = 0$, we also have that H commutes with the operator \vec{L}^2

$$[H, \vec{L}^2] = \sum_{\alpha=x,y,z} L_\alpha [H, L_\alpha] + [H, L_\alpha] L_\alpha = 0. \quad (82)$$

As a third example, consider the hydrogen atom Hamiltonian

$$H = \frac{1}{2\mu}(\vec{p} \cdot \vec{p}) - \frac{e^2}{r}. \quad (83)$$

For the Hamiltonian with this $1/r$ potential, the three components of the Runge–Lenz vector, $\vec{\mathcal{R}}$, are conserved, where classically $\vec{\mathcal{R}} = \frac{1}{\mu}[\vec{p} \times \vec{L}] - \frac{e^2}{r}\vec{r}$. Quantum mechanically, we must convert this into a hermitian operator by using the symmetrized form of the first term. Remembering the interchange of the order of the two vectors in a vector product introduces a minus sign, the symmetrized form for $\vec{\mathcal{R}}$ is

$$\vec{\mathcal{R}} = \frac{1}{2\mu}([\vec{p} \times \vec{L}] - [\vec{L} \times \vec{p}]) - \frac{e^2}{r}\vec{r}. \quad (84)$$

Note,

$$\begin{aligned} \frac{1}{2}([\vec{p} \times \vec{L}]_x - [\vec{L} \times \vec{p}]_x) &= \frac{1}{2}((p_y L_z - p_z L_y) - (L_y p_z - L_z p_y)) \\ &= \frac{1}{2}((p_y L_z + L_z p_y) - (p_z L_y + L_y p_z)). \end{aligned} \quad (85)$$

Note, $p_y L_z$ is not a hermitian operator, because p_y does not commute with $L_z = (xp_y - yp_x)$. The symmetrized form of this operator, $\frac{1}{2}(p_y L_z + L_z p_y)$, however, is hermitian. In making the transition from classical physics quantities to quantum-mechanical operators, the hermitian, symmetrized form of the classical quantities will often give the needed quantum-mechanical operators. The proof that $[H, \mathcal{R}_k] = 0$, where H is the hydrogen atom Hamiltonian, will be left as an exercise (part of problem 13).

As a final example of a conserved operator, consider the space inversion or parity operator, P , where

$$P\Psi(x, y, z, t) = \Psi(-x, -y, -z, t). \quad (86)$$

For a Hamiltonian,

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(x, y, z), \quad \text{with } V(-x, -y, -z) = V(x, y, z), \quad (87)$$

that is, with a potential that is space-inversion invariant, we have

$$\begin{aligned} HP\Psi(\vec{r}, t) &= H\left(\frac{\hbar}{i}\vec{\nabla}, \vec{r}\right)\Psi(-\vec{r}, t) \\ PH\Psi(\vec{r}, t) &= H\left(-\frac{\hbar}{i}\vec{\nabla}, -\vec{r}\right)\Psi(-\vec{r}, t) = H\left(\frac{\hbar}{i}\vec{\nabla}, \vec{r}\right)\Psi(-\vec{r}, t), \end{aligned} \quad (88)$$

so

$$(HP - PH)\Psi(\vec{r}, t) = 0 \quad (89)$$

for all Ψ of our Hilbert space. Hence, $[H, P] = 0$, and P is a conserved quantity. Finally, note also, P is a hermitian operator, because

$$\int d\vec{r}\Psi^*(\vec{r}, t)P\Psi(\vec{r}, t) = \int d\vec{r}\Psi^*(\vec{r}, t)\Psi(-\vec{r}, t) = \int d\vec{r}\Psi^*(-\vec{r}, t)\Psi(\vec{r}, t)$$

$$= \int d\vec{r} \left(P^\dagger \Psi(\vec{r}, t) \right)^* \Psi(\vec{r}, t),$$

where we have made the change of variables, $x \rightarrow -x$, $y \rightarrow -y$, $z \rightarrow -z$, and have changed the order of the integration limits in the three integrals implied by our shorthand notation in the last step of the first line. We see $P^\dagger = P$. Therefore, the expectation value of the operator P must also be real. Finally, because

$$P^2 \Psi(\vec{r}, t) = \Psi(\vec{r}),$$

the operator P^2 has an expectation value of 1. The real expectation value of the operator P can thus be only either +1 or -1. The solutions of the Schrödinger equation for the space-inversion invariant Hamiltonian of eq. (87) must thus either be unchanged or change sign under the space-inversion operation. The wave function must have even or odd parity.

J Quantum-Mechanical Hamiltonians for More General Systems

As an example of a slightly more general system, consider a particle of mass, m , and charge, e , moving in an electromagnetic field derivable from a vector potential, $\vec{A}(\vec{r})$, and a scalar potential, $\Phi(\vec{r})$. The classical Hamiltonian is given by

$$H = \frac{(\vec{p} - \frac{e}{c}\vec{A})^2}{2m} + e\Phi. \quad (90)$$

This relation can be written in the form

$$H = \frac{(\vec{p} \cdot \vec{p})}{2m} - \frac{e}{2mc}(\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) + \frac{e^2}{2mc^2}\vec{A} \cdot \vec{A} + e\Phi. \quad (91)$$

Note, because in general $[p_x, A_x] \neq 0$, we have written the scalar product of \vec{A} with \vec{p} in symmetrized, hermitian form, so the Hamiltonian in the second form is a candidate for the quantum-mechanical Hamiltonian of this system. This relation is indeed the correct quantum-mechanical Hamiltonian. The predictions based on this form of the Hamiltonian are in agreement with the experiment! (We shall study this system in more detail later, where we will discuss the role of the gauge of the potentials, the gauge transformation, the Aharonov–Bohm effect, etc.) For more complicated systems, however, the simple process of symmetrization of a classical Hamiltonian may not be sufficient, particularly if the physically relevant coordinates are a set of complicated curvilinear coordinates, say, in the case of a many-body system in which some of the degrees of freedom are “frozen” or do not come into play at a region of low-energy excitations.

K The Schrödinger Equation for an n -particle System

For the general n -particle system, with the Hamiltonian

$$H = \sum_{k=1}^n \frac{(\vec{p}_k \cdot \vec{p}_k)}{2m_k} + V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n), \quad (92)$$

we are led (as in the case of the single-particle system) to the Schrödinger equation

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = -\sum_k \frac{\hbar^2}{2m_k} \nabla_k^2 \Psi + V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) \Psi. \quad (93)$$

For the two-particle system with no external forces, in particular, it will be useful to make a transformation to relative and center of mass coordinates

$$\vec{r} = \vec{r}_1 - \vec{r}_2, \quad \vec{R} = \frac{(m_1 \vec{r}_1 + m_2 \vec{r}_2)}{(m_1 + m_2)}, \quad (94)$$

and

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2(m_1 + m_2)} \nabla_{\text{C.M.}}^2 \Psi - \frac{\hbar}{2\mu} \nabla_{\text{rel.}}^2 \Psi + V(\vec{r}) \Psi, \quad (95)$$

where μ is the reduced mass, $\mu = m_1 m_2 / (m_1 + m_2)$ and the potential is a function of the relative \vec{r} only (no external fields). In this case, the center of mass motion separates. With $\Psi(\vec{R}, \vec{r}, t) = \Psi_{\text{C.M.}}(\vec{R}, t) \Psi_{\text{rel.}}(\vec{r}, t)$, the center of mass term leads to a plane wave solution

$$\Psi_{\text{C.M.}}(\vec{R}, t) = A e^{i(\vec{P} \cdot \vec{R} - E_{\text{transl.}} t)}, \quad (96)$$

where \vec{P} is the linear momentum associated with the center of mass motion of the system of mass $(m_1 + m_2)$ and $E_{\text{transl.}}$ is the translational energy associated with the center of mass motion, $E_{\text{transl.}} = P^2 / 2(m_1 + m_2)$. The Schrödinger equation is then effectively an equation equivalent to a single-particle equation, provided the mass is replaced by the reduced mass.

$$-\frac{\hbar}{i} \frac{\partial \Psi_{\text{rel.}}}{\partial t} = -\frac{\hbar^2}{2\mu} \nabla_{\text{rel.}}^2 \Psi_{\text{rel.}}(\vec{r}, t) + V(\vec{r}) \Psi_{\text{rel.}}(\vec{r}, t). \quad (97)$$

In n -particle systems, it will be useful to transform from the coordinates x_1, \dots, z_n to a set of generalized coordinates q_s . Often, some of these will not come into play. In a polyatomic molecule, e.g., the ammonia molecule, NH_3 , we have a system with 4 atomic nuclei and 10 electrons, a 14-particle system with 42 degrees of freedom (assuming we can neglect the electron and nuclear spins). These coordinates could be chosen as the 3 center of mass coordinates, which merely describe the free-particle translation of the whole system in space; 3 angular coordinates, say, three Euler angles, ϕ, θ, χ , which describe the orientation of the molecule in space and describe the rotational motion of the molecule; 6 relative coordinates, which describe the relative motions of the atomic nuclei, that is, the vibrational motions of the molecule; and finally 3×10 electronic coordinates

(again ignoring for the moment the electron spins), which describe the electron motions of the molecule. At very low excitation energies, only the rotational degrees of freedom, ϕ, θ, χ , may need to be considered. Therefore, if we can transform the general $3n = 42$ -dimensional Laplacian operator of this 14-particle system from the 3×14 Cartesian coordinates to the physically relevant 42 generalized coordinates, q_s , including ϕ, θ, χ , we arrive at the desired Schrödinger equation, if the variations with all q_s are neglected, except for the variations with the needed ϕ, θ, χ . Even for the 1-particle system, it will generally be useful to express the Schrödinger equation not in terms of the Cartesian coordinates x, y, z , but in terms of some set of curvilinear coordinates, e.g., spherical coordinates r, θ, ϕ .

L The Schrödinger Equation in Curvilinear Coordinates

If we transform from the $3n$ Cartesian coordinates x_1, \dots, z_n to a new set of $3n$ generalized coordinates q_s , with $s = 1, \dots, 3n$, through

$$x_1 = f_1(q_1, q_2, \dots, q_{3n}), \quad \dots, \quad \dots, \quad z_n = f_{3n}(q_1, q_2, \dots, q_{3n}) \quad (98)$$

the classical kinetic energy expression can be written as a homogeneous quadratic function of the q_i ,

$$T = \frac{1}{2} \sum_{i,j} g_{ij} \dot{q}_i \dot{q}_j, \quad (99)$$

where the g_{ij} are in general functions of the q_s . The classical Hamiltonian expressed in the generalized momenta, p_s , canonically conjugate to these q_s , can then be written as

$$H_{\text{class.}} = \frac{1}{2} \sum_{ij} g^{ij} p_i p_j + V(q_1, q_2, \dots, q_{3n}), \quad (100)$$

where the g^{ij} matrix, that is, the superscripted g -matrix, is the inverse of the g_{ij} matrix, that is, the subscripted g -matrix

$$\sum_{\alpha} g_{i\alpha} g^{\alpha j} = \delta_i^j, \quad \text{and} \quad \sum_{\alpha} g^{i\alpha} g_{\alpha j} = \delta^i_j. \quad (101)$$

Note, the g^{ij} are in general complicated functions of the q_s and do not commute with the p_s . A large number of ways would exist of making the kinetic energy term hermitian, so the hermiticity requirement alone does not lead to the correct quantum-mechanical Hamiltonian. We know, however, how to transform the $3n$ -dimensional Laplacian operator from its Cartesian form to the form involving partial derivatives with respect to the new generalized q_s . Therefore, we can write the proper Schrödinger equation. We need, in addition to the g^{ij} , the function g , given by the determinant of the subscripted g -matrix,

$$g = |g_{ij}| = \det(g_{ij}). \quad (102)$$

Writing the 3n-dimensional Laplacian ∇^2 in the curvilinear coordinates, we arrive at the Schrödinger equation

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2} \sum_{ij} \frac{1}{\sqrt{g}} \frac{\partial}{\partial q_i} \left(g^{ij} \sqrt{g} \frac{\partial \Psi}{\partial q_j} \right) + V\Psi. \quad (103)$$

If Ψ is assumed to be a function of only a few of the q_i , the equation will simplify.

Problems

1. A free particle moving in the x-direction, (1-D motion) has a momentum distribution given by

$$\phi(p, t) = \sqrt{\frac{1}{\alpha \sqrt{\pi}}} e^{-\frac{1}{2} \frac{(p-p_0)^2}{\alpha^2}} e^{-\frac{i}{\hbar} \frac{p^2}{2m} t}$$

$$\phi(p, t) = \sqrt{\frac{4}{3\alpha^5 \sqrt{\pi}}} (p - p_0)^2 e^{-\frac{1}{2} \frac{(p-p_0)^2}{\alpha^2}} e^{-\frac{i}{\hbar} \frac{p^2}{2m} t}.$$

For both cases, calculate the spatial probability density amplitude function, $\Psi(x, t)$, for this particle. Calculate $\langle p \rangle$, $\langle p^2 \rangle$, $\langle \Delta p \rangle$, $\langle x \rangle$, $\langle x^2 \rangle$, and $\langle \Delta x \rangle$, and verify the uncertainty principle. Give an interpretation of Δx , in the limit $\hbar \rightarrow 0$, in classical terms.

2. From the “dispersion law,”

$$\frac{E^2}{c^2} - (\vec{p} \cdot \vec{p}) = m_0^2 c^2$$

for a relativistic free particle, derive a wave equation. (This equation is known as the Klein–Gordon equation.) If the probability density current is to have the form

$$\vec{S} = \frac{\hbar}{2mi} \left(\Psi^* \vec{\nabla} \Psi - \Psi \vec{\nabla} \Psi^* \right)$$

with

$$\operatorname{div} \vec{S} + \frac{\partial W}{\partial t} = 0$$

to preserve conservation of probability, show how the probability density, W , must be related to Ψ , $\frac{\partial \Psi}{\partial t}$, Ψ^* , $\frac{\partial \Psi^*}{\partial t}$. Is this an acceptable W ? Is $W \geq 0$ everywhere, for all t ?

3. A particle of charge, e , and mass, m , in an electromagnetic field, derivable from vector and scalar potentials, \vec{A} , Φ , has a Hamiltonian

$$H = \frac{\vec{p}^2}{2m} - \frac{e}{2mc} (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) + \frac{e^2}{2mc^2} \vec{A}^2 + e\Phi.$$

(Note the symmetrized form of the second term.) Write the Schrödinger equation for this case. Find an expression for the probability density current, \vec{S} , with $W = \Psi^* \Psi$. Calculate

$$\frac{d\langle x \rangle}{dt}, \text{ and } \frac{d\langle p_x \rangle}{dt},$$

and show how these are related to the classical equations of motion.

Also, show the wave equation is gauge invariant, and under the transformation

$$\vec{A} \rightarrow \vec{A}' = \vec{A} + \vec{\nabla}\chi, \quad \Phi \rightarrow \Phi' - \frac{1}{c} \frac{\partial \chi}{\partial t},$$

where $\chi = \chi(x, y, z; t)$, the wave equation remains unchanged, provided

$$\Psi \rightarrow \Psi' = \Psi e^{i\epsilon \chi(x, y, z; t)}.$$

4. In describing scattering processes of complex projectiles from nuclei, it is sometimes useful to use a fictitious complex potential

$$V = V_1 + iV_2,$$

where V_1 and V_2 are both real. Assume $V_2 = \text{constant} = W$, inside a sphere of radius, $r_0 = 10^{-12}$ cm, and $V_2 = 0$ for $r > r_0$. Determine, W , magnitude in eV and sign, so the probability is 0.1 per 10^{-21} seconds for the loss of flux of incoming projectile particles. (Incoming α particles, e.g., can be “lost” by conversion to ${}^3\text{He}$ and neutrons, etc. Note, 10^{-21} seconds is a typical traversal time for a fast but nonrelativistic nuclear particle through a heavy nucleus.)

5. The classical kinetic energy for a rigid rotator, e.g., a polyatomic molecule such as H_2O to very good approximation, is given in terms of the three Euler angles, ϕ, θ, χ , and the three principal moments of inertia, A, B, C , by

$$2T = A(\dot{\theta} \cos \chi + \dot{\phi} \sin \theta \sin \chi)^2 + B(-\dot{\theta} \sin \chi + \dot{\phi} \sin \theta \cos \chi)^2 + C(\dot{\chi} + \dot{\phi} \cos \theta)^2.$$

Assuming other degrees of freedom, such as vibrational, translational, and electronic, in the case of the polyatomic molecule, can be neglected, then $V = 0$. Write the Schrödinger equation for the rigid rotator (asymmetric case, $A \neq B \neq C$). For the symmetric rotator, with $A = B$, show the time-independent wave function separates via the Ansatz

$$\psi(\phi, \theta, \chi) = \frac{1}{2\pi} e^{iM\phi} e^{iK\chi} \Theta(\theta),$$

and write the differential equation for $\Theta(\theta)$. (For the asymmetric case, the differential equation approach may not be the best way to solve this problem.)

6. Transpose the Schrödinger equation for the hydrogenic atom, with

$$H = \frac{\vec{p} \cdot \vec{p}}{2\mu} - \frac{Ze^2}{r},$$

where the above \vec{p} and \vec{r} , which are $\vec{p}_{\text{physical}}$, and $\vec{r}_{\text{physical}}$ are transcribed into dimensionless \vec{p} and \vec{r} via

$$\vec{r}_{\text{phys.}} = a_0 \vec{r}, \quad \vec{p}_{\text{phys.}} = \frac{\hbar}{a_0} \vec{p}, \quad \text{with } a_0 = \frac{\hbar^2}{\mu e^2 Z},$$

$$H_{\text{phys.}} = \frac{\mu Z^2 e^4}{\hbar^2} H, \quad E_{\text{phys.}} = \frac{\mu Z^2 e^4}{\hbar^2} \epsilon.$$

Transpose the Schrödinger equation for the hydrogenic atom, further, into an equation written in terms of “stretched parabolic coordinates,” μ, ν, ϕ , defined in terms of the dimensionless $\vec{r} = (x, y, z)$ by

$$\mu = \sqrt{(r+z)[-2\epsilon]^{\frac{1}{4}}}, \quad \nu = \sqrt{(r-z)[-2\epsilon]^{\frac{1}{4}}}, \quad \phi = \tan^{-1}\left(\frac{y}{x}\right),$$

where $r = \sqrt{x^2 + y^2 + z^2}$, and $\epsilon = E/(\mu Z^2 e^4/\hbar^2)$, or

$$x = \frac{\mu\nu}{[-2\epsilon]^{\frac{1}{2}}} \cos\phi, \quad y = \frac{\mu\nu}{[-2\epsilon]^{\frac{1}{2}}} \sin\phi, \quad z = \frac{(\mu^2 - \nu^2)}{2[-2\epsilon]^{\frac{1}{2}}},$$

where this transformation is useful for bound states, with $\epsilon < 0$. Transform the Laplacian into these stretched parabolic coordinates.

Another set of useful coordinates for the hydrogenic atom are the conventional parabolic coordinates, defined in terms of the dimensionless $\vec{r} = (x, y, z)$, by

$$\xi = r - z, \quad \eta = r + z, \quad \phi = \tan^{-1}\left(\frac{y}{x}\right),$$

$$x = \sqrt{\xi\eta} \cos\phi, \quad y = \sqrt{\xi\eta} \sin\phi, \quad z = \frac{1}{2}(\eta - \xi).$$

Transform the Laplacian into these curvilinear coordinates, and write the Schrödinger equation for the hydrogenic atom in these parabolic coordinates.

4

Schrödinger Theory: The Existence of Discrete Energy Levels

A The Time-Independent Schrödinger Equation

The Schrödinger equation for a single particle moving under the influence of a time-independent conservative force

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi = H\Psi \quad (1)$$

can be converted to the time-independent equation for the function $\psi(x, y, z)$ by assuming

$$\Psi = f(t)\psi(x, y, z), \quad (2)$$

with

$$-\frac{1}{f} \left\{ \frac{\hbar}{i} \frac{df}{dt} \right\} = \frac{1}{\psi} \left\{ -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi \right\} = \frac{1}{\psi} (H\psi) = \text{const}, \quad (3)$$

where we have converted a function of the time only on the left-hand side of the equation into a function of x, y, z only on the right-hand side. Because this must hold for all values of t and all x, y, z , the left-hand side and the right-hand side must be equal to a constant. We have separated the equation. The physical significance of the constant can be seen to be the energy, E .

$$f(t) = \exp\left(-\frac{i}{\hbar} Et\right) \quad (4)$$

and

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi. \quad (5)$$

For a 1-D problem, in particular,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))\psi = 0. \quad (6)$$

In this chapter, we shall show the Schrödinger equation, eq. (5), for potentials V , for which the classical motion would be restricted to a bound region of space, will lead to allowed (square-integrable) solutions, the so-called characteristic functions, or “eigenfunctions,” of the equation only for certain discrete allowed energies, the so-called “eigenvalues” or characteristic values of the energies.

B The Simple, Attractive Square Well

The 1-D Schrödinger equation, eq. (6), has particularly simple solutions in regions $a < x < b$, where $V(x)$ can be replaced by a constant, with simple sinusoidal solutions for regions with $E > V$ and simple exponentials for regions with $E < V$. The simplest 1-D problem is that of a single, attractive square well of width $2a$, with

$$V(x) = 0 \quad \text{for } -a \leq x \leq +a, \quad V(x) = +V_0 \quad \text{for } |x| > a, \quad (7)$$

(see Fig. 4.1). The Schrödinger equation becomes

$$\begin{aligned} \frac{d^2\psi}{dx^2} + k^2\psi(x) &= 0, \quad \text{with } k^2 = \frac{2mE}{\hbar^2} \quad \text{for } -a \leq x \leq +a, \\ \frac{d^2\psi}{dx^2} - \kappa^2\psi(x) &= 0, \quad \text{with } \kappa^2 = \frac{2m(V_0 - E)}{\hbar^2} \quad \text{for } |x| \geq a. \end{aligned} \quad (8)$$

In order to have square-integrable solutions, the $\psi(x)$ must be restricted to exponentially decaying solutions outside the potential well; i.e.,

$$\psi(x) = Ce^{-\kappa x} \quad \text{for } x > +a, \quad \psi(x) = De^{+\kappa x} \quad \text{for } x < -a. \quad (9)$$

In the interior, for $-a \leq x \leq +a$, the most general solution is

$$\psi(x) = A \cos kx + B \sin kx.$$

(For the moment, we have not made use of the symmetry of the potential.) In order to have solutions with sensible probability densities, both the probability density and the probability density currents must be continuous functions of x . This solution can be ensured by requiring the continuity of both $\psi(x)$ and its first derivative at the discontinuities of the potential at $x = \pm a$. The continuity of $\psi(x)$ and its first derivative at $x = +a$ leads to the boundary conditions

$$A \cos ka + B \sin ka = Ce^{-\kappa a}, \quad (10)$$

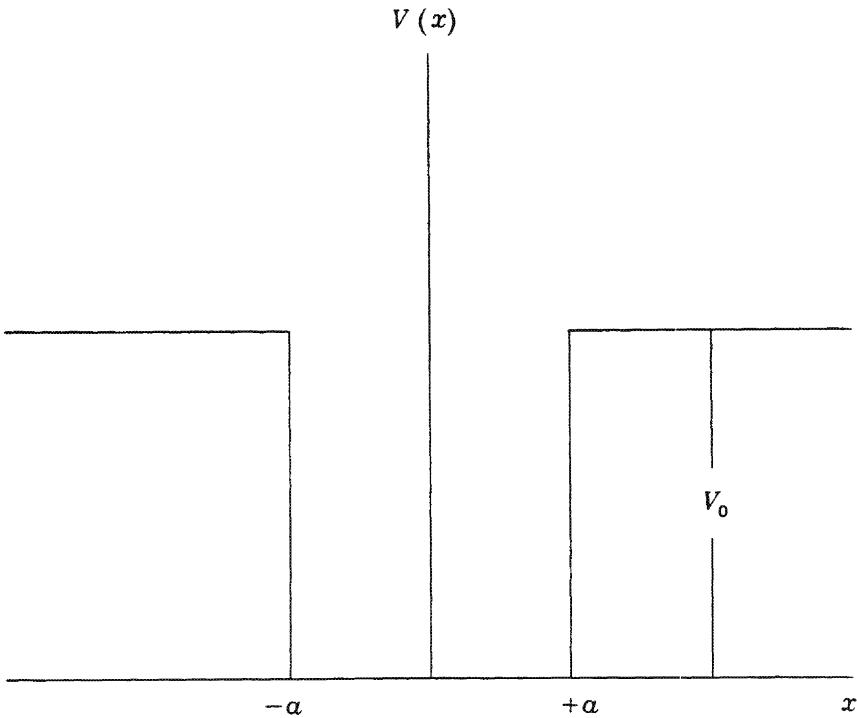


FIGURE 4.1. The attractive square well potential.

$$-Ak \sin ka + Bk \cos ka = -\kappa Ce^{-\kappa a}, \quad (11)$$

and at $x = -a$, we are led to the boundary conditions

$$A \cos ka - B \sin ka = De^{-\kappa a}, \quad (12)$$

$$Ak \sin ka + Bk \cos ka = \kappa De^{-\kappa a}. \quad (13)$$

Eliminating the constant C from eqs. (10) and (11) and the constant D from eqs. (12) and (13), we are led to the further restriction

$$AB = 0,$$

with the two possible solutions:

$$B = 0, \quad D = C, \quad \text{or} \quad A = 0, \quad D = -C. \quad (14)$$

We see the solutions are either even or odd functions of x . This could have been seen at once from the space-reflection symmetry of our potential, $V(-x) = V(x)$. Because the Schrödinger equation is invariant under the 1-D space-inversion operation, $x \rightarrow -x$, our solutions must have good parity; see Section I of Chapter 3. The $\psi(x)$ must be either even or odd functions of x ; either $\cos kx$ or $\sin kx$ functions in the region $|x| < a$. It would have been sufficient to apply the boundary

conditions at $x = +a$. The boundary conditions at $x = -a$ follow from symmetry. The two boundary conditions at $x = +a$, however, are consistent only if

$$\begin{aligned} k \tan ka &= +\kappa, && \text{for even } \psi(x), \\ k \cot ka &= -\kappa, && \text{for odd } \psi(x). \end{aligned} \quad (15)$$

Because k and κ are functions of the energy E , these relations are transcendental equations with solutions only for very specific values of E , the discrete allowed values of the energy. To solve the transcendental equations, it will be convenient to introduce dimensionless coordinates z and z_0 ,

$$z = ka = \sqrt{\frac{2mEa^2}{\hbar^2}}, \quad \text{and} \quad z_0 = \sqrt{\frac{2mV_0a^2}{\hbar^2}}, \quad (16)$$

transforming eq. (15) into

$$\begin{aligned} z \tan z &= +\sqrt{(z_0^2 - z^2)} && \text{for even } \psi(x), \\ z \cot z &= -\sqrt{(z_0^2 - z^2)} && \text{for odd } \psi(x). \end{aligned} \quad (17)$$

These two relations are plotted in Fig. 4.2. The solutions $z(E)$ at the intersections of the curves $z \tan z$ with $+\sqrt{(z_0^2 - z^2)}$ and the curves $z \cot z$ with $-\sqrt{(z_0^2 - z^2)}$ give the allowed values of E . Fig. 4.2 for the case $z_0 = 4$ shows a potential with this depth has three bound states, two with solutions of even parity and only one with a solution of odd parity. Note also, only one even bound state exists if $z_0 < \pi/2$, but at least this one bound state always exists, even in the limit of a shallow potential well, with $V_0 \rightarrow 0$. Note, also, in the limit of an infinitely deep well, as $V_0 \rightarrow \infty$, the solutions are

$$\begin{aligned} z &\rightarrow (2N+1)\frac{\pi}{2}, \quad N = 0, 1, 2, \dots, \quad \text{for even } \psi \\ z &\rightarrow 2N\frac{\pi}{2}, \quad N = 1, 2, \dots, \quad \text{for odd } \psi \end{aligned} \quad (18)$$

or

$$z_n = n\frac{\pi}{2}, \quad \text{thus,} \quad E_n = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}, \quad \text{with } n = 1, 2, \dots \quad (19)$$

Note, in the case, $V_0 \rightarrow \infty$, the wave functions are exactly 0 in the region $|x| > a$, and the interior solutions obey $\psi(\pm a) = 0$. In this case, the derivatives of the wave function are discontinuous at $x = \pm a$. Both the probability density and the probability density current, however, have the value zero at the boundaries and are therefore still continuous at the boundaries.

Note, also, so far we have considered only bound states with $E < V_0$. For $E > V_0$, the solutions of the Schrödinger equation are oscillatory for all values of x , from $-\infty \rightarrow +\infty$. Merely, a change of wavelength ("index of refraction") occurs as the wave traverses the region of the potential well. Because they reach from $x = -\infty$ to $x = +\infty$, the wave functions are no longer square integrable. They still have, however, a sensible probability interpretation. The amplitudes of

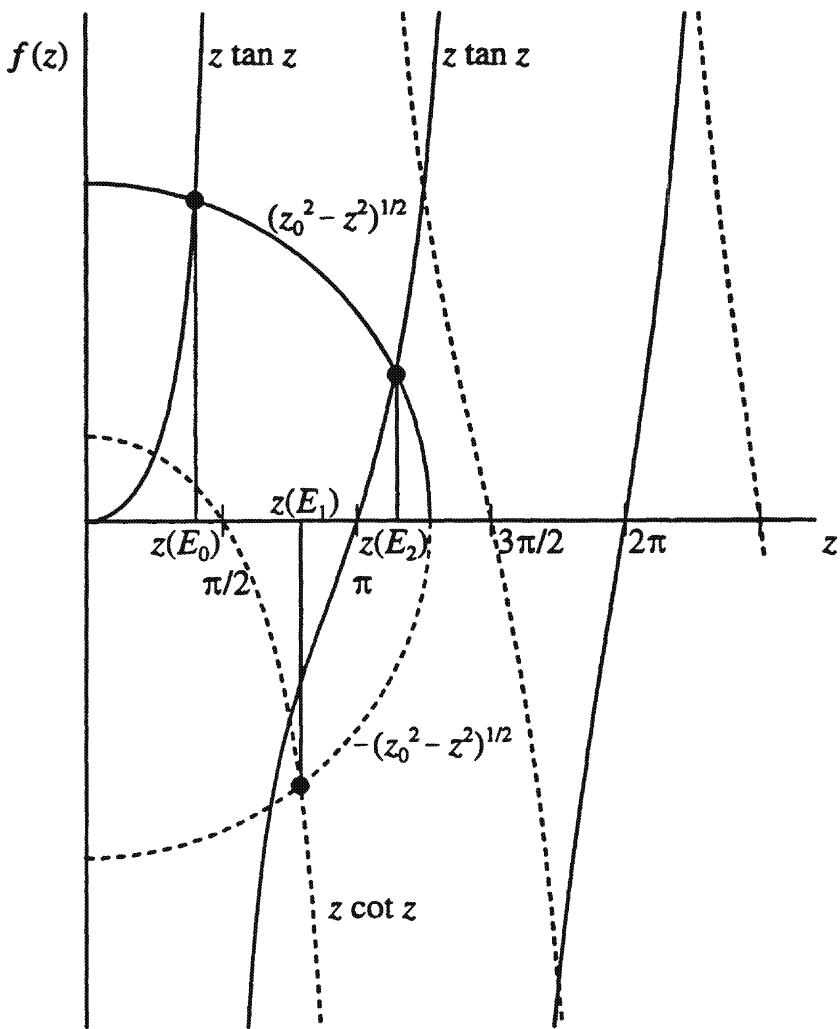


FIGURE 4.2. The transcendental eqs. (17) for the case $z_0 = 4$. Solid lines for even $\psi(x)$. Dashed lines for odd $\psi(x)$.

the sinusoidal waves give the strengths of the probability density current and can therefore be determined from the experimental flux of particles. Note, however, \vec{S} is zero for real $\psi(x)$. The physics of the problem dictates we use complex solutions of the type

$$e^{i(\pm kx - Et)}$$

for particles moving in the $\pm x$ direction. The amplitude of the wave $A e^{i(k_0 x - Et)}$, for $x < -a$, with $k_0 = [2m(E - V_0)/\hbar^2]^{1/2}$, is determined by the flux of particles from a source at $x = -\infty$. These particles can be reflected or transmitted by the

potential step, leading to a reflected wave, $B e^{(-ik_0x - iEt)}$ in the region, $x < -a$, and a transmitted wave $C e^{i(k_0x - Et)}$ in the region $x > +a$. This is a 1-D scattering problem. Scattering of particles by square wells will be treated in Part V of these lectures. For the moment, we content ourselves with noting that all energies for $E > V_0$ are possible. In this energy regime, we therefore have a continuum of allowed energies.

As a final remark, we note the solutions of the simple square well above can also be used to solve a slightly different square well problem with

$$\begin{aligned} V(x) &= \infty, \quad \text{for } x < 0, & V(x) &= 0, \quad \text{for } 0 < x \leq a, \\ V(x) &= V_0 \quad \text{for } x > a; \end{aligned} \tag{20}$$

i.e., the left potential has been replaced by a very high (∞) potential step. Therefore, $\psi(x) = 0$ for $x < 0$. This can therefore also be used for a 3-D spherically symmetric square well leading to a 1-D Schrödinger equation of the above type, where x is replaced by the radial coordinate, r . (Note, the region $r < 0$ is excluded by the fictitious infinite potential for $r < 0$.) Because the boundary condition at $r = 0$ is $\psi(r = 0) = 0$, only the odd solutions of the above potential will be allowed (see the dashed curves of Fig. 4.2). We see a bound state exists for this problem, only if

$$z_0 > \frac{\pi}{2}, \quad \text{or} \quad V_0 a^2 > \frac{\hbar^2}{2m} \frac{\pi^2}{4}. \tag{21}$$

If the sinusoidal radial wave function starting with the value 0 at $r = 0$ does not have enough curvature in the potential well region to have at least a first maximum for $r < a$, it will reach the barrier at $r = a$ with a positive slope that cannot fit onto a negative (decaying) exponential in the region $r > a$ without a discontinuity in slope and, hence, a discontinuity in the probability density current. If the potential well is not deep enough or wide enough, no bound state will exist. The potential of eq. (20) is a reasonably good approximation for the effective potential between neutron and proton in the deuteron. [Note that the mass in eq. (21) must be replaced by the reduced mass of this 2-body problem.] The deuteron has only a single bound state in its 2-particle spin triplet ($S = 1$) state. Moreover, the binding energy of this state, of 2.22 MeV (with $E = V_0 - 2.22$ MeV) is small compared with the expected value of V_0 . The deuteron is therefore a barely bound system with

$$V_0 a^2 \approx \frac{\hbar^2}{2\mu} \frac{\pi^2}{4}.$$

The deuteron has no bound states with 2-particle spin $S = 0$. The potential must therefore be spin dependent. The $S = 0$ potential just misses having a bound state. This property makes itself felt in a large scattering cross section for $E - V_0 \approx 0$, a low-energy resonance. For a detailed discussion of proton-neutron scattering and the bound or nearly bound states of the deuteron, see Chapter 44.

Problems 7–8: Square Well Problems

More complicated square well problems can often be used to gain qualitative solutions for more sophisticated problems. The following two problems can be used to illustrate some interesting physics.

7. The double-minimum potential problem. The square well double-minimum potential, shown in (c) of Fig. P7, can be used as a rough approximation for the potential governing the motion of the N atom relative to the H₃ plane, one of the vibrational degrees of freedom of the ammonia molecule, NH₃ (the degree of freedom responsible for the transition used in the NH₃ MASER, the historical forerunner of all LASERS and MASERS).

$$V = V_0 \quad \text{for } |x| < a \quad \text{Region II,}$$

$$V = 0 \quad \text{for } a < |x| < b \quad \text{Regions I, III,}$$

$$V = \infty \quad \text{for } |x| > b \quad \text{Regions IV.}$$

The mass, μ , is the reduced mass for the N–H₃ pair:

$$\mu = \frac{3m_H m_N}{(3m_H + m_N)}.$$

Exploit $V(x)$ is an even function of x , so the solutions, $\psi(x)$, must be either even or odd functions of x . It is therefore sufficient to find acceptable solutions for $x \geq 0$ and continue these appropriately into the region, $x < 0$. Find the transcendental equations from which the eigenvalues of E , corresponding to both the even and odd eigenfunctions, can be found for the states with $E < V_0$. Show graphically how the solutions can be found. Show, in particular, that for $E \ll V_0$, the solutions follow from

$$k_n(b - a) = n\pi - \Delta\phi, \quad \text{with } \Delta\phi \ll 1, \quad k_n^2 = \frac{2\mu}{\hbar^2} E_n,$$

with slightly different $\Delta\phi$ for the eigenvalues associated with the even and odd solutions, so the eigenvalues of E occur in nearly degenerate pairs, when $E \ll V_0$.

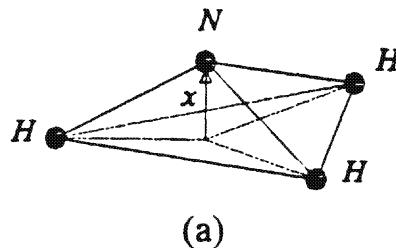
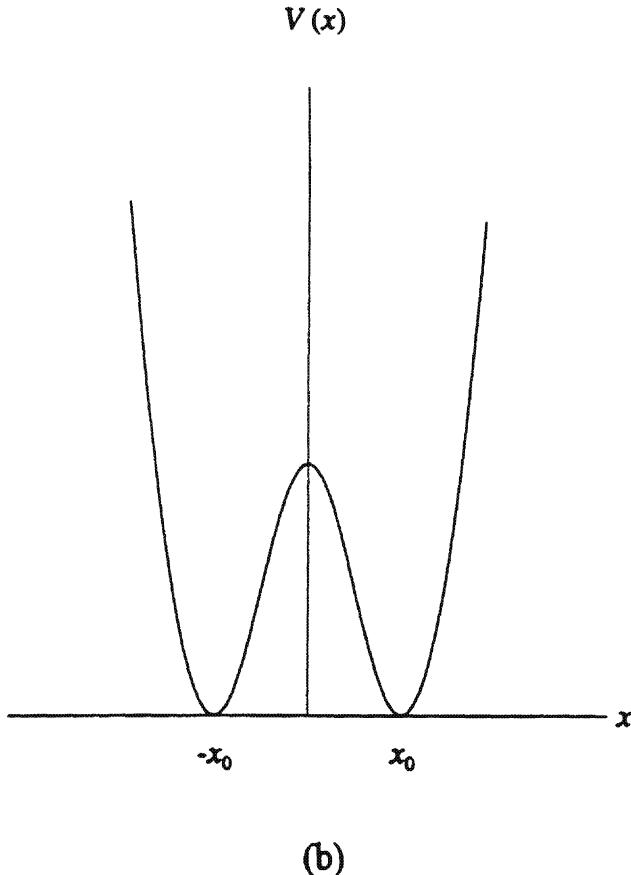


FIGURE P7. (a) The NH₃ inversion coordinate, x .

FIGURE P7. (b) Realistic $V(x)$.

Show, in this case, the splitting, ΔE_n , of the nearly degenerate pair is given by

$$\Delta E_n = (E_n^{\text{odd}} - E_n^{\text{even}}) = \frac{\hbar^3 n^2 \pi^2 \sqrt{8}}{(b-a)^3 \sqrt{\mu^3 (V_0 - E_n)}} e^{-\frac{2a}{\hbar} \sqrt{2\mu(V_0 - E_n)}},$$

where

$$E_n \approx \frac{n^2 \pi^2 \hbar^2}{2\mu(b-a)^2}.$$

Retain only dominant terms in all expansions of $\Delta\phi$ and in powers of E_n / V_0 . Hints: The even (odd) solutions in the central region, II, are of the form $\cosh \kappa x$, $(\sinh \kappa x)$, where $\kappa^2 = 2\mu(V_0 - E)/\hbar^2$. All solutions are of the form $\sin[k(x-b)]$ in region III.

8. Virtually bound states. Assume the potential, $V(r)$, shown in (a) of the Fig. P8, which is an effective potential for the motion of an α -particle relative to a heavy

nucleus, can be approximated by the simpler square well potential of (b). Find solutions, $\psi(r)$, for this square well problem for energies, $E > 0$. The boundary condition at $r = 0$ is $\psi(r = 0) = 0$. Note, all energies, $E > 0$, lead to acceptable oscillatory solutions in region III.

Show, in general, for arbitrary positive energies, E ,

$$\left| \frac{\psi_{\text{III}}}{\psi_1} \right|^2 \text{ is of order } e^G, \quad \text{with } G = \frac{2(b-a)}{\hbar} \sqrt{2\mu(V_1 - E)}.$$

For $|\psi_1|$ and $|\psi_{\text{III}}|$, take the amplitudes of the oscillatory functions in regions I and III.

Show, however, the ratio

$$\left| \frac{\psi_{\text{III}}}{\psi_1} \right|^2 \text{ can be of order } e^{-G}$$

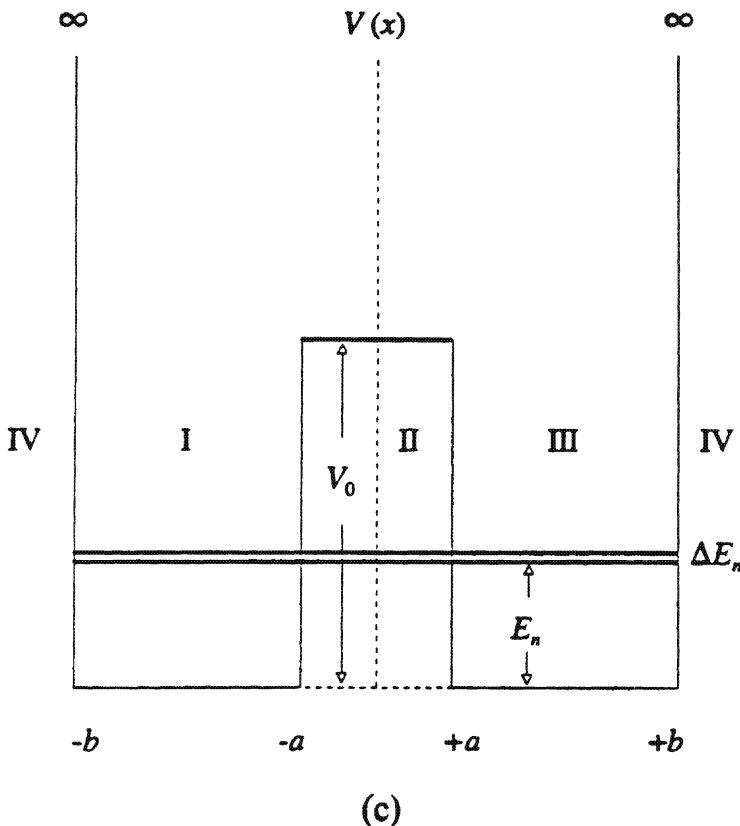


FIGURE P7. (c) Square well analogue.

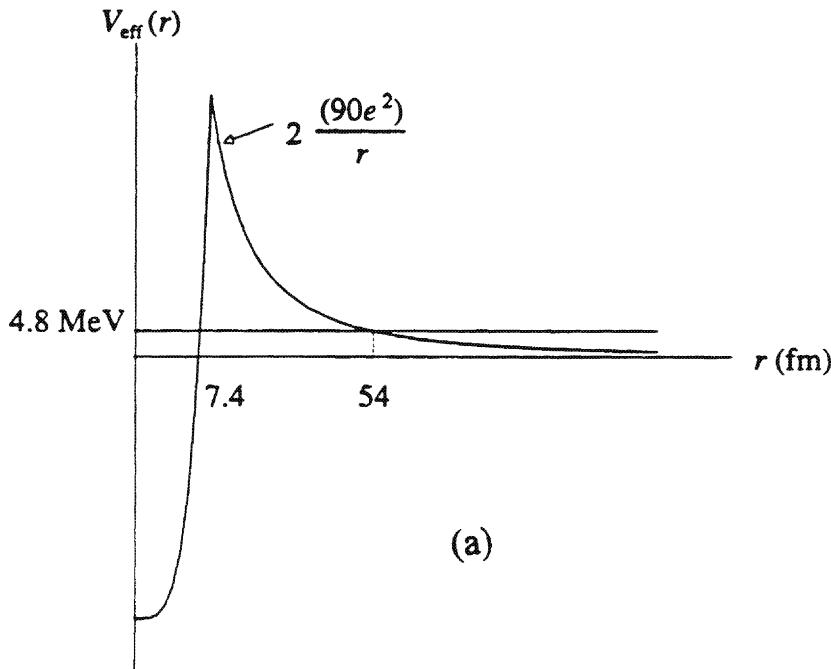


FIGURE P8. (a) Realistic $V_{\text{eff.}}(r)$ for the α - ^{234}Th motion.

for certain, specific values of $E = \bar{E}$. The factor e^{-G} is known as the Gamow penetrability factor. Find the transcendental equation from which these values of \bar{E} can be determined graphically in terms of the parameters, μ , a , b , V_0 , V_1 . Show also, for each such solution, \bar{E} , a range of energies exists, ΔE , about \bar{E} , for which

$$\left| \frac{\psi_{\text{III}}}{\psi_{\text{I}}} \right|^2 \approx e^{-G},$$

and show

$$\Delta E \approx 4 \frac{(V_1 - \bar{E})}{(V_1 + V_0)} \sqrt{\frac{\hbar^2(\bar{E} + V_0)}{2\mu a^2}} \frac{1}{\cos \sqrt{2\mu a^2(\bar{E} + V_0)/\hbar^2}} e^{-G}.$$

Note: A realistic estimate of e^G in a heavy nucleus, e.g., ^{238}U , would be $e^G \approx 10^{38}$.

C The Periodic Square Well Potential

Another interesting case in which a square well approximation may shed considerable light on an important physical problem is that of an N -fold periodic potential. For very large N , this leads to a basic problem in condensed matter physics, the motion of an electron in a crystalline lattice with N lattice points. For very small

N , such as $N = 2$ or $N = 3$, examples of motions in an N -fold periodic potential may be found in the hindered internal rotation of one atomic unit relative to another in a molecule. A symmetrical X_2Y_4 molecule, such as ethylene, C_2H_4 , e.g., has one degree of freedom, ϕ , which describes the highly hindered rotational motion of one essentially rigid CH_2 unit relative to the other on a circle in a plane perpendicular to the C–C symmetry axis, as shown in Fig. 4.3. The wave equation separates approximately, so the hindered internal rotation can be described by the one degree of freedom Schrödinger equation

$$-\frac{\hbar^2}{2I} \frac{d^2\psi}{d\phi^2} + V(\phi)\psi(\phi) = E\psi(\phi), \quad (22)$$

with $I = I_1 I_2 / (I_1 + I_2)$, and $I_1 = I_2 = 2m_Y r_Y^2$. The potential, $V(\phi)$, could be approximated by a purely sinusoidal potential,

$$V(\phi) = \frac{1}{2} V_0 (1 - \cos 2\phi),$$

or, on the other hand, by a square well potential with potential valleys of $V = 0$ and widths $2a$ centered at $\phi = 0$ and at $\phi = \pi$, and potential barriers of constant heights of V_0 and widths w centered at $\phi = \frac{1}{2}\pi$ and at $\phi = \frac{3}{2}\pi$, where $4a + 2w = 2\pi r_Y$.

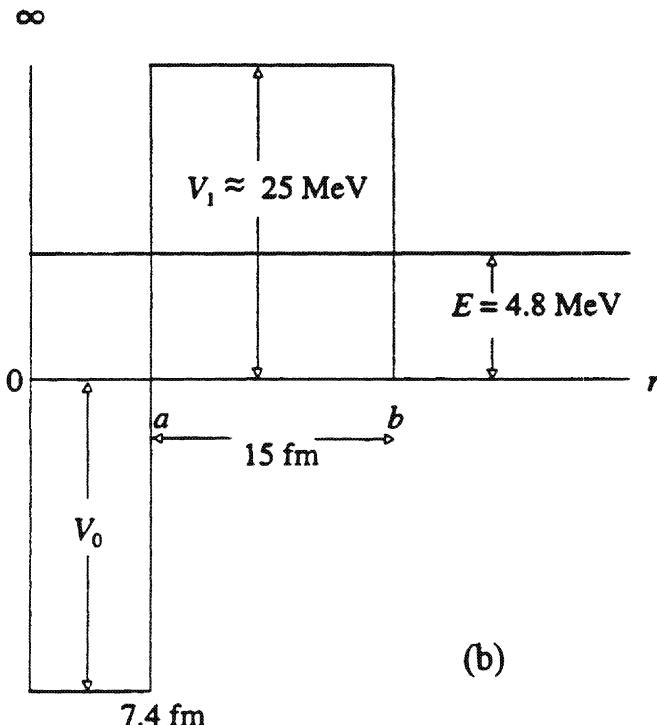
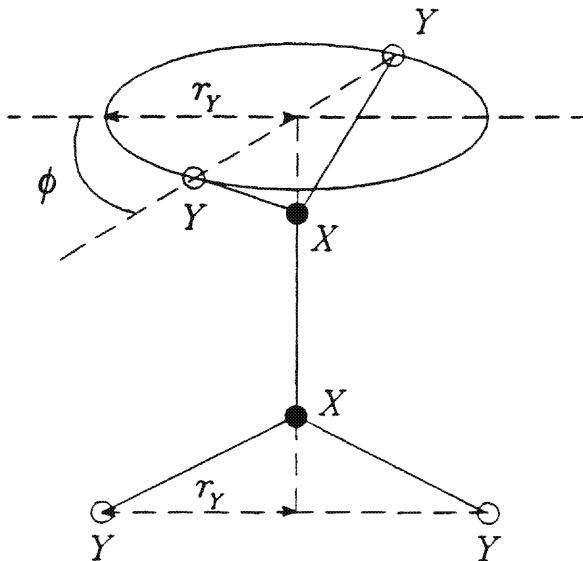


FIGURE P8. (b) Square well analogue.

FIGURE 4.3. The X_2Y_4 molecule and its internal rotational coordinate, ϕ .

The true hindering potential is probably somewhere between these two extremes. The square well approximation leads to the easiest solution; yet it contains the essential physics of the problem. A symmetrical X_2Y_4 molecule such as C_2H_6 (ethane) leads to a similar Schrödinger equation with 3-fold periodicity, i.e., with $N = 3$. The symmetrical CH_3NO_2 molecule furnishes an example with $N = 6$ -fold periodicity. Here, the C–N bond furnishes the symmetry axis for both the CH_3 and NO_2 units of the molecule. In these examples, the $(N + 1)^{\text{st}}$ site of the potential is truly the same point in 3-D space as the first site. In the condensed matter problem with N lattice sites, one usually takes periodic boundary conditions by assuming the $(N + 1)^{\text{st}}$ site is equivalent to the first site, in the limit $N \rightarrow \infty$.

In the square well approximation for the periodic potential, we assume

$$\begin{aligned} V &= 0 && \text{for } (2m - 1)a + mw < x < (2m + 1)a + mw; \\ V &= +V_0 && \text{for } (2m + 1)a + mw < x < (2m + 1)a + (m + 1)w; \\ m &= 0, 1, \dots, N. \end{aligned} \quad (23)$$

We see the m^{th} potential valley is centered at $x = 2ma + mw$, and the m^{th} potential barrier is centered at $x = (2m + 1)a + (m + \frac{1}{2}w)$; see Fig. 4.4. For the moment, we shall seek only solutions for $E < V_0$. (For the hindered internal rotation problems, we can expect the barrier heights, V_0 , to be very large compared with the energies of interest.) For this case, we define

$$k^2 = \frac{2\mu E}{\hbar^2}, \quad \kappa^2 = \frac{2\mu(V_0 - E)}{\hbar^2},$$

where μ is an effective mass for the problem. We expect the following solutions. In the m^{th} valley centered at $x = 2ma + mw$:

$$\psi(x) = C_m \cos k[x - m(2a + w)] + D_m \sin k[x - m(2a + w)];$$

under the m^{th} potential hill, centered at $x = (2m + 1)a + (m + \frac{1}{2}w)$:

$$\psi(x) = A_m \cosh \kappa \left(x - [(2m + 1)a + (m + \frac{1}{2}w)] \right)$$

$$+ B_m \sinh \kappa \left(x - [(2m + 1)a + (m + \frac{1}{2}w)] \right).$$

The potential is invariant under reflections in the planes centered at $x = 2ma + mw$ and at $x = (2m + 1)a + (m + \frac{1}{2}w)$. We might thus be tempted to assume our solutions are either even or odd under these reflection operations and that either $A_m = 0$ or $B_m = 0$, and, similarly, either $C_m = 0$ or $D_m = 0$. These assumptions would be good if all allowed energies were nondegenerate. We shall find, however, most of the allowed energy values are doubly degenerate, with two allowed solutions. We therefore retain the above linear combinations of even and odd functions. To ensure the continuity of the probability density and the probability density currents at the discontinuities of the potential, we shall again require the continuity of the wave functions and their first derivatives at the boundaries between the potential hills and valleys. With the solution under the $(m - 1)^{\text{st}}$ potential hill given by

$$\psi(x) = A_{m-1} \cosh \kappa \left(x - [(2m - 1)a + (m - \frac{1}{2})w] \right)$$

$$+ B_{m-1} \sinh \kappa \left(x - [(2m - 1)a + (m - \frac{1}{2})w] \right),$$

the continuity of ψ and its first derivative at the left boundary of the m^{th} valley, i.e., at $x = (2m - 1)a + mw$, leads to

$$A_{m-1} \cosh \kappa \frac{w}{2} + B_{m-1} \sinh \kappa \frac{w}{2} = C_m \cos ka - D_m \sin ka; \quad (24)$$

$$\kappa \left(A_{m-1} \sinh \kappa \frac{w}{2} + B_{m-1} \cosh \kappa \frac{w}{2} \right) = k(C_m \sin ka + D_m \cos ka). \quad (25)$$

The continuity of ψ and its first derivative at the right boundary of the m^{th} valley, at $x = (2m + 1)a + mw$, leads to

$$C_m \cos ka + D_m \sin ka = A_m \cosh \kappa \frac{w}{2} - B_m \sinh \kappa \frac{w}{2}, \quad (26)$$

$$k(-C_m \sin ka + D_m \cos ka) = \kappa(-A_m \sinh \kappa \frac{w}{2} + B_m \cosh \kappa \frac{w}{2}). \quad (27)$$

Solving eqs. (24) and (25) for C_m and D_m and substituting into eqs. (26) and (27) leads to the relation

$$\begin{pmatrix} A_m \\ B_m \end{pmatrix} = \mathbf{M} \begin{pmatrix} A_{m-1} \\ B_{m-1} \end{pmatrix}, \quad (28)$$

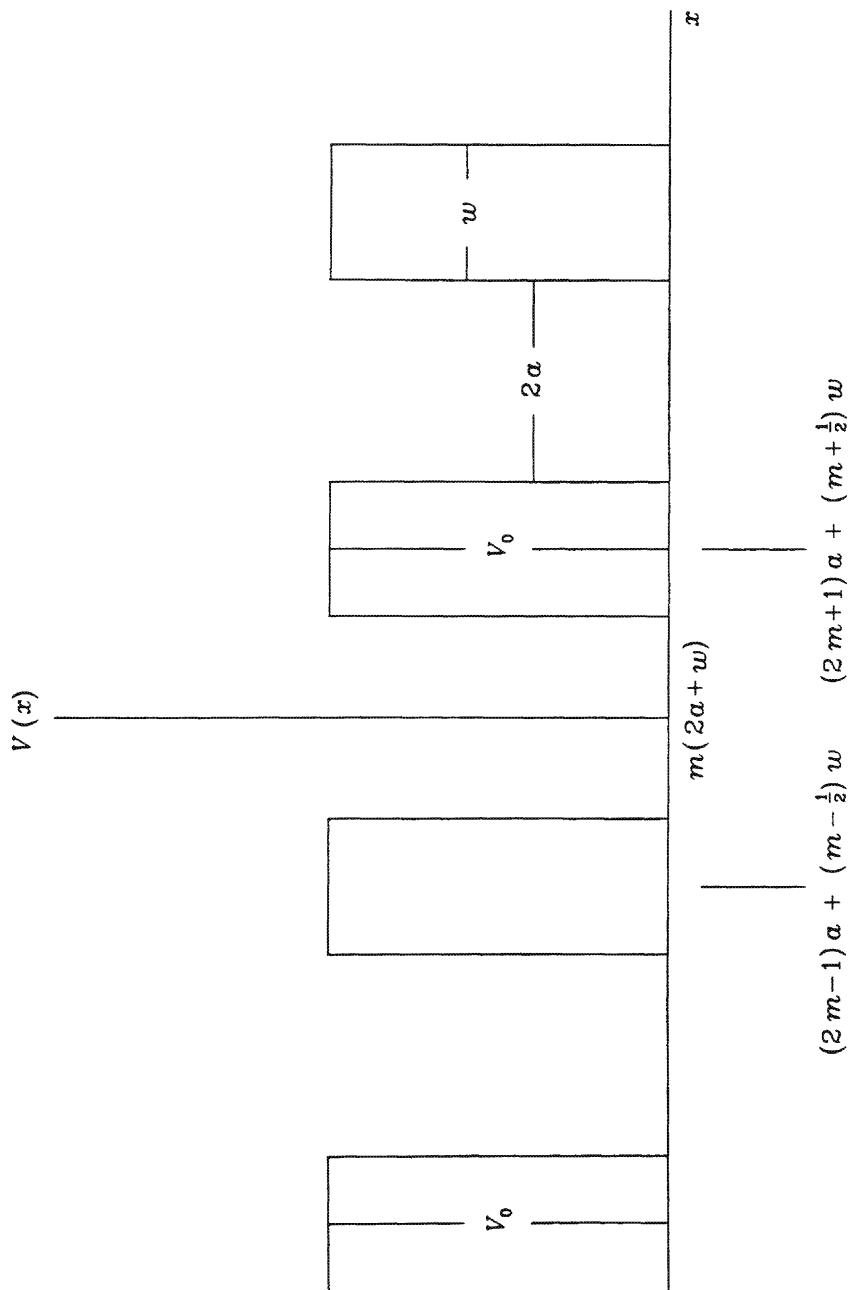


FIGURE 4.4. The periodic square well potential with barrier height, V_0 , width, w , and potential valleys of width, $2a$, with $V = 0$.

where the 2×2 matrix, \mathbf{M} , is given by

$$\mathbf{M} = \cos 2ka \begin{pmatrix} P & Q + \gamma \\ Q - \gamma & P \end{pmatrix}, \quad (29)$$

with

$$\begin{aligned} P &= \cosh \kappa w + \frac{1}{2} \left(\frac{\kappa}{k} - \frac{k}{\kappa} \right) \tan 2ka \sinh \kappa w \\ &= \frac{1}{2} e^{\kappa w} \left[1 + \frac{1}{2} \left(\frac{\kappa}{k} - \frac{k}{\kappa} \right) \tan 2ka \right] + \frac{1}{2} e^{-\kappa w} \left[1 - \frac{1}{2} \left(\frac{\kappa}{k} - \frac{k}{\kappa} \right) \tan 2ka \right], \\ Q &= \sinh \kappa w + \frac{1}{2} \left(\frac{\kappa}{k} - \frac{k}{\kappa} \right) \tan 2ka \cosh \kappa w \\ &= \frac{1}{2} e^{\kappa w} \left[1 + \frac{1}{2} \left(\frac{\kappa}{k} - \frac{k}{\kappa} \right) \tan 2ka \right] - \frac{1}{2} e^{-\kappa w} \left[1 - \frac{1}{2} \left(\frac{\kappa}{k} - \frac{k}{\kappa} \right) \tan 2ka \right], \\ \gamma &= \frac{1}{2} \left(\frac{\kappa}{k} + \frac{k}{\kappa} \right) \tan 2ka. \end{aligned} \quad (30)$$

The continuity of the probability density and the probability density current require

$$\begin{pmatrix} A_N \\ B_N \end{pmatrix} = \mathbf{M}^N \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \pm \begin{pmatrix} A_0 \\ B_0 \end{pmatrix}. \quad (31)$$

In particular, the *wave function* is not single valued for the case of the minus sign in the \pm above. The probability density and the probability density current, however, are single valued. Also, the wave function would diverge as $e^{pN\kappa w}$ as $x \rightarrow pN(2a+w)$ in the above, or as $\phi \rightarrow pN(2\pi)$ in the wave function of eq. (22), as $p \rightarrow \infty$; unless the coefficients of the $e^{+\kappa w}$ terms of P and Q above are precisely equal to zero, or at most of order $e^{-\kappa w}$. We are thus led to the requirement

$$\frac{1}{2} \left(\frac{\kappa}{k} - \frac{k}{\kappa} \right) \tan 2ka = -1 + 2\beta e^{-\kappa w}, \quad (32)$$

where the new parameter, β , may, like k and κ , in general, also be a function of the energy E . Eq. (32) will thus lead to a transcendental equation for the determination of the allowed values of the energy, E , where the parameter, β , must also be fixed to satisfy eq. (31). It will be instructive to examine first the case of high potential barriers, $V_0 \gg E$. This case will actually be of interest for the problems of internal hindered rotations in most molecules. In the limit $V_0 \rightarrow \infty$, we have a problem with N -potential wells with infinitely high walls. In that case we saw [eq. (19)] $ka = \frac{1}{2}n\pi$. For the N -fold periodic square well with large V_0 , we shall therefore try

$$2ka = n\pi + 2(\Delta k)a, \quad (33)$$

where $(\Delta k)a$ are small quantities, dependent on the integer n . Terms of second order in these small quantities will be negligible. Thus,

$$\cos 2ka \approx (-1)^n, \quad \tan 2ka \approx 2(\Delta k)a = -2 \frac{1}{\left(\frac{\kappa}{k} - \frac{k}{\kappa} \right)} (1 - 2\beta e^{-\kappa w}). \quad (34)$$

In the high barrier approximation, we have

$$e^{-\kappa w} \ll \frac{k}{\kappa} \ll 1.$$

With $\beta \approx \text{order}(1)$, we might thus expect the $\beta e^{-\kappa w}$ term to be negligible and obtain an energy shift, given by $(\Delta k)a \approx (-k/\kappa)$, of the $2N$ -fold degenerate zeroth-order energy of $E_n^{(0)} = (\hbar^2 n^2 \pi^2 / 8\mu a^2)$. [The factor 2 in the degeneracy factor, $2N$, comes from the \pm sign in the boundary condition of eq. (31).] Even though the splitting of the $2N$ -fold degenerate levels with $E \ll V_0$ will be smaller than the above shifts by a factor of $e^{-\kappa w}$, this splitting is of primary interest. We will therefore retain this factor in eq. (34). In the high barrier limit, $e^{-\kappa w} \ll (k/\kappa) \ll 1$, the 2×2 matrix \mathbf{M} reduces to

$$\mathbf{M} = (-1)^n \begin{pmatrix} \beta & \beta - 1 \\ \beta + 1 & \beta \end{pmatrix}. \quad (35)$$

For $N = 2$, the matrix needed for eq. (31) is

$$\mathbf{M}^2 = \begin{pmatrix} (2\beta^2 - 1) & 2\beta(\beta - 1) \\ 2\beta(\beta + 1) & (2\beta^2 - 1) \end{pmatrix}. \quad (36)$$

Eq. (31) then has allowed solutions for

$$\begin{aligned} \beta = +1, \quad & \text{with } \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}; \quad \begin{pmatrix} A_2 \\ B_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 4 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = +1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \\ \beta = -1, \quad & \text{with } \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad \begin{pmatrix} A_2 \\ B_2 \end{pmatrix} = \begin{pmatrix} 1 & 4 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = +1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \\ \beta = 0, \quad & \text{with } \begin{pmatrix} A_2 \\ B_2 \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = -1 \begin{pmatrix} A_0 \\ B_0 \end{pmatrix}, \\ & \text{where now } \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ or } \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \end{aligned} \quad (37)$$

For $N = 2$, three solutions exist for the allowed energies: two of them corresponding to $\beta = +1$ and $\beta = -1$ with but a single eigenfunction, corresponding to nondegenerate energy eigenvalues; and one with $\beta = 0$ with two independent solutions (which could be any linear combination of the above solutions), corresponding to a double degeneracy of this energy level. Expanding eq. (34) in powers of (k/κ) , but retaining the dominant energy splitting term, we obtain for $N = 2$

$$E_n = \frac{\hbar^2}{2\mu a^2} \left(\frac{n^2 \pi^2}{4} - n\pi \frac{k_n}{\kappa_n} + \frac{+2n\pi(k_n/\kappa_n)e^{-\kappa_n w}}{-2n\pi(k_n/\kappa_n)e^{-\kappa_n w}} \right), \quad (38)$$

where we can approximate (k_n/κ_n) by $\sqrt{(E_n^{(0)} / V_0)}$, but will retain the $E_n^{(0)}$ term in the exponential factor,

$$e^{-\kappa_n w} \approx e^{-[2\mu(V_0 - E_n^{(0)})w^2/\hbar^2]^{\frac{1}{2}}},$$

because of the sensitivity of the exponential factor on its exponent.

Next, for the three-fold periodic potential with $N = 3$, we have

$$\mathbf{M}^3 = (-1)^n \begin{pmatrix} \beta(4\beta^2 - 3) & (4\beta^2 - 1)(\beta - 1) \\ (4\beta^2 - 1)(\beta + 1) & \beta(4\beta^2 - 3) \end{pmatrix}. \quad (39)$$

The boundary condition of eq. (31) is satisfied for $\beta = +1$ and $\beta = -1$, with nondegenerate solutions

$$\begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \text{respectively,}$$

and for $\beta = +\frac{1}{2}$ and $\beta = -\frac{1}{2}$, where both of these lead to doubly degenerate levels with a linear combination of the above two solutions. The energy $E_n^{(0)}$ is thus split into four levels, a highest and a lowest nondegenerate level and two intermediate doubly degenerate levels.

At this stage, it should be mentioned that the splittings of the ground-state $n = 0$ internal rotation energies in the molecules, C_2H_4 and C_2H_6 , are too small to be observable. The factors, $e^{-\kappa_0 w}$, are too small to be observable in these molecules. In the methyl alcohol molecule, CH_3OH , however, the splittings of the $n = 0$ and higher levels are observable and have been studied extensively by microwave spectroscopy. In this molecule, the internal rotation degree of freedom is strongly coupled with the rotational degrees of freedom of the whole molecule. Since this molecule is an asymmetric rotator, (see Chapter 15), the combined rotation–internal rotation spectrum is very complicated.

For the case of general N , it will be convenient to introduce the new parameter α , via

$$\beta = \cos \alpha.$$

In terms of this new parameter, we have

$$\mathbf{M}^N = (-1)^{nN} \begin{pmatrix} \cos N\alpha & \frac{\sin N\alpha}{\sin \alpha}(\cos \alpha - 1) \\ \frac{\sin N\alpha}{\sin \alpha}(\cos \alpha + 1) & \cos N\alpha \end{pmatrix}. \quad (40)$$

Eqs. (36) and (39) show this is satisfied for $N = 2$ and $N = 3$. Also,

$$\begin{pmatrix} \cos(N-1)\alpha & \frac{\sin(N-1)\alpha}{\sin \alpha}(\cos \alpha - 1) \\ \frac{\sin(N-1)\alpha}{\sin \alpha}(\cos \alpha + 1) & \cos(N-1)\alpha \end{pmatrix} \begin{pmatrix} \cos \alpha & (\cos \alpha - 1) \\ (\cos \alpha + 1) & \cos \alpha \end{pmatrix} \\ = \begin{pmatrix} \cos N\alpha & \frac{\sin N\alpha}{\sin \alpha}(\cos \alpha - 1) \\ \frac{\sin N\alpha}{\sin \alpha}(\cos \alpha + 1) & \cos N\alpha \end{pmatrix}, \quad (41)$$

so that the relation (40) is proved by induction. In this general case, two nondegenerate levels again exist, with $\alpha = 0$, and $\alpha = \pi$, and now $(N - 1)$ doubly degenerate levels with

$$\alpha = \frac{\ell\pi}{N}; \quad \ell = 1, 2, \dots, (N - 1).$$

The energies for the case $E_n^{(0)} \ll V_0$ are given by

$$E_n = \frac{\hbar^2}{2\mu a^2} \left(\frac{n^2\pi^2}{4} - n\pi \sqrt{\frac{E_n^{(0)}}{V_0}} \left[1 - 2 \cos \frac{\ell\pi}{N} e^{-[2\mu(V_0 - E_n^{(0)})w^2/\hbar^2]^{\frac{1}{2}}} \right] \right)$$

$$\ell = 0, 1, \dots, N. \quad (42)$$

For very large N in a crystalline lattice, therefore, we have a set of $(N + 1)$ finely spaced, discrete, allowed energy values, centered about a slightly downward-shifted $E_n^{(0)}$. In the limit, $N \rightarrow \infty$, this becomes a continuous narrow band of allowed energies of bandwidth

$$\Delta E = \frac{\hbar^2}{ma^2} n^2 \pi^2 \sqrt{\frac{\hbar^2}{2ma^2 V_0}} e^{-[2m(V_0 - E_n^{(0)})w^2/\hbar^2]^{\frac{1}{2}}}, \quad (43)$$

where we have set $\mu = m$, the electron mass. These continuous bands of allowed energies are separated by energy gaps of order $(E_{n+1}^{(0)} - E_n^{(0)})$. As $E_n^{(0)}$ approaches V_0 , the bandwidths become larger and the gaps smaller. Of course, as $E_n^{(0)} \rightarrow V_0$, our high V_0 approximations are no longer valid. The bandwidth and gap structure, however, survives even into the region $E > V_0$. (For details, see, e.g., C. Kittel, *Introduction to Solid State Physics*, New York: John Wiley, 1956.) In a real solid, we must of course also deal with a 3-D structure. It is therefore perhaps interesting to note that in a cooler ring of some modern generation heavy ion accelerators we may approximate a truly 1-D crystal of cold (hence, nearly monoenergetic) heavy ions. In the limit of temperature, $T \rightarrow 0$, these form a 1-D crystal of equally spaced monoenergetic heavy ions. Here, indeed, the $(N + 1)^{\text{st}}$ ion is the 1st ion, and the periodic boundary condition of eq. (31) is no longer an approximation. Although the square well solution has all of the qualitative features found with a more realistic potential, an approximate solution for a more realistic $V(x)$ can be found through the WKB approximation to be treated in Chapters 36 and 37 (see, in particular, problem 55).

D The Existence of Discrete Energy Levels: General $V(x)$

For a $V(x)$ that is such that $V \rightarrow \infty$ for both large positive and large negative values of x , the existence of a discrete set of allowed energy levels follows in a general way from the requirement that the solutions be square-integrable, i.e.,

$$\int_{-\infty}^{+\infty} \psi^* \psi dx = \text{finite}, \quad (44)$$

and that ψ and $\frac{d\psi}{dx}$ be continuous. For the type of potential function shown in Fig. 4.5, with an arbitrary E , but $E > V_{\min.}$, we have in region I, with $E > V(x)$, between the left and right classical turning points,

$$\frac{d^2\psi}{dx^2} + k^2(x)\psi = 0. \quad (45)$$

In region I, therefore, the solutions are oscillatory, but with a variable (x -dependent) wavelength because $k(x) = \frac{2\pi}{\lambda}$; i.e., the curvature is always toward the x -axis. In

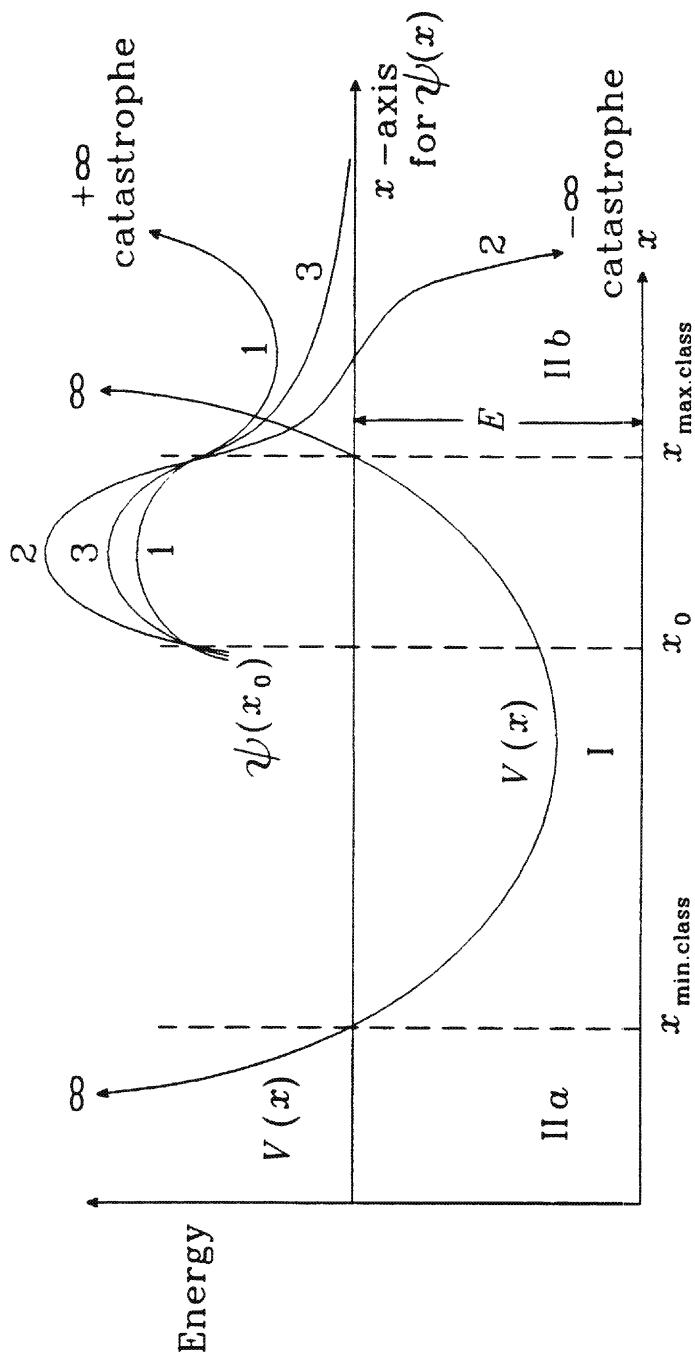


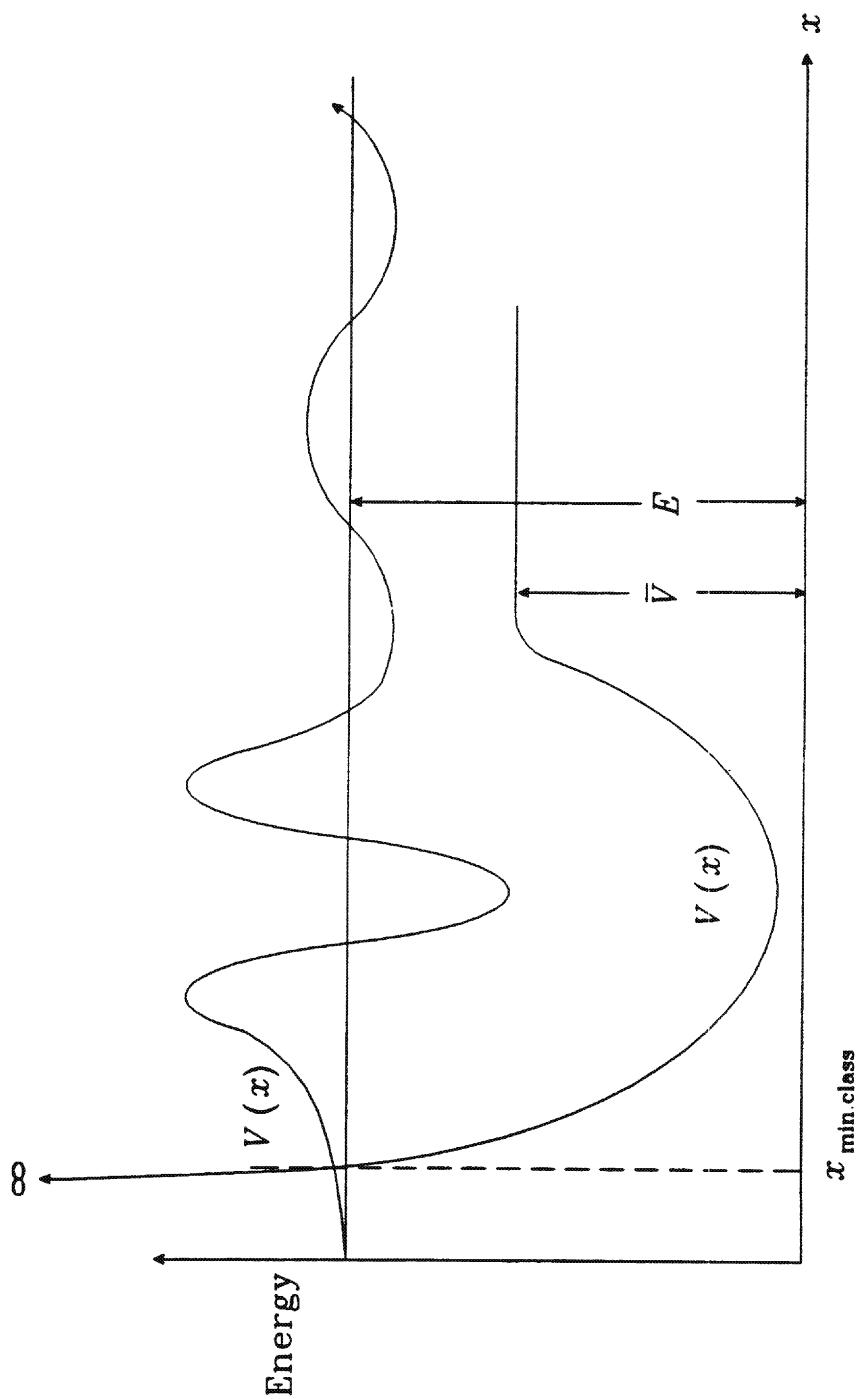
FIGURE 4.5. Solutions, $\psi(x)$, for three different initial conditions at x_0 .

regions II, conversely, for $x > x_{\text{max.class.}}$, or for $x < x_{\text{min.class.}}$, the Schrödinger equation has the form

$$\frac{d^2\psi}{dx^2} - \kappa^2(x)\psi = 0, \quad (46)$$

because $E < V(x)$. In regions II, therefore, the curvature is always away from the axis. To find a solution, start with some assumed initial value for $\psi(x_0)$ and $\frac{d\psi}{dx}|_{x_0}$. The equation then gives us the value of $\psi(x)$ and $\frac{d\psi}{dx}$ at the neighboring points. We could numerically determine the solution, say, from some x_0 in the classically allowed region to the right boundary, where the solution changes from one with curvature toward the axis to one with curvature away from the axis. For the solution, labeled 1, in Fig. 4.5, e.g., the curvature away from the axis will be such that $\psi(x)$ never reaches negative values. The function and its derivative will thus both get larger and larger as x reaches further away from the classically allowed values of x ; and both $\psi(x)$ and $\frac{d\psi}{dx}$ will go to $+\infty$ as $x \rightarrow +\infty$. This is a catastrophe. Such a function is surely not square-integrable. We can, however, start the process over again. Starting with the same $\psi(x_0)$ at x_0 , we can adjust the first derivative at x_0 , as in the curve, labeled 2. Now, as we reach the right classical turning point, the curvature away from the axis can be made less; perhaps we have chosen a derivative at x_0 such that now the solution in the classically forbidden region, IIa, reaches the value 0 and thereafter curves away from the axis becoming more and more negative along with its first derivative, so now both $\psi \rightarrow -\infty$ and $\frac{d\psi}{dx} \rightarrow -\infty$ as $x \rightarrow +\infty$. Again, we have a catastrophe. This solution cannot be square-integrable. We can, however, continue to adjust the first derivative at x_0 until it is just right, so both $\psi(x)$ and $\frac{d\psi}{dx} \rightarrow 0$ together as we penetrate into the classically forbidden region, $x \rightarrow +\infty$, as shown in the solution, labeled 3 in Fig. 4.5. This solution will have only a small probability the particle will be found in the classically forbidden region. This solution can now be continued from x_0 to more negative values of x , but because we have no further freedom of “fixing” the first derivative at x_0 , when the solution reaches the left turning point, it will undoubtedly curve away from the axis such that either both $\psi(x)$ and $\frac{d\psi}{dx} \rightarrow +\infty$ or both $\rightarrow -\infty$ as $x \rightarrow -\infty$. Again, a catastrophe: a nonsquare-integrable solution. For arbitrary values of E , therefore, we will not get an allowed (square-integrable) solution. We can now, however, further adjust the energy E such that once we have fixed the proper behavior as $x \rightarrow +\infty$ we will also have both $\psi(x)$ and $\frac{d\psi}{dx} \rightarrow 0$ as $x \rightarrow -\infty$. This unique situation can only occur for a discrete set of values of E , the allowed values of E : $E_0, E_1, E_2, \dots, E_n, \dots$. This situation exists for a $V(x)$, which $\rightarrow +\infty$ for both $x \rightarrow \pm\infty$.

In Fig. 4.6, we show a potential function that for $E > \bar{V} = V_\infty$ has only a left classically forbidden region. For such a $V(x)$, for $E > \bar{V}$, we can always fix the solution such that both $\psi(x)$ and $\frac{d\psi}{dx}$ together $\rightarrow 0$ as $x \rightarrow -\infty$. For such a potential, all values of $E > \bar{V}$ are allowed. As $x \rightarrow +\infty$, the solution remains oscillatory. The $\psi(x)$ is not square integrable, but the solution has a sensible probability interpretation. It now corresponds to a particle with finite kinetic energy coming in from $+\infty$ being reflected near $x = 0$ and going back out to $+\infty$. This

FIGURE 4.6. $V(x)$ with a continuous spectrum for $E > \bar{V} = V_\infty$.

is a scattering problem, associated with the continuum of allowed energies. The wave function is now normalized to describe a definite flux (value of \vec{S}). Because the solution $\psi(x)$ again has a sensible probability interpretation for values of x as $x \rightarrow +\infty$ for all values of $E > \bar{V}$, all values of $E > \bar{V}$ are allowed leading to a continuum of allowed energies.

Finally, in Fig. 4.7, another potential is shown, of the type perhaps describing the motion of an α -particle relative to a heavy nucleus. For $E > \bar{V} = V_\infty$, we again have an energy continuum; for values of $\bar{V} < E < V_{\text{barrier}}$ and arbitrary values of E , however, we would expect a much greater probability the particle be in region III, outside the barrier. Now, certain states will exist, with a narrow width (narrow range ΔE) about a discrete E for which the probability of finding the particle in region I rather than in region III is overwhelmingly large. These states are the virtually bound states. They are, however, part of the energy continuum and have a finite (perhaps very small) probability the particle will tunnel through the barrier and stream out to $+\infty$ (see problem 8).

E The Energy Eigenvalue Problem: General

For potentials with a discrete spectrum of allowed energy values (as in Fig. 4.5), the Schrödinger equation leads to the allowed solutions

$$H\psi_n(x) = E_n\psi_n(x), \quad (47)$$

with allowed energy values, E_n , the so-called eigenvalues, or characteristic values of E .

1. If the Hamiltonian operator is hermitian, $H = H^\dagger$, the E_n are real.

$$\begin{aligned} & \langle \psi_n, H\psi_n \rangle = E_n \langle \psi_n, \psi_n \rangle = E_n \\ & = \langle (H^\dagger \psi_n), \psi_n \rangle = \langle (H\psi_n), \psi_n \rangle = \langle \psi_n, H\psi_n \rangle^* = E_n^*. \end{aligned} \quad (48)$$

2. The orthogonality of the eigenfunctions, ψ_n , follows from

$$H\psi_n = E_n\psi_n, \quad (49)$$

and

$$H\psi_m^* = E_m\psi_m^*. \quad (50)$$

By multiplying the first of these equations by ψ_m^* , the second by ψ_n , and subtracting, we get

$$\langle \psi_m, H\psi_n \rangle - \langle \psi_n, H\psi_m \rangle^* = (E_n - E_m) \langle \psi_m, \psi_n \rangle. \quad (51)$$

The left-hand side of this equation is zero via the hermiticity of H , so

$$(E_n - E_m) \langle \psi_m, \psi_n \rangle = 0. \quad (52)$$

Thus, with $E_n \neq E_m$, $\langle \psi_m, \psi_n \rangle = 0$. The eigenfunctions are orthogonal to each other.

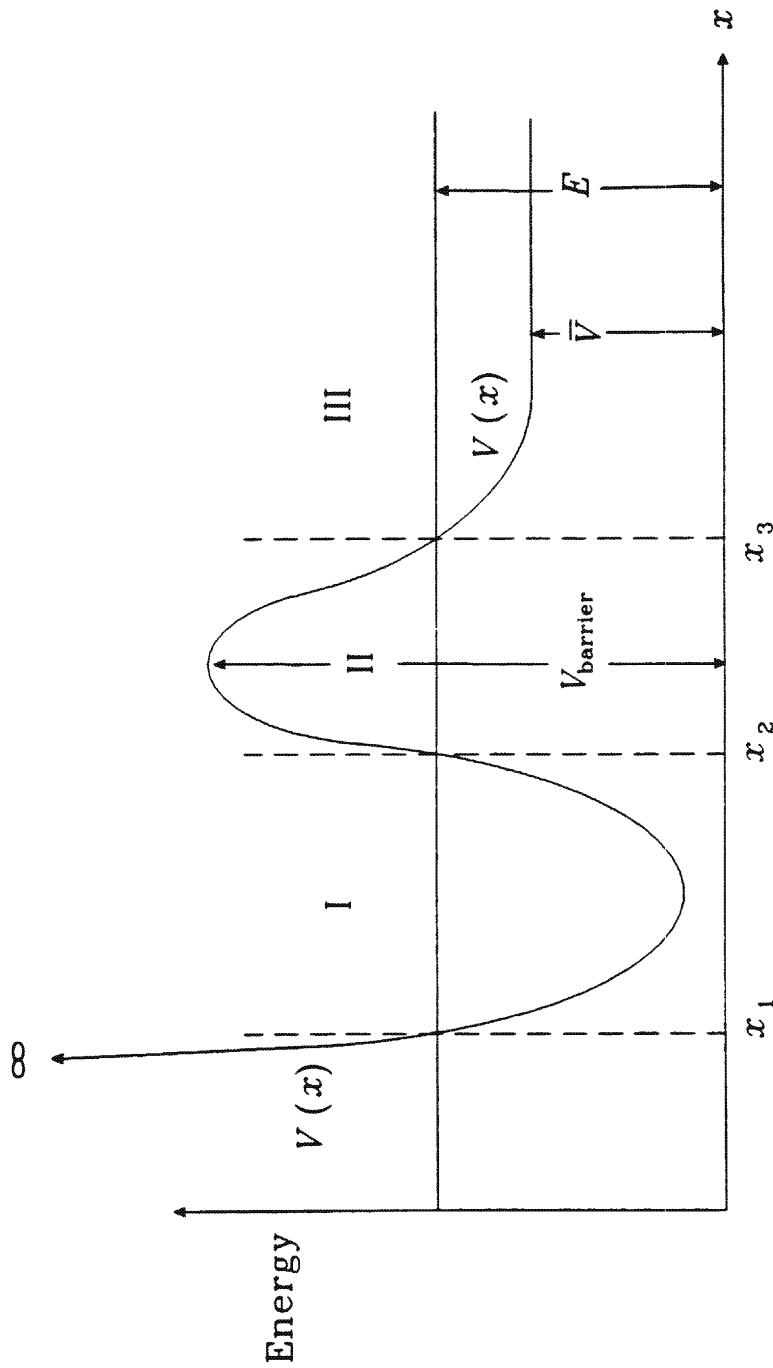


FIGURE 4.7. $V(x)$ with possible virtually bound states for $\bar{V} < E < V_{\text{barrier}}$.

F A Specific Example: The One-Dimensional Harmonic Oscillator

The Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dq^2} \psi(q) + \frac{m\omega_0^2}{2} q^2 \psi(q) = E \psi(q). \quad (53)$$

As a first step in the solution, it will be convenient to introduce a dimensionless coordinate x ; i.e., to define appropriately scaled coordinates. Thus, the physical displacement, q , will be transformed into a dimensionless coordinate, x , where the “yardstick” for q can be obtained from the value of the potential energy which must be proportional to the basic energy scale of the problem, $m\omega_0^2 q^2 = \text{const.}(\hbar\omega_0)$, so a natural yardstick for q is $\sqrt{\hbar/m\omega_0}$:

$$q = \sqrt{\frac{\hbar}{m\omega_0}} x. \quad (54)$$

Similarly,

$$p = \sqrt{\hbar m\omega_0} p_x, \quad p_x = \frac{1}{i} \frac{d}{dx}, \quad (55)$$

$$E = \hbar\omega_0\epsilon, \quad (56)$$

and the wave equation becomes

$$-\frac{1}{2} \frac{d^2}{dx^2} \psi(x) + \frac{1}{2} x^2 \psi(x) = \epsilon \psi(x). \quad (57)$$

The equation has a singular point only at $x = \pm\infty$. The first step is to find the asymptotic form of the solution at $\pm\infty$. The $\epsilon\psi(x)$ term of eq. (57) is negligible compared with the $x^2\psi(x)$ term as $x \rightarrow \pm\infty$. Because

$$\begin{aligned} \frac{d^2}{dx^2} \left(e^{-\frac{x^2}{2}} \right) &= (x^2 - 1)e^{-\frac{x^2}{2}} \rightarrow x^2 e^{-\frac{x^2}{2}} \quad \text{as } x \rightarrow \pm\infty, \\ \psi(x) &\rightarrow e^{-\frac{x^2}{2}} \quad \text{as } x \rightarrow \pm\infty. \end{aligned} \quad (58)$$

(The second possible solution with a + exponential is ruled out by the boundary condition.) We transform the solution into

$$\psi(x) = u(x) e^{-\frac{x^2}{2}}, \quad (59)$$

$$\frac{d^2 u}{dx^2} - 2x \frac{du}{dx} + (2\epsilon - 1)u(x) = 0. \quad (60)$$

For $u(x)$, try a series solution

$$u(x) = \sum_{k=0} a_k x^k, \quad (61)$$

where

$$\sum_{k=2} a_k k(k-1)x^{k-2} = \sum_{k=0} (2k+1-2\epsilon)a_k x^k. \quad (62)$$

Changing the dummy summation index on the left-hand side from $k \rightarrow (k+2)$ and equating coefficients of the k^{th} term leads to the two-term recursion relation

$$\frac{a_{k+2}}{a_k} = \frac{2k+1-2\epsilon}{(k+2)(k+1)}. \quad (63)$$

To examine the behavior of this infinite series at large values of x , look at the asymptotic form as $k \rightarrow \infty$. This form is

$$\frac{a_{k+2}}{a_k} \rightarrow \frac{2}{k} \quad (64)$$

or

$$a_{2m} \rightarrow \frac{1}{m!}, \quad (65)$$

so we would have

$$u(x) \rightarrow e^{+x^2}. \quad (66)$$

Thus, for general values of ϵ , $\psi(x) \rightarrow \infty$, we do not have a square-integrable solution. For the special value

$$2\epsilon = (2n+1), \quad (67)$$

the infinite series of eq. (61) can terminate at the n^{th} term. If n is an even integer and $a_0 \neq 0$, the recursion formula of eq. (63) yields $a_{n+2} = 0$, and, therefore, $a_m = 0$ with $m = n+2k$. If n is an even integer, and if we had $a_1 \neq 0$, however, all a_m with odd integers m would survive up to $m \rightarrow \infty$, and the infinite series would again diverge as e^{+x^2} . If n is an even integer, we must therefore have $a_1 = 0$. Similarly, if n is an odd integer, we must have $a_0 = 0$. The series therefore terminates

$$\begin{aligned} &\text{with } n = \text{even, } a_0 \neq 0, \quad a_1 = 0, \quad a_{n+2} = 0, \\ &\text{with } n = \text{odd, } a_1 \neq 0, \quad a_0 = 0, \quad a_{n+2} = 0. \end{aligned} \quad (68)$$

For these cases, the wave functions of eqs. (59) and (61) are square-integrable and lead to the discrete set of allowed energy eigenvalues

$$2\epsilon = (2n+1); \quad E = \hbar\omega_0(n + \frac{1}{2}). \quad (69)$$

To find the coefficients of the polynomial of degree n , invert the recursion relation:

$$\frac{a_{k-2}}{a_k} = -\frac{k(k-1)}{2(n-k+2)}, \quad (70)$$

leading to

$$\frac{a_{n-2j}}{a_n} = (-1)^j \frac{n(n-1)\cdots(n-2j+2)(n-2j+1)}{2^j 2 \cdot 4 \cdots (2j-2)2j}$$

$$= (-1)^j \frac{n!}{(n-2j)! 2^j j!}. \quad (71)$$

With $a_n = 2^n$, this solution is the standard Hermite polynomial, $H_n(x)$,

$$H_n(x) = \sum_{j=0}^{\lfloor \frac{n}{2} \rfloor} (-1)^j \frac{2^{n-2j} n!}{j!(n-2j)!} x^{n-2j}. \quad (72)$$

The Hermite polynomial can be defined in three ways:

1. Through the regular solutions of the differential equation:

$$H_n''(x) - 2xH_n'(x) + 2nH_n(x) = 0. \quad (73)$$

2. Through a generating function, where the parameter, s , may be an arbitrary complex number:

$$e^{-s^2+2sx} = \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} s^n. \quad (74)$$

3. Through a differential relation, or a Rodrigues-type formula:

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} (e^{-x^2}). \quad (75)$$

Thus,

$$E_n = \hbar\omega_0(n + \frac{1}{2}), \quad \psi_n(x) = N_n H_n(x) e^{-\frac{x^2}{2}}. \quad (76)$$

The normalization constant, N_n , can be evaluated most simply through the Rodrigues-type formula

$$\begin{aligned} |N_n|^2 \int_{-\infty}^{\infty} dx H_n^2(x) e^{-x^2} &= |N_n|^2 \int_{-\infty}^{\infty} dx H_n(x) (-1)^n \frac{d^n}{dx^n} (e^{-x^2}) \\ &= |N_n|^2 \int_{-\infty}^{\infty} dx (e^{-x^2}) \left(\frac{d^n}{dx^n} H_n(x) \right) = |N_n|^2 \int_{-\infty}^{\infty} dx e^{-x^2} n! a_n \\ &= |N_n|^2 \sqrt{\pi} n! 2^n = 1. \end{aligned} \quad (77)$$

Here, we have integrated by parts n times and have used the fact that the integrated parts, to be evaluated at $\pm\infty$, are all dominated by the factor e^{-x^2} . Choosing N_n to be real

$$N_n = \sqrt{\frac{1}{n! 2^n \sqrt{\pi}}}. \quad (78)$$

Final note: Sometimes it is necessary to normalize the wave function in real, physical space, i.e., with

$$\int_{-\infty}^{\infty} dq \psi^* \psi = 1. \quad (79)$$

Then,

$$N_n = \sqrt{\frac{1}{n! 2^n} \sqrt{\frac{m\omega_0}{\hbar\pi}}}. \quad (80)$$

5

Harmonic Oscillator Calculations

A The Bargmann Transform

For many calculations involving 1-D harmonic oscillator wave functions, it is useful to introduce the Bargmann transform through the kernel function

$$A(k, x) = \frac{1}{\pi^{\frac{1}{4}}} \exp(-\frac{1}{2}k^2 + \sqrt{2}kx - \frac{1}{2}x^2), \quad (1)$$

where k is a complex number. Given a square-integrable function, $\psi(x)$, its Bargmann transform, $F(k)$, is given by

$$F(k) = \int_{-\infty}^{\infty} dx \psi(x) A(k, x), \quad (2)$$

where

$$\psi(x) = \frac{1}{\pi} \int d^2k e^{-kk^*} A(k^*, x) F(k), \quad (3)$$

and the integral is over the 2-D complex k -plane; i.e., with $k = a + ib$,

$$\int d^2k \equiv \int_{-\infty}^{\infty} da \int_{-\infty}^{\infty} db. \quad (4)$$

Now, from the definition of $A(k, x)$ and the generating function definition for the Hermite polynomials, with $s = k/\sqrt{2}$,

$$A(k, x) = \sum_{n=0} \left(\frac{H_n(x)}{\sqrt{n!} 2^n \sqrt{\pi}} e^{-\frac{1}{2}x^2} \right) \frac{k^n}{\sqrt{n!}} = \sum_{n=0} \psi_n(x) \frac{k^n}{\sqrt{n!}}. \quad (5)$$

We therefore see

$$\psi_n(x) \quad \text{has Bargmann transform} \quad \frac{k^n}{\sqrt{n!}}. \quad (6)$$

We can transform a scalar product from x -space into k -space, or from k -space into x -space:

$$\begin{aligned} & \frac{1}{\pi} \int d^2k e^{-kk^*} F_1^*(k) F_2(k) \\ &= \frac{1}{\pi} \int d^2k e^{-kk^*} \int dx \psi^{(1)}(x)^* A(k^*, x) \int dx' \psi^{(2)}(x') A(k, x') \\ &= \int dx \psi^{(1)}(x)^* \psi^{(2)}(x), \end{aligned} \quad (7)$$

where we have used, again with $k = a + ib$,

$$\begin{aligned} & \frac{1}{\pi} \int d^2k e^{-kk^*} A(k^*, x) A(k, x') \\ &= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} da e^{-[i\sqrt{2}a - \frac{(x-x')}{2}]^2} e^{-[\frac{(x-x')}{2}]^2} \frac{1}{\pi} \int_{-\infty}^{\infty} db e^{i\sqrt{2}b(x' - x)} \\ &= e^{-[\frac{(x-x')}{2}]^2} \frac{1}{2\pi} \int_{-\infty}^{\infty} db' e^{ib'(x' - x)} = \delta(x' - x). \end{aligned} \quad (8)$$

In the last step, we have used

$$f(x)\delta(x) = f(0)\delta(x). \quad (9)$$

Eq. (7) thus permits us to evaluate a scalar product either in x -space or in k -space. At times, the latter may lead to the easier integral.

B Completeness Relation

The delta-function property of the integral of eq. (8) is also useful to prove the completeness of the set of harmonic oscillator eigenfunctions $\psi_n(x)$. An arbitrary 1-D square-integrable function, $\Psi(x)$, can be expanded in a generalized Fourier series in oscillator eigenfunctions, $\psi_n(x)$,

$$\Psi(x) = \sum_{n=0}^{\infty} c_n \psi_n(x), \quad (10)$$

with coefficient, c_n , evaluated by the Fourier inversion theorem

$$c_n = \int_{-\infty}^{\infty} dx' \Psi(x') \psi_n^*(x'); \quad (11)$$

so

$$\Psi(x) = \sum_{n=0}^{\infty} \int_{-\infty}^{\infty} dx' \Psi(x') \psi_n(x) \psi_n^*(x'). \quad (12)$$

This requires

$$\sum_{n=0}^{\infty} \psi_n(x) \psi_n^*(x') = \delta(x - x'). \quad (13)$$

This is the completeness relation we want to prove. Substituting eq. (5) into the left-hand side of eq. (8), we get

$$\begin{aligned} \frac{1}{\pi} \int d^2k e^{-kk^*} \sum_{n=0}^{\infty} \psi_n^*(x) \frac{k^{*n}}{\sqrt{n!}} \sum_{m=0}^{\infty} \psi_m(x') \frac{k^m}{\sqrt{m!}} = \\ \frac{1}{\pi} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{\psi_n^*(x) \psi_m(x')}{\sqrt{n! m!}} \int d^2k e^{-kk^*} k^{*n} k^m. \end{aligned} \quad (14)$$

Doing the integral in polar coordinates, with $k = \rho e^{i\phi}$,

$$\begin{aligned} \int d^2k e^{-k^*k} k^{*n} k^m &= \int_0^\infty d\rho \rho e^{-\rho^2} \rho^{n+m} \int_0^{2\pi} d\phi e^{i(m-n)\phi} \\ &= \int_0^\infty d\rho \rho e^{-\rho^2} \rho^{n+m} 2\pi \delta_{nm} = \pi n! \delta_{nm}. \end{aligned} \quad (15)$$

Combining eqs. (8) and (14) leads to the needed completeness relation given by eq. (13).

C A Second Useful Application: The matrix $(x)_{nm}$

As a second example, we will use the Bargmann kernel to calculate the following useful integral

$$\int_{-\infty}^{\infty} dx \psi_n^*(x) x \psi_m(x) = \langle \psi_n^*, x \psi_m \rangle \equiv (x)_{nm}. \quad (16)$$

With $m = n$ this integral would be needed to calculate the expectation value of x in the n^{th} eigenstate. Because in that case the integrand is an odd function of x , this expectation value is zero. The particle is equally likely to be in the right half or the left half of the x domain. For general n, m , the two-index quantity defined as $(x)_{nm}$ in eq. (16) will be shown to be a matrix in Chapter 6. For general n, m , we can evaluate the needed integral by considering the integral

$$\int_{-\infty}^{\infty} dx A(l^*, x) x A(k, x) \quad (17)$$

as a function of the arbitrary complex parameters k and l^* in two ways

$$\begin{aligned} \int_{-\infty}^{\infty} dx A(l^*, x) x A(k, x) &= \sum_{n,m} \frac{l^{*n}}{\sqrt{n!}} \frac{k^m}{\sqrt{m!}} \int_{-\infty}^{\infty} dx \psi_n^*(x) x \psi_m(x) \\ &= \frac{1}{\sqrt{\pi}} e^{l^* k} \int_{-\infty}^{\infty} dx' x' e^{-[x - \frac{1}{\sqrt{2}}(l^* + k)]^2} = \frac{1}{\sqrt{\pi}} e^{l^* k} \int_{-\infty}^{\infty} dx' \left(x' + \frac{1}{\sqrt{2}}(l^* + k) \right) e^{-x'^2} \end{aligned}$$

$$\begin{aligned}
&= \frac{1}{\sqrt{2}}(l^* + k)e^{l^*k} = \frac{1}{\sqrt{2}} \sum_{n=0} \frac{(l^{*n+1}k^n + l^{*n}k^{n+1})}{n!} \\
&= \frac{1}{\sqrt{2}} \left(\sum_{n=1} \frac{l^{*n}k^{n-1}}{(n-1)!} + \sum_{n=0} \frac{l^{*n}k^{n+1}}{n!} \right).
\end{aligned} \tag{18}$$

The only surviving terms are those in which the powers of k , viz., m , differ from n by ± 1 . Therefore

$$\begin{aligned}
\int_{-\infty}^{\infty} dx \psi_n^*(x) x \psi_m(x) &= 0 \quad \text{for } m \neq (n \pm 1) \\
&= \sqrt{\frac{(n+1)}{2}} \quad \text{for } m = (n+1) \\
&= \sqrt{\frac{n}{2}} \quad \text{for } m = (n-1).
\end{aligned} \tag{19}$$

Problems

- 9.** For the 1-D harmonic oscillator, calculate all nonzero matrix elements of q^2 , p , and p^2 (for the nonzero matrix elements of q , see eq. (19) above). For a general state

$$\Psi(q, t) = \sum_n c_n \psi_n(q) e^{-\frac{i}{\hbar} E_n t},$$

calculate $\langle q \rangle$, $\langle q^2 \rangle$, $\langle p \rangle$, $\langle p^2 \rangle$, Δq , and Δp as functions of the c_n . Try to determine values of c_n for which the product $(\Delta p)(\Delta q)$ is a minimum. (Hint: Try $c_0 = 1$, all other $c_n = 0$.) For the special case

$$c_0 = \frac{1}{\sqrt{2}}, \quad c_1 = \frac{i}{\sqrt{2}},$$

calculate $\langle q \rangle$, $\langle q^2 \rangle$, and Δq as functions of the time, t . For this special case, also calculate \vec{S} ; that is, calculate as a function of q and t the probability per unit time and unit area normal to the displacement, q , that the particle is streaming in the direction of q .

- 10.** A particle of mass, m , in a 1-D harmonic oscillator potential has a probability density amplitude at $t = 0$, specified by the initial value

$$\Psi(q, t = 0) = \left[\frac{m\omega_0}{\hbar\pi} \right]^{\frac{1}{4}} e^{-\frac{1}{2} \frac{m\omega_0}{\hbar}(q - q_0)^2},$$

that is, by the $n = 0$ eigenfunction displaced by a distance q_0 . Calculate $P(E_n)$, the probability the particle is in an energy eigenstate with energy E_n at $t = 0$ as a function of $x_0 = q_0/\sqrt{\hbar/m\omega_0}$ and n . [Check that $P(E_n) \rightarrow \delta_{n0}$, as $q_0 \rightarrow 0$.] Calculate $\Psi\Psi^*$ at a later time, t , and discuss the motion of the particle. Note: You may be able to sum an infinite series by using the generating function definition

of the Hermite polynomials, $H_n(x)$, or the Bargmann kernel expansion

$$A(k, x) = \sum_{n=0}^{\infty} \psi_n(x) \frac{k^n}{\sqrt{n!}}.$$

11. Repeat problem 10 for the case when

$$\Psi(q, t = 0) = \left[\frac{m\omega_0}{\hbar\pi} \right]^{\frac{1}{4}} \sqrt{\frac{2m\omega_0}{\hbar}} (q - q_0) e^{-\frac{1}{2} \frac{m\omega_0}{\hbar} (q - q_0)^2},$$

that is, by the $n = 1$ eigenfunction displaced by a distance q_0 , or for the case when

$$\Psi(q, t = 0) = \psi_n(q - q_0)$$

for arbitrary n .

Solution for Problem 11

a. The case $n = 1$: Let us write Ψ at $t = 0$ in terms of the dimensionless x and x_0

$$\begin{aligned} \Psi(x, 0) &= \frac{2(x - x_0)}{\sqrt{2}\pi^{\frac{1}{4}}} e^{-\frac{1}{2}(x-x_0)^2} = \sqrt{2}(x - x_0) e^{-\frac{1}{4}x_0^2} \frac{e^{-\frac{1}{2}\left(\frac{x_0}{\sqrt{2}}\right)^2 + \sqrt{2}x\frac{x_0}{\sqrt{2}} - \frac{1}{2}x^2}}{\pi^{\frac{1}{4}}} \\ &= \sqrt{2}(x - x_0) e^{-\frac{1}{4}x_0^2} A\left(\frac{x_0}{\sqrt{2}}, x\right) = \sqrt{2}(x - x_0) e^{-\frac{1}{4}x_0^2} \sum_{n=0}^{\infty} \frac{\psi_n(x)}{\sqrt{n!}} \left(\frac{x_0}{\sqrt{2}}\right)^n, \end{aligned} \quad (1)$$

where we have used the expansion of the Bargmann kernel function, $A(k, x)$, with $k = x_0/\sqrt{2}$, in terms of the normalized $\psi_n(x)$. If we further use

$$x\psi_n(x) = \sqrt{\frac{(n+1)}{2}}\psi_{n+1}(x) + \sqrt{\frac{n}{2}}\psi_{n-1}(x), \quad (2)$$

the above yields

$$\begin{aligned} \Psi(x, 0) &= e^{-\frac{1}{4}x_0^2} \left(-\sqrt{2}x_0 \sum_{n=0}^{\infty} \frac{\psi_n(x)}{\sqrt{n!}} \left(\frac{x_0}{\sqrt{2}}\right)^n \right. \\ &\quad \left. + \sum_{n=0}^{\infty} \sqrt{(n+1)} \frac{\psi_{n+1}(x)}{\sqrt{n!}} \left(\frac{x_0}{\sqrt{2}}\right)^n + \sum_{n=1}^{\infty} \sqrt{n} \frac{\psi_{n-1}(x)}{\sqrt{n!}} \left(\frac{x_0}{\sqrt{2}}\right)^n \right) \\ &= e^{-\frac{1}{4}x_0^2} \sum_{n=0}^{\infty} \left(-\sqrt{2}x_0 \frac{\psi_n(x)}{\sqrt{n!}} \left(\frac{x_0}{\sqrt{2}}\right)^n \right. \\ &\quad \left. + n \frac{\psi_n(x)}{\sqrt{n!}} \left(\frac{x_0}{\sqrt{2}}\right)^{n-1} + \frac{x_0}{\sqrt{2}} \frac{\psi_n(x)}{\sqrt{n!}} \left(\frac{x_0}{\sqrt{2}}\right)^n \right), \end{aligned} \quad (3)$$

where we have shifted indices $n \rightarrow (n-1)$ and $n \rightarrow (n+1)$ in the last two sums above. (The second sum is proportional to a factor n and thus begins at $n = 1$.) We have therefore expanded our $\Psi(x, 0)$ in terms of the $\psi_n(x)$

$$\Psi(x, 0) = \sum_n c_n \psi_n(x), \quad \text{with } c_n = \frac{e^{-\frac{1}{4}x_0^2}}{\sqrt{n!}} \left(\frac{x_0}{\sqrt{2}}\right)^{n-1} \left(n - \frac{1}{2}x_0^2\right). \quad (4)$$

At a later time, we have

$$\begin{aligned}\Psi(x, t) &= \sum_n c_n \psi_n(x) e^{-i\omega_0(n+\frac{1}{2})t} \\ &= e^{-\frac{i}{2}\omega_0 t} \sum_n e^{-\frac{1}{4}x_0^2} \frac{\sqrt{2}}{x_0} \left(n - \frac{x_0^2}{2}\right) \left(\frac{x_0 e^{-i\omega_0 t}}{\sqrt{2}}\right)^n \frac{\psi_n(x)}{\sqrt{n!}}.\end{aligned}\quad (5)$$

We can now sum these infinite series, using the expansion of the Bargmann kernel function, through

$$\begin{aligned}\sum_{n=0}^{\infty} \frac{\psi_n(x)}{\sqrt{n!}} k^n &= A(k, x) = \frac{1}{\pi^{\frac{1}{4}}} e^{-\frac{1}{2}k^2 + \sqrt{2}kx - \frac{1}{2}x^2} \\ \sum_{n=1}^{\infty} n \frac{\psi_n(x)}{\sqrt{n!}} k^{n-1} &= \frac{dA(k, x)}{dk} = (-k + \sqrt{2}x)A(k, x),\end{aligned}\quad (6)$$

now with $k = (x_0 e^{-i\omega_0 t} / \sqrt{2})$. This yields

$$\begin{aligned}\Psi(x, t) &= e^{-\frac{i}{2}\omega_0 t} \left(\left[-\left(\frac{x_0}{\sqrt{2}} e^{-i\omega_0 t}\right) + \sqrt{2}x \right] e^{-i\omega_0 t} - \frac{x_0}{\sqrt{2}} \right) \\ &\quad \times e^{-\frac{1}{4}x_0^2} \left[\frac{e^{-\frac{1}{4}x_0^2 e^{-2i\omega_0 t} + xx_0 e^{-i\omega_0 t} - \frac{1}{2}x^2}}{\pi^{\frac{1}{4}}} \right] \\ &= e^{-\frac{i}{2}\omega_0 t} \left(e^{-i\omega_0 t} \left[\frac{2(x - x_0 \cos \omega_0 t)}{\sqrt{2}} \right] \right) \\ &\quad \times \frac{e^{-\frac{1}{2}(x - x_0 \cos \omega_0 t)^2} e^{-ix_0 \sin \omega_0 t(x - \frac{1}{2}x_0 \cos \omega_0 t)}}{\pi^{\frac{1}{4}}} \\ &= e^{-i\frac{3}{2}\omega_0 t} \frac{2(x - x_0 \cos \omega_0 t)}{\sqrt{2}\pi^{\frac{1}{4}}} e^{-\frac{1}{2}(x - x_0 \cos \omega_0 t)^2} e^{-ix_0 \sin \omega_0 t(x - \frac{1}{2}x_0 \cos \omega_0 t)}. \quad (7)\end{aligned}$$

Therefore,

$$|\Psi(x, t)|^2 = 2 \frac{(x - x_0 \cos \omega_0 t)^2}{\sqrt{\pi}} e^{-(x - x_0 \cos \omega_0 t)^2} = |\psi_1(x - x_0 \cos \omega_0 t)|^2; \quad (8)$$

that is, the probability density is that of the $n = 1$ state, but it oscillates about the origin with the oscillator frequency, (ω_0), with amplitude x_0 , and without change of shape.

Our derivation so far has made use of some simple properties of harmonic oscillator eigenfunctions, [see eq. (2)], and the expansion of the Bargmann kernel function in terms of the $\psi_n(x)$, or, what would be equivalent, the generating function definition of the Hermite polynomials.

b. The case of arbitrary n : To generalize our result to a function $\Psi(x, 0) = \psi_n(x - x_0)$ with arbitrary n , it may prove more convenient to work with the Bargmann transform of $\psi_n(x - x_0)$:

$$F_n(k) = \int_{-\infty}^{\infty} dx \psi_n(x - x_0) A(k, x) = \int_{-\infty}^{\infty} dx' \psi_n(x') A(k, x' + x_0)$$

$$\begin{aligned}
&= e^{\sqrt{2}kx_0 - \frac{1}{2}x_0^2} \int_{-\infty}^{\infty} dx' \psi_n(x') e^{-\frac{1}{2}k^2 - \frac{1}{2}x'^2 + \sqrt{2}(k - \frac{x_0}{\sqrt{2}})x'} \\
&= e^{-\frac{1}{4}x_0^2 + \frac{1}{\sqrt{2}}kx_0} \int_{-\infty}^{\infty} dx' \psi_n(x') A\left(k - \frac{x_0}{\sqrt{2}}, x'\right) \\
&= e^{-\frac{1}{4}x_0^2 + \frac{1}{\sqrt{2}}kx_0} \int_{-\infty}^{\infty} dx' \psi_n(x') \sum_{N=0}^{\infty} \frac{\psi_N(x')}{\sqrt{N!}} \left(k - \frac{x_0}{\sqrt{2}}\right)^N \\
&= e^{-\frac{1}{4}x_0^2 + \frac{1}{\sqrt{2}}kx_0} \frac{\left(k - \frac{x_0}{\sqrt{2}}\right)^n}{\sqrt{n!}}, \tag{9}
\end{aligned}$$

where we have used the reality and the orthonormality of the harmonic oscillator eigenfunctions. To obtain the expansion coefficients, $c_m^{(n)}$,

$$c_m^{(n)} = \int_{-\infty}^{\infty} dx \psi_m^*(x) \psi_n(x - x_0) = \frac{1}{\pi} \int d^2 k e^{-kk^*} F_n(k) \frac{k^{*m}}{\sqrt{m!}}, \tag{10}$$

it is sufficient to expand $F_n(k)$ in powers of k and use the k -space orthonormality relation

$$\frac{1}{\pi} \int d^2 k e^{-kk^*} \frac{k^m}{\sqrt{m!}} \frac{k^{*l}}{\sqrt{l!}} = \delta_{ml}. \tag{11}$$

For this purpose, therefore, we expand

$$\begin{aligned}
F_n(k) &= e^{-\frac{1}{4}x_0^2 + \frac{x_0}{\sqrt{2}}k} \frac{\left(k - \frac{x_0}{\sqrt{2}}\right)^n}{\sqrt{n!}} \\
&= e^{-\frac{1}{4}x_0^2} \frac{1}{\sqrt{n!}} \sum_{b=0}^{\infty} \sum_{a=0}^n \frac{1}{b!} \left(\frac{x_0}{\sqrt{2}}\right)^b \frac{n!}{a!(n-a)!} \left(-\frac{x_0}{\sqrt{2}}\right)^{n-a} k^{a+b} \\
&= \sum_{m=0}^{\infty} \left[\frac{1}{\sqrt{n!}} e^{-\frac{1}{4}x_0^2} \sum_{a=0}^n \frac{n!}{a!(n-a)!} \frac{(-1)^{n-a}}{(m-a)!} \left(\frac{x_0}{\sqrt{2}}\right)^{n+m-2a} \right] k^m, \tag{12}
\end{aligned}$$

so

$$c_m^{(n)} = \frac{1}{\sqrt{n!}} \frac{1}{\sqrt{m!}} e^{-\frac{1}{4}x_0^2} \sum_{a=0}^n (-1)^{n-a} \frac{n!}{a!(n-a)!} \frac{m!}{(m-a)!} \left(\frac{x_0}{\sqrt{2}}\right)^{n+m-2a}. \tag{13}$$

For the time-dependent function, we then get

$$\Psi(x, t) = \sum_m c_m^{(n)} \psi_m(x) e^{-i\omega_0(m+\frac{1}{2})t}, \tag{14}$$

and we could perform the m sums via

$$\sum_m \frac{m!}{(m-a)!} \psi_m(x) \frac{k^m}{\sqrt{m!}} = \frac{d^a}{dk^a} A(k, x), \quad \text{now with } k = \frac{x_0 e^{-i\omega_0 t}}{\sqrt{2}}. \tag{15}$$

For small values of n , where the a sum contributes only $n+1$ terms, this method works well, as you could again verify for the special case, $n = 1$. For arbitrary values of n , particularly for large values of n , we could use the summed form of

the Bargmann transform, $F_n(k)$. From the above expansion in powers of k ,

$$\text{If } \Psi(x, 0) \text{ has Bargmann transform } F_n(k),$$

then $\Psi(x, t)$ has Bargmann transform $F_n(k, t) = e^{-\frac{i}{2}\omega_0 t} F_n(k e^{-i\omega_0 t})$.

Therefore, for us,

$$\begin{aligned} F_n(k, t) &= e^{-\frac{i}{2}\omega_0 t} e^{-\frac{1}{4}x_0^2} e^{[\frac{x_0}{\sqrt{2}}ke^{-i\omega_0 t}]} \frac{(ke^{-i\omega_0 t} - \frac{x_0}{\sqrt{2}})^n}{\sqrt{n!}} \\ &= e^{-i(n+\frac{1}{2})\omega_0 t} e^{-\frac{1}{4}x_0^2} e^{[\frac{x_0}{\sqrt{2}}ke^{-i\omega_0 t}]} \frac{(k - \frac{x_0 e^{-i\omega_0 t}}{\sqrt{2}})^n}{\sqrt{n!}}. \end{aligned} \quad (16)$$

The function, $\Psi(x, t)$, then follows at once from the inverse Bargmann transform

$$\Psi(x, t) = \frac{1}{\pi} \int d^2 k e^{-kk^*} A(k^*, x) F_n(k, t). \quad (17)$$

To do this integral, it will now be convenient to make the substitution

$$k' = \left(k - \frac{x_0 e^{i\omega_0 t}}{\sqrt{2}} \right),$$

so

$$\begin{aligned} \Psi(x, t) &= \frac{e^{-i(n+\frac{1}{2})\omega_0 t}}{\pi} \int d^2 k' e^{-(k' + \frac{x_0 e^{i\omega_0 t}}{\sqrt{2}})(k'^* + \frac{x_0 e^{-i\omega_0 t}}{\sqrt{2}})} \\ &\times \frac{e^{-\frac{1}{2}(k'^* + \frac{x_0 e^{-i\omega_0 t}}{\sqrt{2}})^2}}{\pi^{\frac{1}{4}}} e^{\sqrt{2}k'^* x + x_0 e^{-i\omega_0 t}} e^{-\frac{1}{2}x^2} e^{[\frac{x_0}{\sqrt{2}}k' e^{-i\omega_0 t}]} e^{+\frac{x_0^2}{4} \left[\frac{k'^n}{\sqrt{n!}} \right]} \\ &= \frac{e^{-i(n+\frac{1}{2})\omega_0 t}}{\pi} \int d^2 k' e^{-k'^* k'} \frac{e^{[-\frac{1}{2}k'^* 2 + \sqrt{2}k'^*(x - x_0 \cos \omega_0 t) - \frac{1}{2}(x - x_0 \cos \omega_0 t)^2]}}{\pi^{\frac{1}{4}}} \\ &\times \left[\frac{k'^n}{\sqrt{n!}} \right] e^{-i x_0 \sin \omega_0 t (x - \frac{x_0}{2} \cos \omega_0 t)} \\ &= e^{-i(n+\frac{1}{2})\omega_0 t} \left[\frac{1}{\pi} \int d^2 k' e^{-k'^* k'} A(k'^*, (x - x_0 \cos \omega_0 t)) \left[\frac{k'^n}{\sqrt{n!}} \right] \right] \\ &\times e^{-i x_0 \sin \omega_0 t (x - \frac{x_0}{2} \cos \omega_0 t)} \\ &= \psi_n(x - x_0 \cos \omega_0 t) e^{-i(n+\frac{1}{2})\omega_0 t} e^{-i x_0 \sin \omega_0 t (x - \frac{x_0}{2} \cos \omega_0 t)}. \end{aligned} \quad (18)$$

For arbitrary n ,

$$|\Psi(x, t)|^2 = |\psi_n(x - x_0 \cos \omega_0 t)|^2, \quad \text{if } \Psi(x, 0) = \psi_n(x - x_0). \quad (19)$$

For arbitrary n , therefore, the probability density oscillates without change of shape about the origin with the oscillator frequency, (ω_0), and with amplitude x_0 , if the initial state is the n^{th} oscillator state displaced in the x -direction through a distance x_0 . This extremely simple property is unique for the harmonic oscillator and does not follow for the energy eigenstates of more complicated Hamiltonians. Also, the use of the Bargmann transform greatly facilitated the proof for general, n .

12. The 2-D isotropic harmonic oscillator with Hamiltonian

$$H + \frac{1}{2m}(p_x^2 + p_y^2) + \frac{m\omega_0^2}{2}(x^2 + y^2)$$

has eigenfunctions

$$\psi_{n_1 n_2}(x, y) = \psi_{n_1}(x)\psi_{n_2}(y),$$

with eigenvalues, $E_{n_1 n_2} = \hbar\omega_0(n_1 + n_2 + 1)$. Show that H is invariant to rotations

$$x' = x \cos \theta + y \sin \theta,$$

$$y' = -x \sin \theta + y \cos \theta,$$

where θ is a constant. Show by means of the Bargmann kernel that an eigenfunction in which only the x' degree of freedom is excited can be expanded in terms of the above $\psi_{n_1 n_2}$; i.e., find the expansion coefficients, $c_{n_1 n_2}^{(N)}$:

$$\psi_N(x')\psi_0(y') = \sum_{n_1 n_2} c_{n_1 n_2}^{(N)} \psi_{n_1}(x)\psi_{n_2}(y).$$

13. For the conservation laws for the hydrogen atom, the three components of the Runge–Lenz vector are

$$\vec{\mathcal{R}} = \frac{1}{2\mu} \left([\vec{p} \times \vec{L}] - \vec{L} \times \vec{p} \right) - \frac{Ze^2}{r} \vec{r}.$$

Show that they are hermitian when written in the above form. Also, show that they commute with the hydrogen atom Hamiltonian

$$H = \frac{(\vec{p} \cdot \vec{p})}{2\mu} - \frac{Ze^2}{r}.$$

In the above, $\vec{\mathcal{R}}$ and H are expressed in terms of the physical quantities, $\vec{r}_{\text{phys.}}$, $\vec{p}_{\text{phys.}}$, $\vec{L}_{\text{phys.}}$, and $H_{\text{phys.}}$. If these are expressed in terms of dimensionless quantities, \vec{r} , \vec{p} , \vec{L} , H , through

$$\vec{r}_{\text{phys.}} = a_0 \vec{r}, \quad \vec{p}_{\text{phys.}} = \frac{\hbar}{a_0} \vec{p}, \quad \vec{L}_{\text{phys.}} = \hbar \vec{L},$$

$$H_{\text{phys.}} = \frac{\mu Z^2 e^4}{\hbar^2} H, \quad \text{with } a_0 = \frac{\hbar^2}{\mu Ze^2},$$

the Runge vector in physical units, as given above, can be expressed in terms of a dimensionless $\vec{\mathcal{R}}$ by

$$\vec{\mathcal{R}}_{\text{phys.}} = Ze^2 \vec{\mathcal{R}}.$$

Show that this dimensionless $\vec{\mathcal{R}}$ can also be expressed as

$$\vec{\mathcal{R}} = [\vec{p} \times \vec{L}] - i \vec{p} - \frac{\vec{r}}{r} = \vec{r}(\vec{p} \cdot \vec{p}) - \vec{p}(\vec{r} \cdot \vec{p}) - \frac{\vec{r}}{r}.$$

Also,

$$(\vec{\mathcal{R}} \cdot \vec{\mathcal{R}}) = \left(\vec{p} \cdot \vec{p} - \frac{2}{r} \right) (\vec{L} \cdot \vec{L} + 1) + 1 = 2H(\vec{L} \cdot \vec{L} + 1) + 1,$$

and

$$\vec{\mathcal{R}} \cdot \vec{L} = \vec{L} \cdot \vec{\mathcal{R}} = 0.$$

6

Further Interpretation of the Wave Function

Consider a quantum-mechanical system with a Hamiltonian that has a discrete spectrum only, with allowed energies, E_n , and eigenfunctions, ψ_n . In general, the state of this quantum system can be specified by a wave function

$$\Psi(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r}) e^{-\frac{i}{\hbar} E_n t} \quad (1)$$

describing a system for which the energy is not uniquely specified. If it is a single particle,

$$\langle \Psi, \Psi \rangle = 1 = \sum_n c_n^* c_n \langle \psi_n, \psi_n \rangle + \sum_{n \neq m} c_n^* c_m \langle \psi_n, \psi_m \rangle e^{\frac{i}{\hbar} (E_n - E_m)t}. \quad (2)$$

Because $\langle \psi_n, \psi_m \rangle = 0$ for $n \neq m$,

$$\langle \Psi, \Psi \rangle = \sum_n |c_n|^2. \quad (3)$$

Similarly,

$$\langle E \rangle = \langle \Psi, H\Psi \rangle = \sum_n |c_n|^2 E_n, \quad (4)$$

$$\langle E^k \rangle = \langle \Psi, H^k \Psi \rangle = \sum_n |c_n|^2 E_n^k. \quad (5)$$

It is natural to interpret $|c_n|^2$ as $P(E_n)$, the probability the particle be found in the state with energy E_n . Without a coupling of our system to an outside field, that is, without an outside perturbation, these $P(E_n)$ are independent of the time.

A Application 1: Tunneling through a Barrier

As a simplest application, consider the NH_3 molecule system, where the motion of the N-atom relative to the H_3 plane is governed by the double-minimum potential of problem 7. The lowest-energy eigenfunction was an even function of x ; the first excited state, at an excitation energy, ΔE , above the ground state (see Fig. 6.1), has an eigenfunction that is an odd function of x , but otherwise almost identical with the lowest-energy eigenfunction (see Fig. 6.2). If we actually make a measurement of the position of the N-atom when the x -vibrational motion is not excited, we will find the N-atom either above the H_3 plane, $x > 0$, or below it, $x < 0$. Suppose at $t = 0$ we make a measurement telling us the N-atom is above the H_3 plane. Then,

$$\Psi(x, t = 0) = \frac{1}{\sqrt{2}}(\psi_{0,\text{even}} + \psi_{0,\text{odd}}) = \psi_{\text{Right}}. \quad (6)$$

Note $\sum_n |c_n|^2 = 1$. At any later time,

$$\begin{aligned} \Psi(x, t) &= \frac{1}{\sqrt{2}}(\psi_{0,\text{even}} e^{-\frac{i}{\hbar}E_{0,\text{even}}t} + \psi_{0,\text{odd}} e^{-\frac{i}{\hbar}E_{0,\text{odd}}t}) \\ &= \frac{1}{\sqrt{2}}e^{-\frac{i}{\hbar}E_{0,\text{even}}t}(\psi_{0,\text{even}} + \psi_{0,\text{odd}} e^{-\frac{i}{\hbar}\Delta Et}). \end{aligned} \quad (7)$$

In particular, when

$$t = \frac{\hbar\pi}{\Delta E}, \quad (8)$$

$$\Psi(x, t) = \frac{1}{\sqrt{2}}e^{-\frac{i}{\hbar}E_{0,\text{even}}t}(\psi_{0,\text{even}} - \psi_{0,\text{odd}}), \quad |\Psi(x, t)| = |\psi_{\text{Left}}|. \quad (9)$$

In this time, therefore, the N-atom has tunneled from the right potential minimum through the barrier to the left potential minimum. In twice this time, we will again find the N-atom in the right minimum. The N-atom tunnels back and forth through the potential barrier with a frequency given by

$$\nu_{\text{tunneling}} = \frac{\Delta E}{2\pi\hbar}. \quad (10)$$

From the solution of problem 7, ΔE is proportional to the Gamow factor, e^{-G} , with $G = 2a\sqrt{[2\mu(V_0 - E)/\hbar^2]}$ for the square well barrier of width $2a$. For a more general $V(x)$, this would be replaced by

$$G = \int_{-a}^{+a} dx \sqrt{[2\mu(V(x) - E)/\hbar^2]},$$

as will be shown in Chapter 37, where the Gamow factor, e^{-G} , is the most crucial part for the probability of tunneling through the barrier.

We end with a parenthetic remark: In the above discussion, we have used another result of problem 7. The lowest-state eigenfunction for our symmetric potential, with $V(-x) = V(x)$, is an even function of x . This result seems to be universally

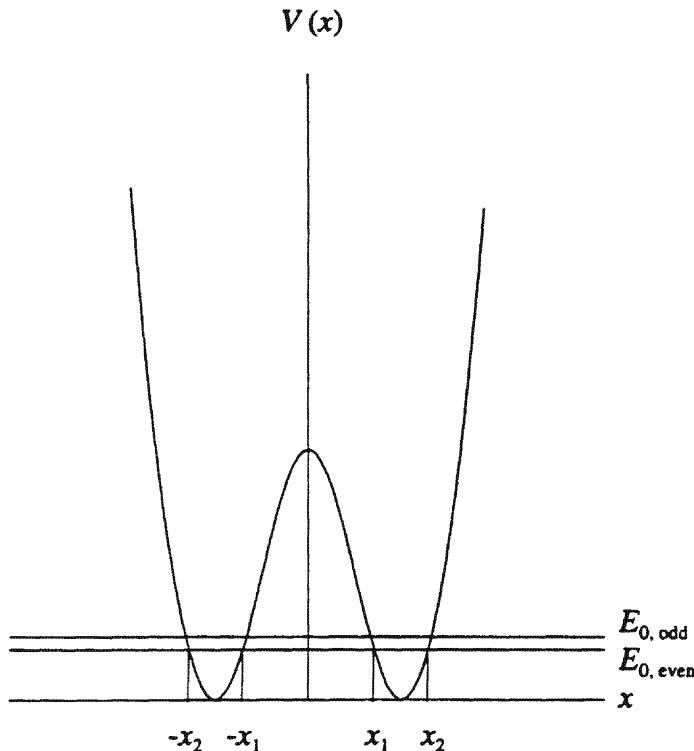


FIGURE 6.1. The ground-state doublet of the NH_3 double minimum potential.

true for symmetric potentials, which can be understood in terms of the curvature of the eigenfunctions. For two similar eigenfunctions of opposite parity, the function of odd parity must have a node in the center at $x = 0$ and must therefore have a somewhat greater curvature to “fit” into the potential, leading to a greater positive value of the expectation value of the kinetic energy. It is, however, not completely clear this property could be negated by the expectation value of the potential energy for a “pathological” potential perhaps having a large contribution to $\langle V \rangle$ from the region near $x = 0$. In fact, the double minimum potential of this section, in which the central potential barrier is sufficiently infinite, is such a “pathological” case for which the ground state wave function is a degenerate doublet of an even and odd function. The ground-state wave function is no longer a pure even function of x .

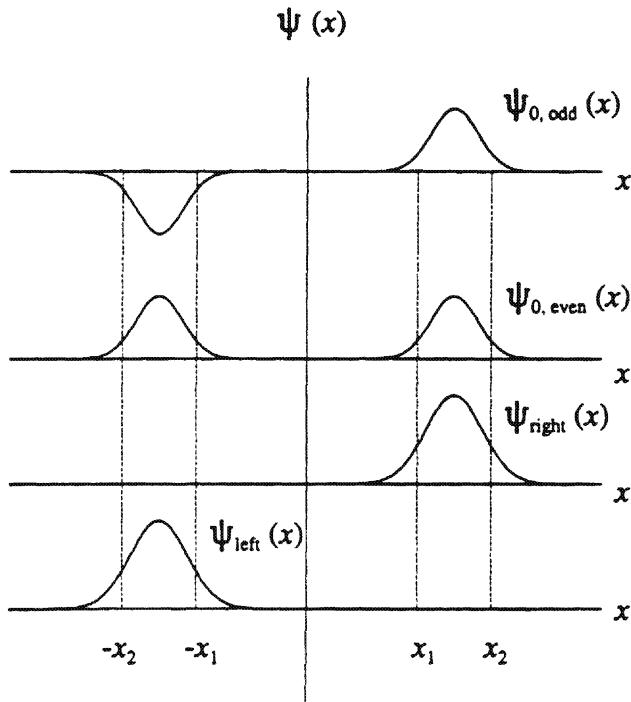


FIGURE 6.2. The eigenfunctions $\psi_{0,\text{odd}}$ and $\psi_{0,\text{even}}$ of the ground state doublet and $\psi_{\text{right/left}} = \sqrt{\frac{1}{2}}(\psi_{0,\text{even}} \pm \psi_{0,\text{odd}})$.

B Application 2: Time-dependence of a general oscillator $\langle q \rangle$

The probability amplitudes c_n can tell us the quantum mechanical expectation value of any operator, O, through

$$\langle O \rangle = \sum_{n,m} c_n^* c_m \langle \psi_n, O \psi_m \rangle e^{\frac{i}{\hbar}(E_n - E_m)t}. \quad (11)$$

As a particular example, let $O = q$, the physical displacement coordinate of the 1-D harmonic oscillator. The two-index quantities $(q)_{nm} = \langle \psi_n, q \psi_m \rangle$ for the harmonic oscillator were nonzero only for $m = n \pm 1$ (see Chapter 5). Thus,

$$\begin{aligned} \langle q \rangle &= \sqrt{\frac{\hbar}{m\omega_0}} \langle x \rangle = \sqrt{\frac{\hbar}{2m\omega_0}} \sum_n [c_n^* c_{n-1} \sqrt{n} e^{i\omega_0 t} + c_n^* c_{n+1} \sqrt{n+1} e^{-i\omega_0 t}] \\ &= \sum_n \sqrt{\frac{\hbar n}{2m\omega_0}} [c_n^* c_{n-1} e^{i\omega_0 t} + c_{n-1}^* c_n e^{-i\omega_0 t}] \end{aligned}$$

$$\begin{aligned}
&= \sum_n \sqrt{\frac{\hbar n}{2m\omega_0}} [2\text{Real}(c_n^* c_{n-1}) \cos \omega_0 t - 2\text{Im}(c_n^* c_{n-1}) \sin \omega_0 t] \\
&= \sum_n \sqrt{\frac{\hbar n}{2m\omega_0}} A_n \cos(\omega_0 t + \phi_n),
\end{aligned} \tag{12}$$

where we have defined $2c_n^* c_{n-1} \equiv A_n e^{i\phi_n}$. If we use $\langle q \rangle$ to describe the quantum-mechanical motion of the simple 1-D harmonic oscillator, the result is very similar to the classical motion.

C Matrix Representations

For the expectation value, $\langle O \rangle$, of eq. (11), it is tempting to interpret the two-index quantity, $O_{nm} \equiv \langle \psi_n, O \psi_m \rangle$, as the nm^{th} matrix element of an infinite-dimensional matrix. (The set of numbers, O_{nm} , contain all experimentally observable information about the dynamical quantity represented by the operator, O .) To prove O_{nm} is a matrix, all laws of matrix algebra must be satisfied:

- 1) multiplication by a scalar (a complex number or “c-number”), λO :

$$\langle \psi_n, \lambda O \psi_m \rangle = \lambda O_{nm}. \tag{13}$$

- 2) addition of two matrices, $O_1 + O_2$:

$$\langle \psi_n, (O_1 + O_2) \psi_m \rangle = (O_1)_{nm} + (O_2)_{nm}. \tag{14}$$

- 3) matrix multiplication, $O_2 O_1$:

$$\langle \psi_n, O_2 O_1 \psi_m \rangle = ? \tag{15}$$

To prove the law of matrix-multiplication, the new function obtained by acting with O_1 on ψ_m can be expanded in terms of the ψ_k in a generalized Fourier series

$$O_1 \psi_m = \sum_k c_k \psi_k, \quad \text{with } c_k = \langle \psi_k, O_1 \psi_m \rangle = (O_1)_{km}, \tag{16}$$

so

$$\langle \psi_n, O_2 O_1 \psi_m \rangle = \sum_k \langle \psi_n, O_2 \psi_k \rangle \langle \psi_k, O_1 \psi_m \rangle, \tag{17}$$

or

$$(O_2 O_1)_{nm} = \sum_k (O_2)_{nk} (O_1)_{km}. \tag{18}$$

This relation is the familiar law of matrix multiplication. The matrix elements,

$$O_{nm} = \langle \psi_n, O \psi_m \rangle = \int dx \psi_n^*(x) O \psi_m(x),$$

were introduced here with the concept of the Schrödinger wave equation and the use of the energy eigenfunctions of this wave equation. Heisenberg first introduced

such matrix elements of dynamical quantities entirely without the concept of a wave equation or a wave function.

D Heisenberg Matrix Mechanics

We are therefore now at a stage where we can make a short historical remark about the Heisenberg derivation of the laws of quantum mechanics. Heisenberg did not think in terms of a wave equation or in terms of a wave function. He started by thinking about the laws of classical dynamics for a periodic (or more generally a multiple-periodic or quasiperiodic system) in terms of a Fourier analysis of the classical generalized coordinates, q . For a simple periodic system,

$$q(t) = \sum_n q_n e^{in\omega t}, \quad \text{with } \omega = 2\pi\nu, \quad (19)$$

where q_n is the Fourier amplitude for the n^{th} overtone of the classical fundamental ω . (For a multiple-periodic system, $n\omega$ would be replaced by $n_1\omega_1 + n_2\omega_2 + \dots + n_f\omega_f$, and the sum would be over f overtone indices, and the Fourier coefficients would depend on f integers, $q_{\vec{n}} = q_{n_1 n_2 \dots n_f}$.)

Now, Heisenberg reasoned: Because the n^{th} overtone has to be replaced by a two-index quantity, via the Bohr frequency relation,

$$n\omega \rightarrow \frac{E_n - E_m}{\hbar} = \omega_{nm} \quad \text{Bohr,} \quad (20)$$

the Fourier coefficient q_n should also be replaced by a two-index quantity

$$q_n \rightarrow q_{nm} \quad \text{Heisenberg matrix.} \quad (21)$$

Moreover, these q_{nm} are the only observable (physically meaningful) quantities. In addition, because matrices do not commute, the quantum mechanically meaningful p and q matrices do not commute. In particular, Heisenberg introduced the Planck constant into his matrix algebra with the simple *assumption*

$$\sum_k (p_{nk} q_{km} - q_{nk} p_{km}) = \frac{\hbar}{i} \delta_{nm}. \quad (22)$$

In the limit, $\hbar \rightarrow 0$, p and q do commute as they should in the classical limit, when \hbar becomes too small to matter. The genius of the Heisenberg approach is contained in this *Heisenberg relation*, which we have already met in Section 3G in the framework of the Schrödinger approach.

Using the p, q matrix commutation relation, the relation between $H(p, q)$ and E , and the commutators $[p, H(p, q)]$ and $[q, H(p, q)]$, which follow from eq. (22), Heisenberg found the allowed energy values and the matrix elements of p and q via matrix algebra for the 1-D harmonic oscillator and other simple dynamical systems, *without* the use of a wave equation. The equivalence between the Heisenberg q_{nm} and the Schrödinger $\langle \psi_n, q \psi_m \rangle$ was demonstrated by Schrödinger in 1926. (Wolfgang Pauli in an unpublished letter to P. Jordan is reputed to have shown

this equivalence even earlier). In these lectures, we shall give the Heisenberg derivation for the energy eigenvalues, E_n , and the matrix elements q_{nm} and p_{nm} of the simple harmonic oscillator in Chapter 19 after we have gained some facility in the calculation of matrix elements of dynamical quantities by both Schrödinger and algebraic (Heisenberg) techniques.

7

The Eigenvalue Problem

One of the basic problems needing to be solved in quantum theory is the general eigenvalue problem, for some hermitian operator, say, A , with $A^\dagger = A$,

$$A\psi_a(x) = \lambda_a \psi_a(x). \quad (1)$$

We shall learn how to solve such problems by purely algebraic techniques, without introducing wave functions and differential equations. For the moment, however, let us go back to the coordinate representation, and, in particular, let us choose $A = H$, where H is the Hamiltonian for a single particle in three dimensions, or for the two-particle problem after transformation to center of mass and relative coordinates. Keeping the center of mass fixed, the eigenvalue problem for the relative motion of the two-particle system is given by the Schrödinger equation

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi + V(x, y, z)\psi = E\psi. \quad (2)$$

If the potential is a function of the scalar distance r only, spherical coordinates will be natural and

$$-\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \right) \psi + \frac{2\mu}{\hbar^2} (V(r) - E)\psi = 0. \quad (3)$$

Now, let

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi) = R(r)\Theta(\theta)\Phi(\phi). \quad (4)$$

Substituting into the equation, and subsequently dividing by $\psi = R\Theta\Phi$, and then multiplying from the left with r^2 , leads to a separation of the wave equation

$$\frac{r^2}{R} \left[\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} \right] + \frac{2\mu r^2}{\hbar^2} (E - V(r)) = -\frac{1}{\Theta} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \Theta}{\partial \theta} \right] - \frac{1}{\Phi \sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2}. \quad (5)$$

Now, we have a function of r only, on the left-hand side of the equation, equaling a function of θ and ϕ only on the right. Hence, each function must be equal to the same constant, to be named, λ_0 . By multiplying the right-hand side by $\sin^2 \theta$, we can further separate the θ and ϕ -dependent pieces. Letting the new separation constant be named m^2 , we get the three separated equations

$$-\frac{\hbar^2}{2\mu} \left[\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} \right] + \left[\frac{\hbar^2}{2\mu r^2} \lambda_0 + V(r) \right] R(r) = E R(r), \quad (6)$$

$$-\frac{d^2 \Theta}{d\theta^2} - \cot \theta \frac{d\Theta}{d\theta} + \frac{m^2}{\sin^2 \theta} \Theta(\theta) = \lambda_0 \Theta(\theta), \quad (7)$$

$$-\frac{d^2 \Phi}{d\phi^2} = m^2 \Phi(\phi). \quad (8)$$

The solution to the last equation is trivial

$$\Phi(\phi) = e^{\pm im\phi}. \quad (9)$$

We shall prove later the separation constant, m , must be an integer. We shall defer the proof to later, but we note that it does *not* follow from the requirement that the wave function be single valued. It is $\psi\psi^*$ and the probability density current, \vec{S} , that must be single valued, i.e., have the same value at ϕ and $(\phi + 2\pi)$. The r and θ equations can be simplified by eliminating the first derivative term to make them have the form of a 1-D Schrödinger equation. Because the volume element in spherical coordinates has the weighting factor $r^2 \sin \theta$, and we require the normalization

$$\int_0^\infty dr r^2 |R(r)|^2 \int_0^\pi d\theta \sin \theta |\Theta|^2 \int_0^{2\pi} d\phi |\Phi|^2 = 1, \quad (10)$$

(we will find it convenient to make each integral separately equal to unity), it will be useful to “one-dimensionalize” by transforming to new 1-D functions, u ,

$$r R(r) = u(r), \quad \sqrt{\sin \theta} \Theta(\theta) = u(\theta), \quad \Phi(\phi) = u(\phi). \quad (11)$$

The 1-D equations are then

$$\left(-\frac{d^2}{dr^2} + \frac{2\mu}{\hbar^2} \left[V(r) + \frac{\hbar^2 \lambda_0}{2\mu r^2} \right] \right) u(r) = \frac{2\mu}{\hbar^2} E u(r) = \lambda u(r), \quad (12)$$

$$\left(-\frac{d^2}{d\theta^2} + \frac{(m^2 - \frac{1}{4})}{\sin^2 \theta} \right) u(\theta) = (\lambda_0 + \frac{1}{4}) u(\theta) = \lambda u(\theta), \quad (13)$$

$$-\frac{d^2u}{d\phi^2} = m^2 u(\phi) = \lambda u(\phi). \quad (14)$$

The generic eigenvalue problem we want to solve has the form

$$\left(-\frac{d^2}{dx^2} + r(x, m)\right)u_{\lambda m}(x) = \lambda u_{\lambda m}(x). \quad (15)$$

The effective potential term often contains a parameter, named m in the generic equation, such as the parameter, m , in the θ equation, or the parameter λ_0 in the r equation.

One of the methods used by Schrödinger to solve this type of problem is the so-called factorization method, which naturally leads to a constructive process via ladder operators. The introduction of such ladder operators will ease the transition to the algebraic techniques, which we will use later to solve such eigenvalue problems, beginning with Chapter 14, where we reexamine many of these problems in a new light.

A The Factorization Method: Ladder Operators

[A good reference for this method is: L. Infeld and T. E. Hull, *Reviews of Modern Physics* **23** (1951) 21. The table of factorizations at the end of the article gives a listing of 31 wave equations for which solutions are known in analytic form.]

In the factorization method, an attempt is made to solve the eigenvalue problem of eq. (15) by factoring the Schrödinger operator containing a second derivative operator into a product of two factors, each containing only a first derivative operator. Defining

$$\begin{aligned} O_+(m) &= -\frac{d}{dx} + k(x, m), \\ O_-(m) &= +\frac{d}{dx} + k(x, m), \end{aligned} \quad (16)$$

which through the basic second-order equation, eq. (15), satisfy the two equations

$$\begin{aligned} \text{I : } \quad O_+(m)O_-(m)u_{\lambda m}(x) &= [\lambda - \mathcal{L}(m)]u_{\lambda m}(x), \\ \text{II : } \quad O_-(m+1)O_+(m+1)u_{\lambda m}(x) &= [\lambda - \mathcal{L}(m+1)]u_{\lambda m}(x). \end{aligned} \quad (17)$$

For the specific case of the θ equation, our eq. (13), the function

$$k(\theta, m) = (m - \frac{1}{2}) \cot \theta \quad (18)$$

will do the trick. Our equation (I) becomes

$$\begin{aligned} &\left(-\frac{d}{d\theta} + (m - \frac{1}{2}) \cot \theta\right) \left(+\frac{d}{d\theta} + (m - \frac{1}{2}) \cot \theta\right) u_{\lambda m}(\theta) \\ &= \left(-\frac{d^2}{d\theta^2} + \frac{(m^2 - \frac{1}{4})}{\sin^2 \theta} - (m - \frac{1}{2})^2\right) u_{\lambda m}(\theta) \end{aligned}$$

$$= [\lambda - (m - \frac{1}{2})^2] u_{\lambda m}(\theta). \quad (19)$$

Equation (II) becomes

$$\begin{aligned} & \left(+ \frac{d}{d\theta} + (m + \frac{1}{2}) \cot \theta \right) \left(- \frac{d}{d\theta} + (m + \frac{1}{2}) \cot \theta \right) u_{\lambda m}(\theta) \\ &= \left(- \frac{d^2}{d\theta^2} + \frac{(m^2 - \frac{1}{4})}{\sin^2 \theta} - (m + \frac{1}{2})^2 \right) u_{\lambda m}(\theta) \\ &= [\lambda - (m + \frac{1}{2})^2] u_{\lambda m}(\theta). \end{aligned} \quad (20)$$

The proposed factorization works for the θ equation and leads in this case to

$$\mathcal{L}(m) = (m - \frac{1}{2})^2. \quad (21)$$

We will postpone the question, treated in detail by Infeld and Hull, for which “potentials” does the factorization work? Let us first prove a number of theorems.

Theorem I:

If $u_{\lambda m}(x)$ is an eigenfunction of the generic equation with parameter, m , and eigenvalue λ , then $[O_-(m)u_{\lambda m}(x)]$ is an eigenfunction of the equation with parameter, $m - 1$, and the same eigenvalue λ , and $[O_+(m+1)u_{\lambda m}(x)]$ is an eigenfunction of the equation with parameter, $m + 1$, and the same eigenvalue λ .

That is,

$$\begin{aligned} O_-(m)u_{\lambda m}(x) &= \text{const.} u_{\lambda(m-1)}(x), \\ O_+(m+1)u_{\lambda m}(x) &= \text{const.} u_{\lambda(m+1)}(x). \end{aligned} \quad (22)$$

To see the first, act on equation (I) from the left with $O_-(m)$ to give

$$O_-(m)O_+(m) \left[O_-(m)u_{\lambda m} \right] = [\lambda - \mathcal{L}(m)] \left[O_-(m)u_{\lambda m} \right]; \quad (23)$$

that is, $O_-(m)u_{\lambda m}$ is a solution of equation (II), with m replaced by $(m - 1)$. Similarly, acting on equation (II) from the left with $O_+(m + 1)$ gives

$$O_+(m+1)O_-(m+1) \left[O_+(m+1)u_{\lambda m} \right] = [\lambda - \mathcal{L}(m+1)] \left[O_+(m+1)u_{\lambda m} \right]; \quad (24)$$

that is, $O_+(m+1)u_{\lambda m}$ is a solution of equation (I), now with m replaced by $m + 1$. Thus, $O_-(m)$ and $O_+(m + 1)$ are m step-down, or step-up, operators that can ladder from a known solution to other solutions. Still to be answered: Are the new functions square-integrable if the original $u_{\lambda m}$ were square-integrable? Do the m -ladders continue indefinitely to smaller or larger values? These questions still need to be answered. To see these, we need additional theorems.

Theorem II:

$$O_-(m) = O_+(m)^\dagger, \quad O_+(m) = O_-(m)^\dagger. \quad (25)$$

These relations follow from the adjoint properties of the two parts of the operators

$$\left[- \frac{d}{dx} \right] = \left[+ \frac{d}{dx} \right]^\dagger; \quad k(x, m) = k(x, m)^\dagger. \quad (26)$$

We can use this theorem to investigate the square-integrability of $u_{\lambda(m\pm 1)}$. Assuming $u_{\lambda m}$ is square-integrable, over an interval from a to b , consider

$$\begin{aligned} & \int_a^b dx u_{\lambda m+1}^*(x) u_{\lambda m+1}(x) \\ &= |\text{const.}|^2 \int_a^b dx [O_+(m+1)u_{\lambda m}(x)]^* [O_+(m+1)u_{\lambda m}(x)] \\ &= |\text{const.}|^2 \int_a^b dx u_{\lambda m}^*(x) O_-(m+1) O_+(m+1) u_{\lambda m}(x) \\ &= |\text{const.}|^2 [\lambda - \mathcal{L}(m+1)] \int_a^b dx u_{\lambda m}^*(x) u_{\lambda m}(x). \end{aligned} \quad (27)$$

If the number $[\lambda - \mathcal{L}(m+1)]$ is a positive number, the final result is a patently positive quantity, and $u_{\lambda m+1}$ is square-integrable and can be normalized to one by an appropriate choice of the constant. If $\mathcal{L}(m)$ is an increasing function of m (see Fig. 7.1), however, an m -value will come such that $\mathcal{L}(m+1)$ will be greater than λ . Eq. (27) then would say that a patently positive quantity on the left-hand side of the equation would have to be a patently negative quantity on the right-hand side. This cannot be. Hence, the assumption that the solution $u_{\lambda m}$ was square-integrable must have been wrong. The only way out of the soup comes if the m step-up process quits; i.e., if a maximum possible value of m exists, m_{\max} , such that

$$O_+(m_{\max} + 1)u_{\lambda m_{\max}}(x) = 0, \quad (28)$$

which would require

$$\lambda = \mathcal{L}(m_{\max} + 1). \quad (29)$$

Eq. (28) is a first-order equation, which can in principle always be integrated

$$-\frac{du_{\lambda m_{\max}}}{dx} + k(x, m_{\max} + 1)u_{\lambda m_{\max}} = 0. \quad (30)$$

For example, in the case of our θ equation,

$$\frac{du_{\lambda m_{\max}}}{u_{\lambda m_{\max}}} = (m_{\max} + \frac{1}{2}) \cot \theta d\theta, \quad (31)$$

leading to

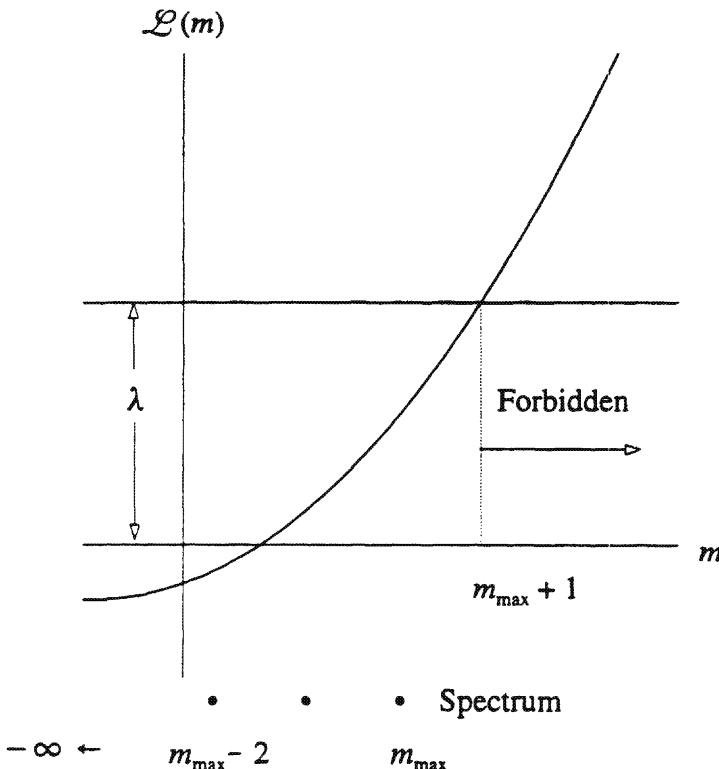
$$\ln u_{\lambda m_{\max}} = [\ln(\sin \theta)]^{m_{\max} + \frac{1}{2}}. \quad (32)$$

If we name

$$m_{\max} = l, \quad (33)$$

we can write this solution

$$u(\theta) = N_l \sin^{(l+\frac{1}{2})} \theta, \quad \Theta(\theta) = N_l \sin^l \theta; \quad (34)$$

FIGURE 7.1. Case 1. A monotonically increasing $\mathcal{L}(m)$.

recalling that $\sqrt{\sin \theta} \Theta(\theta) = u(\theta)$. The normalization constant, N_l , can be evaluated to be

$$|N_l| = \sqrt{\frac{(2l+1)!!}{2(2l)!!}} = \sqrt{\frac{1 \cdot 3 \cdot 5 \cdots (2l+1)}{2[2 \cdot 4 \cdot 6 \cdots 2l]}}. \quad (35)$$

These considerations lead us to theorem IIIa.

Theorem IIIa:

If $\mathcal{L}(m)$ is an increasing function of m , a highest value of m exists, m_{\max} , such that $O_+(m_{\max} + 1)u_{\lambda m_{\max}} = 0$, and the eigenvalue, λ , is restricted by $\lambda = \mathcal{L}(m_{\max} + 1)$. In this case, normalized square-integrable eigenfunctions $u_{\lambda m}$ can be obtained from

$$u_{\lambda m-1}(x) = \mathcal{O}_-(m)u_{\lambda m}(x), \quad (36)$$

where

$$\mathcal{O}_-(m) \equiv \frac{O_-(m)}{\sqrt{[\lambda - \mathcal{L}(m)]}}. \quad (37)$$

That is, we can use a ladder process to ladder down from the eigenfunction with maximum possible m to arbitrary m , by repeated application of this operation.

Theorem IIIb:

If $\mathcal{L}(m)$ is a decreasing function of m , (see, e.g., Fig. 7.2), a lowest value of m exists, m_{\min} , such that $O_-(m_{\min})u_{\lambda m_{\min}} = 0$, and the eigenvalue λ is restricted by $\lambda = \mathcal{L}(m_{\min})$. In this case, normalized, square-integrable eigenfunctions $u_{\lambda m}$ can be obtained through a step-up procedure, starting with the eigenfunction with the minimum possible value of m , via

$$u_{\lambda m+1}(x) = \mathcal{O}_+(m+1)u_{\lambda m}(x), \quad (38)$$

where

$$\mathcal{O}_+(m+1) \equiv \frac{O_+(m+1)}{\sqrt{[\lambda - \mathcal{L}(m+1)]}}. \quad (39)$$

Theorem IIIb follows from

$$\begin{aligned} & \int_a^b dx u_{\lambda m-1}^*(x) u_{\lambda m-1}(x) \\ &= |\text{const.}|^2 \int_a^b dx [O_-(m)u_{\lambda m}(x)]^* O_-(m)u_{\lambda m}(x) \\ &= |\text{const.}|^2 \int_a^b dx u_{\lambda m}^*(x) [O_+(m)O_-(m)u_{\lambda m}(x)] \\ &= |\text{const.}|^2 [\lambda - \mathcal{L}(m)] \int_a^b dx u_{\lambda m}^*(x) u_{\lambda m}(x). \end{aligned} \quad (40)$$

Now if $[\lambda - \mathcal{L}(m)]$ is a positive quantity, $u_{\lambda m-1}$ is square-integrable, if $u_{\lambda m}$ is square-integrable. If $\mathcal{L}(m)$ is a decreasing function of m , as in Fig. 7.2, however, a value of m would (in general) come such that $[\lambda - \mathcal{L}(m-1)]$ would be a negative quantity, and again we would have a patently positive quantity on the left-hand side of the equation equal to a patently negative quantity on the right. The initial assumption that $u_{\lambda m}$ be square-integrable must have been wrong. In the special case when $\lambda = \mathcal{L}(m_{\min})$, however, the laddering process quits at the value m_{\min} , and now no inconsistency exist.

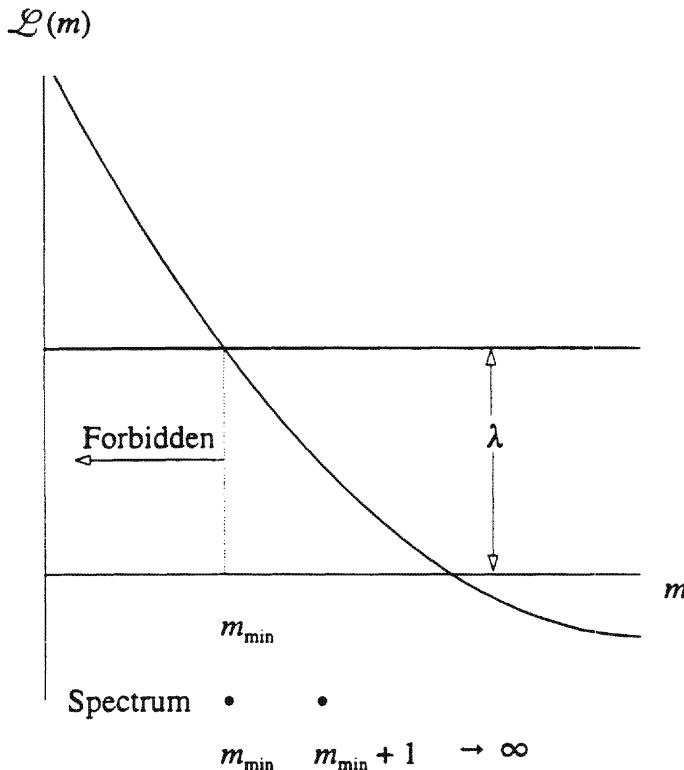
In this case,

$$O_-(m_{\min})u_{\lambda m_{\min}} = 0, \quad (41)$$

$$+ \frac{du_{\lambda m_{\min}}}{dx} + k(x, m_{\min})u_{\lambda m_{\min}}(x) = 0. \quad (42)$$

In this case, if $\mathcal{L}(m)$ is a *monotonic*, decreasing function of m , (see Fig. 7.2), the spectrum of allowed m values runs from $m_{\min}, m_{\min} + 1, m_{\min} + 2, \dots$, on to $+\infty$; the functions with higher m values being generated by repeated action with $\mathcal{O}_+(m+1)$.

So far, we have considered cases with $\mathcal{L}(m)$ being monotonic increasing or decreasing functions of m . Our special example of the θ equation, however, with $\mathcal{L}(m) = (m - \frac{1}{2})^2$, see Fig. 7.3, is an increasing function of m for positive m values and a decreasing function of m for negative m values. In this case, the laddering process will lead to square-integrable functions only if both a minimum value of

FIGURE 7.2. Case 2. A monotonically decreasing $\mathcal{L}(m)$.

m and a maximum value of m exist. The spectrum of allowed m values is restricted to a finite number $= (m_{\max} - m_{\min} + 1)$.

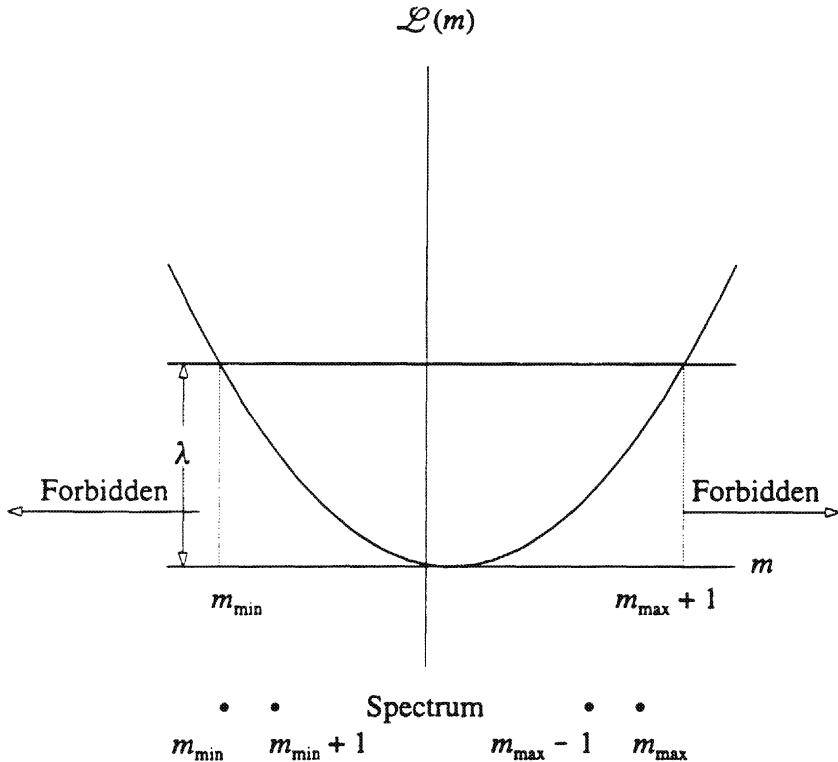
In the special case of the θ -equation, we have both

$$\lambda = \mathcal{L}(m_{\min}) = \mathcal{L}(m_{\max} + 1) = (m_{\min} - \frac{1}{2})^2 = (m_{\max} + \frac{1}{2})^2, \quad (43)$$

$$\text{and thus } m_{\min}^2 - m_{\min} = m_{\max}^2 + m_{\max}. \quad (44)$$

This quadratic equation for m_{\min} has the two roots, $m_{\min} = -m_{\max}$ and $m_{\min} = +(m_{\max} + 1)$. Clearly, the last equation violates the meaning of m_{\min} . Thus, with $m_{\max} \equiv l$, the allowed m values range from $+l$ in steps of one down to $-l$. Because $(m_{\max} - m_{\min}) = 2l$ must be an integer, we have the result, $2l$ must be an integer. Thus, seemingly l can be either an integer or a $\frac{1}{2}$ -integer. Later, we shall prove only the integer values are allowed for the orbital or θ equation.

Finally, the function $\mathcal{L}(m)$ could be a decreasing function of m for large positive values of m and an increasing function of m for negative values of m (see Fig. 7.4). In this case for a $\lambda < \mathcal{L}_{\max}$, now two ranges of m values exist, one beginning at an m_{\min} and going in integer steps on to $+\infty$, and a second beginning at an m_{\max} and going in integer steps onto $-\infty$. If $\lambda > \mathcal{L}_{\max}$, then all m values would

FIGURE 7.3. Case 3. An $\mathcal{L}(m)$ with an allowed spectrum such that $m_{\min} \leq m \leq m_{\max}$.

be allowed. In this last case, therefore, λ also has a continuous spectrum for all values of $\lambda > \mathcal{L}_{\max}$. In this case, the normalization integral should have the delta function form

$$\int_{-\infty}^{\infty} dx u_{\lambda'm}^*(x) u_{\lambda m}(x) = \delta(\lambda' - \lambda). \quad (45)$$

With $\lambda > \mathcal{L}(m)$ for all possible m , the normalized ladder operators, $\mathcal{O}_+(m+1)$ and $\mathcal{O}_-(m)$ exist. Moreover, they will preserve this normalization. If the $u_{\lambda m}(x)$ are normalized according to eq. (45), then

$$\begin{aligned} \int_{-\infty}^{\infty} dx u_{\lambda'(m-1)}^*(x) u_{\lambda(m-1)}(x) &= \frac{\int_{-\infty}^{\infty} dx u_{\lambda'm}^* [O_+(m) O_-(m) u_{\lambda m}]}{\sqrt{[\lambda' - \mathcal{L}(m)][\lambda - \mathcal{L}(m)]}} \\ &= \sqrt{\frac{[\lambda - \mathcal{L}(m)]}{[\lambda' - \mathcal{L}(m)]}} \int_{-\infty}^{\infty} dx u_{\lambda'm}^*(x) u_{\lambda m}(x) = \delta(\lambda' - \lambda). \end{aligned} \quad (46)$$

In this case, however, it may be difficult to find a solution for a starting value, $u_{\lambda m_0}(x)$.

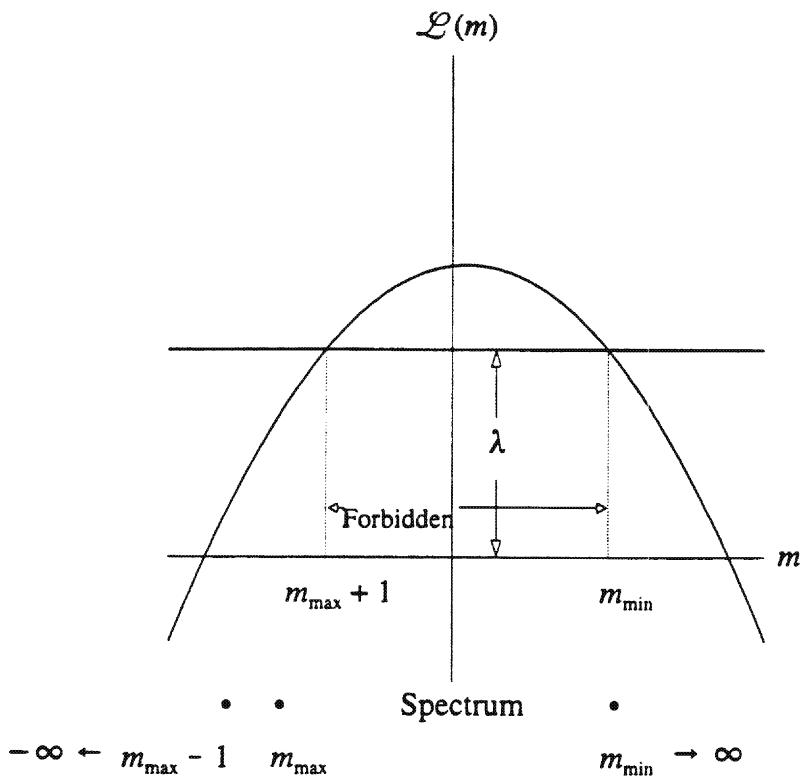


FIGURE 7.4. Case 4. An $\mathcal{L}(m)$ with two allowed branches: $m = m_{\max} \rightarrow -\infty$, and $m = m_{\min} \rightarrow +\infty$.

8

Spherical Harmonics, Orbital Angular Momentum

We are now in a position to calculate the full angular functions for the general central force problem, using the ladderizing techniques for the θ equation to construct the full set of angular functions $\Theta(\theta)$ via the normalized step-down operators. Because the eigenvalue $\lambda = \lambda_0 + \frac{1}{4}$ is a function of $m_{\max} \equiv l$, we will replace the index λ by the integer l . [Recall that $\lambda = \mathcal{L}(m_{\max} + 1) = (l + \frac{1}{2})^2$.] The full angular functions are the spherical harmonics

$$Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\Phi_m(\phi) = \frac{u_{lm}(\theta)}{\sqrt{\sin \theta}} \frac{e^{im\phi}}{\sqrt{2\pi}}. \quad (1)$$

To get the standard (universally accepted) phases for the spherical harmonics, we need to multiply the normalization coefficient in the starting function u_{ll} , with $m_{\max} = l$, by the phase factor $(-1)^l$

$$u_{ll}(\theta) = (-1)^l \sqrt{\frac{(2l+1)!!}{2[2l]!!}} \sin^{l+\frac{1}{2}}(\theta). \quad (2)$$

In addition, we need to multiply the normalized step-operators $\mathcal{O}_-(m)$ and $\mathcal{O}_+(m+1)$ of eqs. (37) and (39) of Chapter 7 by a phase factor (-1) . Thus,

$$Y_{l(m-1)} = -\frac{e^{-i\phi}}{\sqrt{\sin \theta}} \frac{\left[\left(\frac{d}{d\theta} + (m - \frac{1}{2}) \cot \theta \right) u_{lm}(\theta) \right]}{\sqrt{(l + \frac{1}{2})^2 - (m - \frac{1}{2})^2}} \frac{e^{im\phi}}{\sqrt{2\pi}}. \quad (3)$$

Setting $u_{lm}(\theta) = \sqrt{\sin \theta} \Theta_{lm}(\theta)$ in this equation, this becomes

$$Y_{l(m-1)} = \frac{e^{-i\phi}}{\sqrt{(l+m)(l-m+1)}} \left[\left(-\frac{d}{d\theta} - m \cot \theta \right) \Theta_{lm}(\theta) \right] \frac{e^{im\phi}}{\sqrt{2\pi}}. \quad (4)$$

Finally, putting

$$me^{im\phi} = -i \frac{\partial}{\partial \phi} e^{im\phi}, \quad (5)$$

we obtain

$$Y_{l(m-1)}(\theta, \phi) = \frac{e^{-i\phi}}{\sqrt{(l+m)(l-m+1)}} \left[-\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right] Y_{lm}(\theta, \phi). \quad (6)$$

Similarly, using the normalized, standard-phase step-up operator $-\mathcal{O}_+(m+1)$,

$$Y_{l(m+1)}(\theta, \phi) = \frac{e^{+i\phi}}{\sqrt{(l-m)(l+m+1)}} \left[+\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right] Y_{lm}(\theta, \phi). \quad (7)$$

A Angular Momentum Operators

It will now be useful to express the operators converting the Y_{lm} into $Y_{l(m\pm 1)}$ in terms of dimensionless angular momentum operators, such as

$$\frac{L_z}{\hbar} = \frac{1}{i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \quad (8)$$

Transforming to spherical coordinates

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta, \quad (9)$$

and using

$$\begin{aligned} \frac{\partial r}{\partial x} &= \sin \theta \cos \phi, & \frac{\partial r}{\partial y} &= \sin \theta \sin \phi, & \frac{\partial r}{\partial z} &= \cos \theta, \\ \frac{\partial \theta}{\partial x} &= \frac{\cos \theta \cos \phi}{r}, & \frac{\partial \theta}{\partial y} &= \frac{\cos \theta \sin \phi}{r}, & \frac{\partial \theta}{\partial z} &= -\frac{\sin \theta}{r}, \\ \frac{\partial \phi}{\partial x} &= -\frac{\sin \phi}{r \sin \theta}, & \frac{\partial \phi}{\partial y} &= \frac{\cos \phi}{r \sin \theta}, & \frac{\partial \phi}{\partial z} &= 0, \end{aligned} \quad (10)$$

we get

$$\frac{L_z}{\hbar} \equiv L_0 = \frac{1}{i} \frac{\partial}{\partial \phi}, \quad (11)$$

$$\frac{(L_x \pm i L_y)}{\hbar} \equiv L_{\pm} = e^{\pm i\phi} \left(\pm \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right), \quad (12)$$

and

$$\frac{(\vec{L} \cdot \vec{L})}{\hbar^2} = L_0^2 + \frac{1}{2} (L_+ L_- + L_- L_+) = - \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right). \quad (13)$$

Hence, the spherical harmonics are simultaneous eigenfunctions of the operators, $(\vec{L} \cdot \vec{L})$, and L_z , with

$$\begin{aligned} L_z Y_{lm}(\theta, \phi) &= \hbar m Y_{lm}(\theta, \phi), \\ (\vec{L} \cdot \vec{L}) Y_{lm}(\theta, \phi) &= \hbar^2 \lambda_0 Y_{lm}(\theta, \phi) = \hbar^2 l(l+1) Y_{lm}(\theta, \phi). \end{aligned} \quad (14)$$

In addition, eqs. (6) and (7) can be put into the form

$$L_- Y_{lm} = \sqrt{(l+m)(l-m+1)} Y_{l(m-1)}, \quad (15)$$

$$L_+ Y_{lm} = \sqrt{(l-m)(l+m+1)} Y_{l(m+1)}. \quad (16)$$

The $Y_{lm}(\theta, \phi)$ form an orthonormal complete set over the surface of the unit sphere. Thus, the matrix elements of the operators L_\pm are

$$\langle Y_{l'm'}, L_- Y_{lm} \rangle = \delta_{l'l} \delta_{m'(m-1)} \sqrt{(l+m)(l-m+1)}, \quad (17)$$

$$\langle Y_{l'm'}, L_+ Y_{lm} \rangle = \delta_{l'l} \delta_{m'(m+1)} \sqrt{(l-m)(l+m+1)}, \quad (18)$$

and

$$\langle Y_{l'm'}, L_0 Y_{lm} \rangle = \delta_{l'l} \delta_{m'm}. \quad (19)$$

These matrix elements can also be used to obtain the matrix elements of L_x and L_y .

$$\begin{aligned} \langle Y_{l'm'}, L_x Y_{lm} \rangle &= \frac{\hbar}{2} \langle Y_{l'm'}, (L_+ + L_-) Y_{lm} \rangle \\ &= \delta_{l'l} \frac{\hbar}{2} \left(\delta_{m'(m+1)} \sqrt{(l-m)(l+m+1)} \right. \\ &\quad \left. + \delta_{m'(m-1)} \sqrt{(l+m)(l-m+1)} \right). \end{aligned} \quad (20)$$

Similarly,

$$\begin{aligned} \langle Y_{l'm'}, L_y Y_{lm} \rangle &= \frac{\hbar}{2} \langle Y_{l'm'}, (-iL_+ + iL_-) Y_{lm} \rangle \\ &= \delta_{l'l} \frac{\hbar}{2} \left(-i \delta_{m'(m+1)} \sqrt{(l-m)(l+m+1)} \right. \\ &\quad \left. + i \delta_{m'(m-1)} \sqrt{(l+m)(l-m+1)} \right). \end{aligned} \quad (21)$$

The infinite-dimensional matrices for L_x , L_y , and L_z thus factor into $(2l+1)$ by $(2l+1)$ submatrices. As a simple, specific example, the submatrices for $l=1$ are (in units of \hbar),

$$\mathbf{L}_x = \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 \end{pmatrix},$$

$$\mathbf{L}_y = \begin{pmatrix} 0 & \frac{-i}{\sqrt{2}} & 0 \\ \frac{+i}{\sqrt{2}} & 0 & \frac{-i}{\sqrt{2}} \\ 0 & \frac{+i}{\sqrt{2}} & 0 \end{pmatrix},$$

$$\mathbf{L}_z = \begin{pmatrix} +1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

where rows and columns are labeled in the conventional order, $m = +1, 0, -1$.

Because the spherical harmonics form a complete orthonormal set, we can translate the operators L_{\pm} into the following functional forms. For example,

$$L_+ = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=+l} Y_{l(m+1)}(\theta, \phi) Y_{lm}^*(\theta, \phi) (\sqrt{(l-m)(l+m+1)}). \quad (22)$$

In our method of constructing the $(2l+1)$ spherical harmonics for a particular l , we have started with the eigenfunction with $m = m_{\max} = l$, and we have then used the normalized step-down operators, $\mathcal{O}_-(m)$, to calculate the remaining $2l$ eigenfunctions. Alternatively, we could have started with $m = m_{\min}$ and laddered with $\mathcal{O}_+(m+1)$. A third possibility would be to start with the spherical harmonics with $m = 0$ and use successive application of L_{\pm} to calculate the spherical harmonics with $\pm m$.

$$Y_{lm} = \frac{(L_+)^m Y_{l0}}{\sqrt{l(l-1) \cdots (l-m+1)(l+1)(l+2) \cdots (l+m)}} \\ = \sqrt{\frac{(l-m)!}{(l+m)!}} (L_+)^m Y_{l0}, \quad (23)$$

and

$$Y_{l-m} = \frac{(L_-)^m Y_{l0}}{\sqrt{l(l-1) \cdots (l-m+1)(l+1)(l+2) \cdots (l+m)}} \\ = \sqrt{\frac{(l-m)!}{(l+m)!}} (L_-)^m Y_{l0}. \quad (24)$$

Now, because

$$(L_+)^* = -(L_-), \quad (25)$$

we see

$$Y_{l-m}(\theta, \phi) = (-1)^m Y_{lm}^*(\theta, \phi). \quad (26)$$

Thus, it is sufficient to calculate the spherical harmonics with $m \geq 0$. As a final remark, the three operators L_x, L_y, L_z are all hermitian, and hence,

$$L_+^\dagger = L_-; \quad L_-^\dagger = L_+. \quad (27)$$

9

ℓ -Step operators for the θ Equation

In the last section, we calculated the matrix elements of the operators, L_x , L_y , L_z . These operators are functions only of θ , ϕ , and $\frac{\partial}{\partial\theta}$, $\frac{\partial}{\partial\phi}$. It will also be extremely useful to have the matrix elements of the angular parts of the position vector of the particle, viz. $\frac{x}{r} = \sin\theta \cos\phi$, $\frac{y}{r} = \sin\theta \sin\phi$, and $\frac{z}{r} = \cos\theta$. To get these, it would be useful to interchange the role of the quantum numbers l , and m , in the factorization method and derive expressions for ladder operators changing l to $l \pm 1$, keeping m fixed.

For this purpose, rewrite the 1-D θ equation in the form

$$-\sin^2\theta \frac{d^2\Theta}{d\theta^2} - \sin\theta \cos\theta \frac{d\Theta}{d\theta} - l(l+1) \sin^2\theta \Theta = -m^2\Theta. \quad (1)$$

If we can find a change of variable transforming the derivative operators into 1-D form, we will have succeeded, because $-m^2$ can then play the role of the fixed λ , whereas the parameter l is in a position to be stepped. The transformation achieving the desired result is

$$z = \ln\left(\tan \frac{\theta}{2}\right), \quad \theta = 0 \rightarrow z = -\infty, \quad \theta = \pi \rightarrow z = +\infty. \quad (2)$$

Note,

$$\frac{d}{d\theta} = \frac{dz}{d\theta} \frac{d}{dz} = \frac{1}{\sin\theta} \frac{d}{dz}, \quad \frac{d^2}{d\theta^2} = -\frac{\cos\theta}{\sin^2\theta} \frac{d}{dz} + \frac{1}{\sin^2\theta} \frac{d^2}{dz^2}, \quad (3)$$

so

$$-\sin^2\theta \frac{d^2}{d\theta^2} - \sin\theta \cos\theta \frac{d}{d\theta} = -\frac{d^2}{dz^2}. \quad (4)$$

Also,

$$\cosh z = \frac{1}{\sin \theta}, \quad \tanh z = -\cos \theta. \quad (5)$$

Now, with

$$\Theta(\theta(z)) = v(z), \quad (6)$$

eq. (1) is transformed into

$$\left[-\frac{d^2}{dz^2} - \frac{l(l+1)}{\cosh^2(z)} \right] v_{\lambda l}(z) = -m^2 v_{\lambda l}(z) = \lambda v_{\lambda l}(z). \quad (7)$$

Now, with $\lambda = -m^2$, the role of m and l have been interchanged, l being a parameter in the “potential function.” This equation is now factorizable with the factors

$$O_{\pm}(l) = \left(\mp \frac{d}{dz} + l \tanh z \right), \quad (8)$$

with

$$\begin{aligned} O_+(l) O_-(l) v_{\lambda l} &= \left[-\frac{d}{dz} + l \tanh z \right] \left[+\frac{d}{dz} + l \tanh z \right] v_{\lambda l} \\ &= \left(\left[-\frac{d^2}{dz^2} - \frac{l(l+1)}{\cosh^2 z} \right] + l^2 \right) v_{\lambda l} \\ &= [\lambda - \mathcal{L}(l)] v_{\lambda l}, \end{aligned} \quad (9)$$

and

$$\begin{aligned} O_-(l+1) O_+(l+1) v_{\lambda l} &= \left[+\frac{d}{dz} + (l+1) \tanh z \right] \left[-\frac{d}{dz} + (l+1) \tanh z \right] v_{\lambda l} \\ &= \left(\left[-\frac{d^2}{dz^2} - \frac{l(l+1)}{\cosh^2 z} \right] + (l+1)^2 \right) v_{\lambda l} \\ &= [\lambda - \mathcal{L}(l+1)] v_{\lambda l}, \end{aligned} \quad (10)$$

so

$$\mathcal{L}(l) = -l^2. \quad (11)$$

$\mathcal{L}(l)$ is a decreasing function of l and, with the negative $\lambda = -m^2$, must be such that a minimum value of l exists, with

$$\lambda = -m^2 = \mathcal{L}(l_{min}) = -l_{min}^2. \quad (12)$$

The starting function, with $l = l_{min} = m$, is obtained from

$$O_-(l_{min}) v_{\lambda l_{min}=m} = \left(\frac{d}{dz} + m \tanh z \right) v_{\lambda m}, \quad (13)$$

so

$$\frac{dv_{\lambda m}}{v_{\lambda m}} = -m \tanh z dz, \quad \text{with} \quad \ln v_{\lambda m} = \ln(\cosh z)^{-m}. \quad (14)$$

This leads to

$$v_{\lambda m} = \frac{N_m}{(\cosh z)^m} = N_m (\sin \theta)^m, \quad (15)$$

which agrees with our earlier solution for $\Theta(\theta)$, with $l = m$. The remaining solutions with $l > m$ can be obtained through the normalized step-up operators, via

$$\begin{aligned} v_{\lambda(l+1)} &= \frac{1}{\sqrt{[\lambda - \mathcal{L}(l+1)]}} \left(-\frac{d}{dz} + (l+1) \tanh z \right) v_{\lambda l} \\ &= \frac{1}{\sqrt{[-m^2 + (l+1)^2]}} \left(-\frac{d}{dz} + (l+1) \tanh z \right) v_{\lambda l}. \end{aligned} \quad (16)$$

Similarly,

$$v_{\lambda(l-1)} = \frac{1}{\sqrt{[-m^2 + l^2]}} \left(+\frac{d}{dz} + l \tanh z \right) v_{\lambda l}. \quad (17)$$

Note, however, the normalization preserved by these $v_{\lambda l}(z)$ is

$$\int_{-\infty}^{\infty} dz |v_{\lambda l}(z)|^2 = 1, \quad (18)$$

whereas, with $\Theta_{lm}(\theta(z)) = v_{\lambda l}(z)$, $d\theta = \sin \theta dz$, and $\cosh z = \frac{1}{\sin \theta}$, we should have normalized with a weighting factor in z -space

$$\int_0^\pi d\theta \sin \theta |\Theta(\theta)|^2 = \int_{-\infty}^{\infty} dz (\cosh^{-2}(z)) |v_{\lambda l}(z)|^2 = 1. \quad (19)$$

The lack of the weighting factor $\cosh^{-2}(z)$ means our functions $\Theta_{lm}(\theta(z))$ can be identified with the $v_{\lambda m}(z)$ only with the inclusion of an additional normalization factor, c_{lm} , via

$$\Theta_{lm}(\theta) = c_{lm} v_{\lambda l}(z). \quad (20)$$

With $\frac{d}{dz} = \sin \theta \frac{d}{d\theta}$, and $\tanh z = -\cos \theta$, eqs. (16) and (17) translate into

$$\Theta_{(l+1)m}(\theta) = -\frac{(c_{(l+1)m}/c_{lm})}{\sqrt{(l+1+m)(l+1-m)}} \left[-\sin \theta \frac{d}{d\theta} - (l+1) \cos \theta \right] \Theta_{lm}(\theta), \quad (21)$$

$$\Theta_{(l-1)m}(\theta) = -\frac{(c_{(l-1)m}/c_{lm})}{\sqrt{(l+m)(l-m)}} \left[\sin \theta \frac{d}{d\theta} - l \cos \theta \right] \Theta_{lm}(\theta). \quad (22)$$

We have again introduced an extra minus sign to agree with the standard phase conventions for spherical harmonics. This minus sign is the analog of that introduced in eqs. (4) and (7) of Chapter 8.

To calculate the ratios of c_{lm} coefficients, we shall calculate $\Theta_{(l+1)(m+1)}(\theta)$ in two ways, by stepping from (l, m) to $(l+1, m+1)$ along two different paths in the l, m parameter space.

For path (1), step first from (l, m) to $(l, m + 1)$ via the m step-up operator of eq. (7) of Chapter 8:

$$\frac{1}{\sqrt{(l-m)(l+m+1)}} \left[\frac{d}{d\theta} - m \cot \theta \right], \quad (23)$$

and follow this relation with a step from $(l, m + 1)$ to $(l + 1, m + 1)$ with the l step-up operator.

For path (2), step first from (l, m) to $(l + 1, m)$ and follow this with a step from $(l + 1, m)$ to $(l + 1, m + 1)$.

Path (1) leads to:

$$\begin{aligned} \Theta_{(l+1)(m+1)} &= \frac{c_{(l+1)(m+1)}}{c_{l(m+1)}} \left[\frac{\sin \theta \frac{d}{d\theta} + (l+1) \cos \theta}{\sqrt{(l+m+2)(l-m)}} \right] \left[\frac{\frac{d}{d\theta} - m \cot \theta}{\sqrt{(l-m)(l+m+1)}} \right] \Theta_{lm} \\ &= \frac{(c_{(l+1)(m+1)}/c_{l(m+1)})}{(l-m)\sqrt{(l+m+1)(l+m+2)}} \left(\sin \theta \left[\frac{d^2}{d\theta^2} + \cot \theta \frac{d}{d\theta} \right] \right. \\ &\quad \left. + (l-m) \cos \theta \frac{d}{d\theta} - m(l+1) \frac{\cos^2 \theta}{\sin \theta} + \frac{m}{\sin \theta} \right) \Theta_{lm}. \end{aligned} \quad (24)$$

Now use

$$\left[\frac{d^2}{d\theta^2} + \cot \theta \frac{d}{d\theta} \right] = \left[\frac{m^2}{\sin^2 \theta} - l(l+1) \right] \quad (25)$$

via the θ equation, and simplify the above by factoring out the factor $(l-m)$ to yield

$$\Theta_{(l+1)(m+1)} = \frac{(c_{(l+1)(m+1)}/c_{l(m+1)})}{\sqrt{(l+m+1)(l+m+2)}} \left[\cos \theta \frac{d}{d\theta} - \frac{m}{\sin \theta} - (l+1) \sin \theta \right] \Theta_{lm}. \quad (26)$$

Similarly, using path (2), we get

$$\Theta_{(l+1)(m+1)} = \frac{(c_{(l+1)m}/c_{lm})}{\sqrt{(l+m+1)(l+m+2)}} \left[\cos \theta \frac{d}{d\theta} - \frac{m}{\sin \theta} - (l+1) \sin \theta \right] \Theta_{lm}. \quad (27)$$

We see

$$\frac{c_{(l+1)(m+1)}}{c_{l(m+1)}} = \frac{c_{(l+1)m}}{c_{lm}}. \quad (28)$$

That is, the ratio is independent of m , and we can calculate it by setting $m = l$

$$\frac{c_{(l+1)m}}{c_{lm}} = \frac{c_{(l+1)l}}{c_{ll}}. \quad (29)$$

Setting $m = l$ in eq. (26), and using eqs. (28) and (29), leads to

$$\begin{aligned} \Theta_{(l+1)(l+1)} &= N_{l+1} \sin^{l+1} \theta \\ &= \frac{(c_{(l+1)l}/c_{ll})}{\sqrt{(2l+1)(2l+2)}} \left[\cos \theta \frac{d}{d\theta} - \frac{l}{\sin \theta} - (l+1) \sin \theta \right] N_l \sin^l \theta \end{aligned}$$

$$= -\frac{c_{(l+1)l}}{c_{ll}} \sqrt{\frac{(2l+1)}{(2l+2)}} N_l \sin^{l+1} \theta. \quad (30)$$

Therefore, with

$$\frac{N_{l+1}}{N_l} = -\sqrt{\frac{(2l+3)}{(2l+2)}}, \quad (31)$$

[see eq. (2) of Chapter 8],

$$\frac{c_{(l+1)l}}{c_{ll}} = \sqrt{\frac{(2l+3)}{(2l+1)}} = \frac{c_{(l+1)m}}{c_{lm}}. \quad (32)$$

Using this result, we can now rewrite the l -step equations [eqs. (21) and (22)], as

$$\Theta_{(l+1)m} = \sqrt{\frac{(2l+3)/(2l+1)}{(l+1+m)(l+1-m)}} \left[\sin \theta \frac{d}{d\theta} + (l+1) \cos \theta \right] \Theta_{lm}, \quad (33)$$

$$\Theta_{(l-1)m} = \sqrt{\frac{(2l-1)/(2l+1)}{(l+m)(l-m)}} \left[-\sin \theta \frac{d}{d\theta} + l \cos \theta \right] \Theta_{lm}. \quad (34)$$

Adding these two equations, after multiplication of each by the inverse of the square root factor, leads to

$$\begin{aligned} & \cos \theta \Theta_{lm} \\ &= \sqrt{\frac{(l+1+m)(l+1-m)}{(2l+1)(2l+3)}} \Theta_{(l+1)m} + \sqrt{\frac{(l+m)(l-m)}{(2l+1)(2l-1)}} \Theta_{(l-1)m}. \end{aligned} \quad (35)$$

Also, using the c-ratio of eq. (32), eq. (26) can now be rewritten explicitly as

$$\Theta_{(l+1)(m+1)} = \sqrt{\frac{(2l+3)/(2l+1)}{(l+m+1)(l+m+2)}} \left[\cos \theta \frac{d}{d\theta} - \frac{m}{\sin \theta} - (l+1) \sin \theta \right] \Theta_{lm}. \quad (36)$$

Similarly, using step-operations from (l, m) to $(l, m+1)$ and then from $(l, m+1)$ to $(l-1, m+1)$, eliminating the second derivative term via the differential equation, as for eq. (26), we get the companion equation

$$\Theta_{(l-1)(m+1)} = \sqrt{\frac{(2l-1)/(2l+1)}{(l-m)(l-m-1)}} \left[\cos \theta \frac{d}{d\theta} - \frac{m}{\sin \theta} + l \sin \theta \right] \Theta_{lm}. \quad (37)$$

Eqs. (36) and (37) can now be combined to give

$$\sin \theta \Theta_{lm} =$$

$$-\sqrt{\frac{(l+m+2)(l+m+1)}{(2l+3)(2l+1)}} \Theta_{(l+1)(m+1)} + \sqrt{\frac{(l-m)(l-m-1)}{(2l+1)(2l-1)}} \Theta_{(l-1)(m+1)}. \quad (38)$$

Finally, using the products of m step-down, and l step-up or down operators, we get

$$\Theta_{(l+1)(m-1)} = \sqrt{\frac{(2l+3)/(2l+1)}{(l+2-m)(l+1-m)}} \left[-\cos \theta \frac{d}{d\theta} - \frac{m}{\sin \theta} + (l+1) \sin \theta \right] \Theta_{lm}, \quad (39)$$

$$\Theta_{(l-1)(m-1)} = \sqrt{\frac{(2l-1)/(2l+1)}{(l+m)(l+m-1)}} \left[-\cos \theta \frac{d}{d\theta} - \frac{m}{\sin \theta} - l \sin \theta \right] \Theta_{lm}. \quad (40)$$

Eqs. (39) and (40) can now be combined to give

$$\sin \theta \Theta_{lm} =$$

$$\sqrt{\frac{(l+2-m)(l+1-m)}{(2l+3)(2l+1)}} \Theta_{(l+1)(m-1)} - \sqrt{\frac{(l+m)(l+m-1)}{(2l+1)(2l-1)}} \Theta_{(l-1)(m-1)}. \quad (41)$$

Finally, by multiplying eq. (35) by $e^{im\phi}/\sqrt{2\pi}$, eq. (38) by $e^{i(m+1)\phi}/\sqrt{2\pi}$, and eq. (41) by $e^{i(m-1)\phi}/\sqrt{2\pi}$, these operators can be converted to equations involving the full spherical harmonics, $Y_{lm}(\theta, \phi)$:

$$\cos \theta Y_{lm} = \sqrt{\frac{(l+1+m)(l+1-m)}{(2l+1)(2l+3)}} Y_{(l+1)m} + \sqrt{\frac{(l+m)(l-m)}{(2l+1)(2l-1)}} Y_{(l-1)m}, \quad (42)$$

$$e^{i\phi} \sin \theta Y_{lm} =$$

$$-\sqrt{\frac{(l+m+2)(l+1+m)}{(2l+3)(2l+1)}} Y_{(l+1)(m+1)} + \sqrt{\frac{(l-m)(l-m-1)}{(2l+1)(2l-1)}} Y_{(l-1)(m+1)}, \quad (43)$$

$$e^{-i\phi} \sin \theta Y_{lm} =$$

$$\sqrt{\frac{(l+2-m)(l+1-m)}{(2l+3)(2l+1)}} Y_{(l+1)(m-1)} - \sqrt{\frac{(l+m)(l+m-1)}{(2l+1)(2l-1)}} Y_{(l-1)(m-1)}. \quad (44)$$

Now, because the $Y_{lm}(\theta, \phi)$ form a complete orthonormal set over the surface of a sphere, we can use eqs. (42)–(44) to find the matrix elements of the operators $\cos \theta, e^{\pm i\phi} \sin \theta$. These operators give us the matrix elements of the angular parts of x, y, z , because

$$\frac{(x \pm iy)}{r} = e^{\pm i\phi} \sin \theta, \quad \frac{z}{r} = \cos \theta. \quad (45)$$

Matrix elements of higher powers of x, y , and z (angular parts) can then be obtained from these operators by matrix multiplication.

Final remark: The angular functions $\Theta_{lm}(\theta)$ are not by themselves orthogonal for different values of m . Thus, in general,

$$\int_0^\pi d\theta \sin \theta \Theta_{lm'}^*(\theta) \Theta_{lm}(\theta) \neq \delta_{m'm}. \quad (46)$$

$l \ m$	$Y_{lm}(\theta, \phi)$	$\mathcal{Y}_{lm} = r^l Y_{lm}$
0 0	$\frac{1}{\sqrt{4\pi}}$	$\frac{1}{\sqrt{4\pi}}$
1 0	$\sqrt{\frac{3}{4\pi}} \cos \theta$	$\sqrt{\frac{3}{4\pi}} z$
1 ± 1	$\mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$	$\mp \sqrt{\frac{3}{8\pi}} (x \pm iy)$
2 0	$\sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$	$\sqrt{\frac{5}{16\pi}} (2z^2 - x^2 - y^2)$
2 ± 1	$\mp \sqrt{\frac{15}{8\pi}} \cos \theta \sin \theta e^{\pm i\phi}$	$\mp \sqrt{\frac{15}{8\pi}} z(x \pm iy)$
2 ± 2	$\sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$	$\sqrt{\frac{15}{32\pi}} (x \pm iy)^2$
3 0	$\sqrt{\frac{7}{16\pi}} (5 \cos^3 \theta - 3 \cos \theta)$	$\sqrt{\frac{7}{16\pi}} z[2z^2 - 3(x^2 + y^2)]$
3 ± 1	$\mp \sqrt{\frac{21}{64\pi}} (5 \cos^2 \theta - 1) \sin \theta e^{\pm i\phi}$	$\mp \sqrt{\frac{21}{64\pi}} (4z^2 - x^2 - y^2)(x \pm iy)$
3 ± 2	$\sqrt{\frac{105}{32\pi}} \cos \theta \sin^2 \theta e^{\pm 2i\phi}$	$\sqrt{\frac{105}{32\pi}} z(x \pm iy)^2$
3 ± 3	$\mp \sqrt{\frac{35}{64\pi}} \sin^3 \theta e^{\pm 3i\phi}$	$\mp \sqrt{\frac{35}{64\pi}} (x \pm iy)^3$

The orthogonality in m comes via the functions $\Phi(\phi)$. For this reason, eqs. (38) and (41) were set up so that both terms on the right-hand sides have the *same* values of m .

A table of some of the simplest spherical harmonics is included here. These harmonics can be calculated very trivially through eqs. (1) and (2) of Chapter 8 with a few applications of the laddering operations of eq. (6) of Chapter 8 and the use of the symmetry property, eq. (26) of Chapter 8. They are given here so they can be combined with a tabulation of solid harmonics, defined by

$$\mathcal{Y}_{lm} = r^l Y_{lm}(\theta, \phi). \quad (47)$$

These can be expressed as homogeneous polynomials of degree l in x, y, z by acting on

$$\mathcal{Y}_{ll} = N_l (x + iy)^l, \quad \text{with} \quad N_l = (-1)^l \sqrt{\frac{(2l+1)!!}{2(2l)!! 2\pi}}, \quad (48)$$

$(l-m)$ times in succession with the m step-down operator, $\mathcal{O}_-(m)$, where

$$\begin{aligned} \mathcal{O}_-(m) &= -\frac{e^{-i\phi}}{\sqrt{(l+m)(l-m+1)}} \left[\frac{d}{d\theta} + m \cot \theta \right] \\ &= -\frac{(x+iy)^{-1}}{\sqrt{(l+m)(l-m+1)}} \left[z \left(x \frac{d}{dx} + y \frac{d}{dy} + m \right) - (x^2 + y^2) \frac{d}{dz} \right], \end{aligned} \quad (49)$$

and

$$\mathcal{O}_-(m)\mathcal{Y}_{lm} = \mathcal{Y}_{l,m-1}. \quad (50)$$

This relation leads to

$$\mathcal{Y}_{lm} = (-1)^{l-m} N_{ll} \sqrt{\frac{(l+m)!}{(2l)!(l-m)!}} \sum_{\alpha=0}^{\lfloor \frac{l-m}{2} \rfloor} c_{\alpha}^{(m)} (x+iy)^m z^{l-m-2\alpha} (x^2+y^2)^{\alpha} \quad (51)$$

for the states with $m \geq 0$. The coefficients are related by

$$c_{\alpha=0}^{(m-1)} = 2mc_{\alpha=0}^{(m)}, \quad (52)$$

and, for $\alpha = 1, \dots, \lfloor \frac{l-m}{2} \rfloor$,

$$c_{\alpha}^{(m-1)} = 2(m+\alpha)c_{\alpha}^{(m)} - (l-m-2\alpha+2)c_{\alpha-1}^{(m)}. \quad (53)$$

The solution gives

$$\begin{aligned} \mathcal{Y}_{lm} &= (-1)^m \sqrt{\frac{(l+m)!(2l+1)!!}{(l-m)!(2l)!2(2l)!!2\pi}} \\ &\times \sum_{\alpha=0}^{\lfloor \frac{l-m}{2} \rfloor} (-1)^{\alpha} \frac{2^{l-m-2\alpha} l!(l-m)!}{\alpha!(m+\alpha)!(l-m-2\alpha)!} (x+iy)^m z^{l-m-2\alpha} (x^2+y^2)^{\alpha}. \end{aligned} \quad (54)$$

As an additional footnote, this result can also be used to find a solution to the following useful problem: Express the solid spherical harmonics in the relative motion vector, $\vec{r}_1 - \vec{r}_2$, as functions of the solid harmonics in \vec{r}_1 and \vec{r}_2 ; i.e., express the $\mathcal{Y}_{lm}(\vec{r}_1 - \vec{r}_2)$ as functions of $\mathcal{Y}_{lm}(\vec{r}_1)$ and $\mathcal{Y}_{lm}(\vec{r}_2)$. It will be useful first to define \mathcal{Z}_{lm} via

$$\mathcal{Y}_{lm} \equiv -(1)^m \sqrt{\frac{(l+m)!(2l+1)!!}{(l-m)!(2l)!2^{l+1}l!2\pi}} \mathcal{Z}_{lm}, \quad (55)$$

so

$$\mathcal{Z}_{lm} = \sum_{\alpha=0}^{\lfloor \frac{l-m}{2} \rfloor} (-1)^{\alpha} \frac{2^{l-m-2\alpha} l!(l-m)!}{\alpha!(m+\alpha)!(l-m-2\alpha)!} (x+iy)^{m+\alpha} (x-iy)^{\alpha} z^{l-m-2\alpha}, \quad (56)$$

or

$$\begin{aligned} \mathcal{Z}_{lm}(\vec{r}_1 - \vec{r}_2) &= \sum_{\alpha=0}^{\lfloor \frac{l-m}{2} \rfloor} (-1)^{\alpha} \frac{2^{l-m-2\alpha} l!(l-m)!}{\alpha!(m+\alpha)!(l-m-2\alpha)!} \\ &\times [(x_1 + iy_1) - (x_2 + iy_2)]^{m+\alpha} [(x_1 - iy_1) - (x_2 - iy_2)]^{\alpha} (z_1 - z_2)^{l-m-2\alpha} \\ &= \sum_{\alpha=0}^{\lfloor \frac{l-m}{2} \rfloor} \sum_{\beta=0}^{m+\alpha} \sum_{\gamma=0}^{\alpha} \sum_{\delta=0}^{l-m-2\alpha} (-1)^{\alpha+\beta+\gamma+\delta} \\ &\times \frac{2^{l-m-2\alpha} l!(l-m)!}{\beta!(m+\alpha-\beta)!\gamma!(\alpha-\gamma)!\delta!(l-m-2\alpha-\delta)!} \\ &\times (x_1 + iy_1)^{m+\alpha-\beta} (x_1 - iy_1)^{\alpha-\gamma} z_1^{l-m-2\alpha-\delta} (x_2 + iy_2)^{\beta} (x_2 - iy_2)^{\gamma} z_2^{\delta}, \end{aligned} \quad (57)$$

where, renaming $\gamma = \alpha_2$, we have $\gamma = \alpha_2$, $\beta = m_2 + \alpha_2$; and $\delta = l_2 - m_2 - 2\alpha_2$. In addition, with $m = m_1 + m_2$, and $l = l_1 + l_2$, and, defining α_1 through $\alpha = \alpha_1 + \alpha_2$, we have

$$m + \alpha - \beta = m_1 + \alpha_1, \quad \alpha - \gamma = \alpha_1, \quad l - m - 2\alpha - \delta = l_1 - m_1 - 2\alpha_1.$$

The above expression for $Z_{lm}(\vec{r}_1 - \vec{r}_2)$ can then be rewritten as

$$\begin{aligned} Z_{lm}(\vec{r}_1 - \vec{r}_2) &= \sum_{l_1(l_1)m_2(m_1)} \sum_{\alpha_1=0}^{\lfloor \frac{l_1-m_1}{2} \rfloor} \sum_{\alpha_2=0}^{\lfloor \frac{l_2-m_2}{2} \rfloor} (-1)^{l_2+\alpha_1+\alpha_2} \\ &\times \frac{l!(l-m)!2^{l_1-m_1-2\alpha_1+l_2-m_2-2\alpha_2}}{\alpha_1!\alpha_2!(m_1+\alpha_1)!(m_2+\alpha_2)!(l_1-m_1-2\alpha_1)!(l_2-m_2-2\alpha_2)!} \\ &\times (x_1 + iy_1)^{m_1+\alpha_1} (x_1 - iy_1)^{\alpha_1} z_1^{l_1-m_1-2\alpha_1} \\ &\times (x_2 + iy_2)^{m_2+\alpha_2} (x_2 - iy_2)^{\alpha_2} z_2^{l_2-m_2-2\alpha_2} \\ &= \sum_{l_2(l_1)m_2(m_1)} (-1)^{l_2} \frac{l!(l-m)!}{l_1!(l_1-m_1)!l_2!(l_2-m_2)!} Z_{l_1m_1}(\vec{r}_1) Z_{l_2m_2}(\vec{r}_2). \end{aligned} \quad (58)$$

Finally, using the definition of Z_{lm} , we get

$$\begin{aligned} Y_{lm}(\vec{r}_1 - \vec{r}_2) &= \sum_{l_2(l_1)} \sum_{m_2(m_1)} (-1)^{l_2} Y_{l_1m_1}(\vec{r}_1) Y_{l_2m_2}(\vec{r}_2) \times \\ &\left[\frac{(l+m)!(l-m)!l!(2l+1)!!(2l_1)!(2l_2)!4\pi}{(2l)!(l_1+m_1)!(l_1-m_1)!l_1!(2l_1+1)!!(l_2+m_2)!(l_2-m_2)!l_2!(2l_2+1)!!} \right]^{\frac{1}{2}}. \end{aligned} \quad (59)$$

10

The Radial Functions for the Hydrogenic Atom

Because we have solved the angular part of the one-body problem for a spherically symmetric $V(r)$ (or, equivalently, the angular part for the relative motion of a two-body problem), it would be good to provide a detailed example for a particular potential, $V(r)$. Because the Coulomb problem is soluble via the factorization method, let us solve the radial problem for the general hydrogenic atom, i.e., the one electron atom (with $Z = 1, 2, 3, \dots$) for hydrogen, once-ionized Helium, twice-ionized Lithium, and so on, where

$$V(r) = -\frac{Ze^2}{r}. \quad (1)$$

The one-dimensionalized radial equation is

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \left[-\frac{Ze^2}{r} + \frac{\hbar^2 l(l+1)}{2\mu r^2} \right] \right) u(r) = Eu(r), \quad (2)$$

where the coordinate r in this equation is the “physical” r , measured in centimeters or Angstrom units and E is the energy measured in eV, for example. Let us first switch to dimensionless quantities, and let the $r_{phys.}$ and E of the above equation be replaced by dimensionless quantities r , and ϵ

$$r_{phys.} = \frac{a_0}{Z} r, \quad \text{with} \quad a_0 = \frac{\hbar^2}{\mu e^2}, \quad E = \frac{\mu Z^2 e^4}{\hbar^2} \epsilon, \quad (3)$$

leading to the radial equation in dimensionless quantities

$$\left(-\frac{d^2}{dr^2} - \frac{2}{r} + \frac{l(l+1)}{r^2} \right) u_{\lambda l}(r) = 2\epsilon u_{\lambda l}(r) = \lambda u_{\lambda l}(r). \quad (4)$$

This equation is factorizable via the factors

$$O_{\pm}(l) = \left(\mp \frac{d}{dr} + \frac{l}{r} - \frac{1}{l} \right), \quad (5)$$

with

$$O_+(l)O_-(l)u_{\lambda l} = \left(-\frac{d^2}{dr^2} - \frac{2}{r} + \frac{l(l+1)}{r^2} + \frac{1}{l^2} \right) u_{\lambda l} = \left[\lambda + \frac{1}{l^2} \right] u_{\lambda l}, \quad (6)$$

$$\begin{aligned} O_-(l+1)O_+(l+1)u_{\lambda l} &= \left(-\frac{d^2}{dr^2} - \frac{2}{r} + \frac{l(l+1)}{r^2} + \frac{1}{(l+1)^2} \right) u_{\lambda l} \\ &= \left[\lambda + \frac{1}{(l+1)^2} \right] u_{\lambda l}, \end{aligned} \quad (7)$$

so the factorization works, and

$$\mathcal{L}(l) = -\frac{1}{l^2}. \quad (8)$$

Because \mathcal{L} is an increasing function of l for positive l , and because ϵ and, hence, λ must be a negative quantity for bound states, $[\lambda - \mathcal{L}(l+1)]$ will be a positive quantity only up through a maximum l -value. Thus,

$$\lambda = \mathcal{L}(l_{max} + 1) = -\frac{1}{(l_{max} + 1)^2} = 2\epsilon. \quad (9)$$

Renaming the integer l_{max} : $l_{max} + 1 = n$, or $l_{max} = (n - 1)$, we obtain the hydrogen result

$$\epsilon = -\frac{1}{2n^2}, \quad E = -\frac{\mu Z^2 e^4}{\hbar^2} \frac{1}{2n^2}. \quad (10)$$

The starting function is obtained from

$$O_+(l_{max} + 1)u_{\lambda l_{max}} = O_+(n)u_{n,l=(n-1)} = \left(-\frac{d}{dr} + \frac{n}{r} - \frac{1}{n} \right) u_{n,n-1} = 0, \quad (11)$$

leading to the normalized solution

$$u_{n,l=n-1} = N_n r^n e^{-\frac{r}{n}}, \quad \text{with} \quad N_n = \sqrt{\left(\frac{2}{n}\right)^{2n+1} \frac{1}{(2n)!}}. \quad (12)$$

The radial functions for the lower l values for a definite n can be obtained from these by action with the normalization-preserving step-down operators, $\mathcal{O}_-(l)$,

$$\mathcal{O}_-(l) = \frac{1}{\sqrt{[\lambda - \mathcal{L}(l)]}} \left(\frac{d}{dr} + \frac{l}{r} - \frac{1}{l} \right) = \frac{nl}{\sqrt{(n-l)(n+l)}} \left(\frac{d}{dr} + \frac{l}{r} - \frac{1}{l} \right). \quad (13)$$

For example, for $n = 2$, the starting function with $l = 1$ is given by

$$u_{n=2,l=1}(r) = \frac{1}{2\sqrt{6}} r^2 e^{-\frac{r}{2}}. \quad (14)$$

The eigenfunction with $l = 0$ is obtained via

$$\begin{aligned} u_{n=2,l=0}(r) &= \frac{2}{\sqrt{3}} \left(\frac{d}{dr} + \frac{1}{r} - 1 \right) \frac{1}{2\sqrt{6}} r^2 e^{-\frac{r}{2}} \\ &= \frac{1}{2\sqrt{2}} r(2-r)e^{-\frac{r}{2}}. \end{aligned} \quad (15)$$

We tabulate a few of the radial eigenfunctions obtained in this way for the lower n values. With $r R(r) = u(r)$, the $R(r)$ are given by

$$\begin{aligned} \text{For } n = 1, l = 0 : R_{10}(r) &= 2e^{-r}, \\ \text{For } n = 2, l = 1 : R_{21}(r) &= \frac{1}{2\sqrt{6}} r e^{-\frac{r}{2}}, \\ \text{For } n = 2, l = 0 : R_{20}(r) &= \frac{1}{2\sqrt{2}} (2-r) e^{-\frac{r}{2}}, \\ \text{For } n = 3, l = 2 : R_{32}(r) &= \frac{2\sqrt{2}}{3^4\sqrt{15}} r^2 e^{-\frac{r}{3}}, \\ \text{For } n = 3, l = 1 : R_{31}(r) &= \frac{2\sqrt{2}}{3^4\sqrt{3}} r(6-r) e^{-\frac{r}{3}}, \\ \text{For } n = 3, l = 0 : R_{30}(r) &= \frac{2}{3^4\sqrt{3}} (27 - 18r + 2r^2) e^{-\frac{r}{3}}. \end{aligned} \quad (16)$$

Here, the dimensionless r is $r = (Zr_{\text{phys.}}/a_0)$. To convert to a normalization in physical space $\int_0^\infty dr_{\text{phys.}} r_{\text{phys.}}^2 |R(r_{\text{phys.}})|^2 = 1$, the above results must be multiplied with the additional normalization factor $(Z/a_0)^{\frac{3}{2}}$.

Shape-Invariant Potentials: Soluble One-Dimensional Potential Problems

Having seen and used a number of examples, let us now look at the factorization method in a more general way. For the factorization method to work, we must have

$$[O_+(m)O_-(m) + \mathcal{L}(m)]u_{\lambda m} = \lambda u_{\lambda m}, \quad (1)$$

$$\left(\left[-\frac{d}{dx} + k(x, m) \right] \left[\frac{d}{dx} + k(x, m) \right] + \mathcal{L}(m) \right) u_{\lambda m} = \lambda u_{\lambda m}, \quad (2)$$

$$\begin{aligned} & \left(-\frac{d^2}{dx^2} + [k^2(x, m) - k'(x, m) + \mathcal{L}(m)] \right) u_{\lambda m} = \\ & \left(-\frac{d^2}{dx^2} + V(x, m) \right) u_{\lambda m} = \lambda u_{\lambda m}, \end{aligned} \quad (3)$$

where the potential function $V(x, m)$ is expressed in terms of $k(x, m)$ and its first derivative is expressed by a prime. We must also have

$$[O_-(m+1)O_+(m+1) + \mathcal{L}(m+1)]u_{\lambda m} = \lambda u_{\lambda m}. \quad (4)$$

Eqs. (1) and (4) are the two conditions, I and II, of eq. (17) of Chapter 7, which must be satisfied for the factorization method to work. Now, shifting the index m to $(m-1)$ in eq. (4)

$$\begin{aligned} & [O_-(m)O_+(m) + \mathcal{L}(m)]u_{\lambda(m-1)} = \lambda u_{\lambda(m-1)} \\ & = \left(\left[\frac{d}{dx} + k(x, m) \right] \left[-\frac{d}{dx} + k(x, m) \right] + \mathcal{L}(m) \right) u_{\lambda(m-1)} = \lambda u_{\lambda(m-1)} \end{aligned} \quad (5)$$

$$\begin{aligned} & \left(-\frac{d^2}{dx^2} + [k^2(x, m) + k'(x, m) + \mathcal{L}(m)] \right) u_{\lambda(m-1)} \\ & = \left(-\frac{d^2}{dx^2} + V(x, m-1) \right) u_{\lambda(m-1)} = \lambda u_{\lambda(m-1)}, \end{aligned} \quad (6)$$

where

$$V(x, m) = k^2(x, m) - k'(x, m) + \mathcal{L}(m), \quad (7)$$

$$V(x, m-1) = k^2(x, m) + k'(x, m) + \mathcal{L}(m), \quad (8)$$

or

$$V(x, m) - V(x, m-1) = -2k'(x, m). \quad (9)$$

In general, of course, this equation will not be satisfied for arbitrary $k(x, m)$. The factorization method works only if this condition is satisfied. Iterating this equation for $m-1, m-2, \dots$, down to $m=1$, we are lead to the relation

$$\begin{aligned} V(x, m) - V(x, 0) &= [k^2(x, m) - k'(x, m) + \mathcal{L}(m) - k^2(x, 0) \\ &\quad + k'(x, 0) - \mathcal{L}(0)] = -2 \sum_{n=1}^{m-1} k'(x, n). \end{aligned} \quad (10)$$

Infeld and Hull studied the question: What kind of $k(x, m)$ can satisfy this equation? Trying first a Taylor series in m

$$k(x, m) = k_0(x) + k_1(x)m + \dots, \quad (11)$$

they found the potential collapses to a constant independent of x (hence, a trivial unimportant case), if terms quadratic in m or higher powers of m are included. Nevertheless, the possible functions $k_0(x)$ and $k_1(x)$ lead to a number of interesting equations. Similarly, trying Laurent series in m

$$k(x, m) = \dots + \frac{k_{-1}(x)}{m} + k_0(x) + k_1(x)m + \dots, \quad (12)$$

they again found inverse quadratic and higher inverse powers of m lead to potentials independent of x and, hence, trivial. With the inverse first power in m , however, they found a number of new interesting cases.

It would of course be much nicer if we could immediately answer the question: Given a potential, $V(x, m)$, can we find solutions for the Schrödinger equation by the factorization method, or, what is equivalent: Can we find expressions for its eigenfunctions and eigenvalues in simple analytic form? Because this question has no simple general answer, we shall be content to follow the backward approach of Infeld and Hull, and starting with a set of possible $k(x, m)$ discover quite a number of soluble problems. Recall again that the factorization method involves nothing more mathematically challenging than the integration of a first-order differential equation and the taking of first derivatives in the laddering process.

A Shape-Invariant Potentials

If the potentials $V(x, m)$ and $V(x, m - 1)$ are related as of eq. (9), the following is true.

1. The factorization method works.
2. The spectrum of allowed eigenvalues, λ , for the potential $V(x, m - 1)$ is the same as that for $V(x, m)$, except the eigenvalue, $\lambda = \mathcal{L}(m_{\min})$, does not exist in the spectrum for $V(x, m - 1)$, because $u_{\lambda, m_{\min} - 1}$ does not exist, assuming for now we are dealing with a case for which $\mathcal{L}(m)$ is a decreasing function of m . This follows because the eigenvalue λ does not change when we shift m to $m - 1$ in equation (II).
3. The potentials $V(x, m)$ and $V(x, m - 1)$ are said to have the same shape, because the dependence on x is the same, and only the value of m is replaced by $m - 1$ (“Shape invariance” of the potential).

Now, had we written equation (I) of the factorized form with m replaced by $m - 1$, and then shifted $m - 1$ to $m - 2$ in equation (II), we see the equation for $V(x, m - 2)$ has the same spectrum as that for $V(x, m - 1)$, except the eigenvalue $\lambda = \mathcal{L}(m_{\min} - 1)$ is now missing. Thus, we can have a whole set of potentials with the same shape, all with the same spectrum, except the lowest eigenvalue of $V(x, m)$ is missing in $V(x, m - 1)$, the lowest eigenvalue of $V(x, m - 1)$, and hence the two lowest eigenvalues of $V(x, m)$ are missing for $V(x, m - 2)$, and so on. Thus, the spectrum for $V(x, m - n)$ is the same as that for $V(x, m)$, except the lowest n eigenvalues of $V(x, m)$ are missing in the spectrum for $V(x, m - n)$, provided the factorization is such that the eigenvalues are given by $\lambda = \mathcal{L}(m_{\min})$, that is, cases for which $\mathcal{L}(m)$ is a decreasing function of m . Similar arguments can be made for the other case, i.e., if $\mathcal{L}(m)$ is an increasing function of m . In that case, setting $m \rightarrow m + 1$ in eqs. (3) and (6), we see $V(x, m + 1)$ has the same spectrum of λ values, now with $\lambda = \mathcal{L}(m_{\max} + 1)$, except $\lambda = \mathcal{L}(m_{\max} + 1)$, which exists in the spectrum for $V(x, m)$ with eigenfunction $u_{\lambda, m_{\max}}$, does not exist in the spectrum for $V(x, m + 1)$, because $u_{\lambda, m_{\max} + 1}$ does not exist. Similarly, in the spectrum for $V(x, m + n)$, the eigenvalues $\lambda = \mathcal{L}(m_{\max} + 1), \mathcal{L}(m_{\max} + 2), \dots, \mathcal{L}(m_{\max} + n)$ do not exist. The lowest eigenvalue for $V(x, m + n)$ is $\lambda = \mathcal{L}(m_{\max} + n + 1)$, which is also the n^{th} eigenvalue for $V(x, m)$.

B A Specific Example

As a very specific example, consider a 1-D Schrödinger equation for a particle moving in the domain $0 \leq x \leq a$ under the potential

$$\begin{aligned} V(x) &= \frac{\mathcal{V}_0}{\sin^2(\frac{\pi x}{a})}, & 0 \leq x \leq a, \\ &= \infty, & x \leq 0, \quad x \geq a, \end{aligned} \tag{13}$$

$$-\frac{\hbar}{2m} \frac{d^2}{dx^2} u(x) + \frac{V_0}{\sin^2(\frac{\pi x}{a})} u(x) = Eu(x), \quad (14)$$

or, with

$$\frac{\pi x}{a} = \theta, \quad E = \epsilon \left(\frac{\hbar^2 \pi^2}{2ma^2} \right), \quad V_0 = V_0 \left(\frac{\hbar^2 \pi^2}{2ma^2} \right), \quad (15)$$

$$-\frac{d^2 u}{d\theta^2} + \frac{V_0}{\sin^2 \theta} u = \epsilon u(\theta), \quad (16)$$

to be compared with our factorizable equation

$$-\frac{d^2 u}{d\theta^2} + \frac{[m_0^2 - \frac{1}{4}]}{\sin^2 \theta} u = \lambda u = \epsilon u. \quad (17)$$

Now, we let

$$V_0(\theta, m_0) = \frac{[m_0^2 - \frac{1}{4}]}{\sin^2 \theta}, \quad \text{with} \quad V_0 + \frac{1}{4} = m_0^2. \quad (18)$$

In order to work in the m region near m_{\min} , we shall choose the negative root for m_0

$$m_0 = -\sqrt{V_0 + \frac{1}{4}} = -|m_0|. \quad (19)$$

(We will subsequently investigate the region of m values near the positive root to show these give the same result.) For the above θ equation, we found $\mathcal{L}(m) = (m - \frac{1}{2})^2$, and with $m_{\min} = m_0 = -|m_0|$, we get the lowest eigenvalue, $\lambda_0 = \epsilon_0$,

$$\lambda_0 = \mathcal{L}(m_0) = (m_0 - \frac{1}{2})^2 = (|m_0| + \frac{1}{2})^2 = (\sqrt{V_0 + \frac{1}{4}} + \frac{1}{2})^2. \quad (20)$$

The eigenfunction for the ground state of V_0 is obtained from

$$O_{-(m_0)} u_{\lambda_0 m_0} = \frac{du}{d\theta} + (m_0 - \frac{1}{2}) \cot \theta u(\theta) = 0, \quad (21)$$

with the solution

$$u_{\lambda_0 m_0} = N \left(\sin(\theta) \right)^{\frac{1}{2} - m_0}. \quad (22)$$

This is a square-integrable function, with $m_0 = -|m_0|$. The companion potential $V(\theta, m_0 - 1) = V(\theta, (-|m_0| - 1))$ has ground-state eigenvalue $\lambda = (-|m_0| - 1 - \frac{1}{2})^2 = (|m_0| + 1 + \frac{1}{2})^2$. Let us name this potential V_1 , its ground state eigenvalue λ_1 , and note that this is the first excited state, λ_1 , for the potential V_0 . Similarly, the n^{th} -companion potential $V(\theta, m_0 - n) = V(\theta, (-|m_0| - n))$ has lowest eigenvalue λ_n , where we name this potential V_n :

$$\lambda_n = (m_0 - n - \frac{1}{2})^2 = (|m_0| + n + \frac{1}{2})^2. \quad (23)$$

This is the ground state for the potential V_n and the n^{th} excited state for V_0 . The ground state wave function for the potential V_n is

$$u_{\lambda_n(m_0-n)} = \sqrt{\frac{\pi}{a}} \frac{\Gamma(|m_0| + n + \frac{3}{2})}{\Gamma(\frac{1}{2})\Gamma(|m_0| + n + 1)} \sin^{(|m_0|+n+\frac{1}{2})}(\theta) = N_n \sin^{(|m_0|+n+\frac{1}{2})}(\theta), \quad (24)$$

where we have now included the normalization factor explicitly. Recall

$$\int_0^\pi d\theta \sin^{2\alpha} \theta = B(\frac{1}{2}, \alpha + \frac{1}{2}) = \frac{\Gamma(\frac{1}{2})\Gamma(\alpha + \frac{1}{2})}{\Gamma(\alpha + 1)},$$

where B is the Beta function expressed in terms of Γ functions. To get the eigenfunction for the first excited state of the potential V_{n-1} , with this energy λ_n , we need to act with the normalized step-up operator $\mathcal{O}_+(m_0 - n + 1)$,

$$u_{\lambda_n(m_0-n+1)} = \frac{\mathcal{O}_+(-|m_0| - n + 1)}{\sqrt{[\lambda_n - \mathcal{L}(m_0 - n + 1)]}} u_{\lambda_n(m_0-n)}, \quad (25)$$

with

$$\lambda_n = (|m_0| + n + \frac{1}{2})^2, \quad \mathcal{L}(m_0 - n + 1) = (|m_0| + n - \frac{1}{2})^2. \quad (26)$$

Finally, to get the eigenfunction for the n^{th} excited state with this energy λ_n in the potential V_0 , we need to act n -times with such step-up operators (laddering along the horizontal λ_n -line in Fig. 11.1):

$$\begin{aligned} u_{\lambda_n m_0}(\theta) &= \mathcal{O}_+(-|m_0|) \cdots \mathcal{O}_+((-|m_0| - n + 2)\mathcal{O}_+(-|m_0| - n + 1) \\ &\quad \times N_n \sin^{(|m_0|+n+\frac{1}{2})}(\theta)) \\ &= \frac{\left(-\frac{d}{d\theta} - (|m_0| + \frac{1}{2}) \cot \theta \right)}{\sqrt{[\lambda_n - (|m_0| + \frac{1}{2})^2]}} \cdots \frac{\left(-\frac{d}{d\theta} - (|m_0| + n - \frac{3}{2}) \cot \theta \right)}{\sqrt{[\lambda_n - (|m_0| + n - \frac{3}{2})^2]}} \\ &\quad \times \frac{\left(-\frac{d}{d\theta} - (|m_0| + n - \frac{1}{2}) \cot \theta \right)}{\sqrt{[\lambda_n - (|m_0| + n - \frac{1}{2})^2]}} N_n \sin^{(|m_0|+n+\frac{1}{2})}(\theta). \end{aligned} \quad (27)$$

In Fig. 11.1, a family of shape-invariant potentials of this $(1/\sin^2 \theta)$ shape are shown, where we have chosen $m_0 = -1.1$, so the strength of V_0 is $(-1.1)^2 - \frac{1}{4} = 0.96$, leading to potentials V_1, V_2, V_3, V_4 with strengths of 4.16, 9.36, 16.56, 25.76, respectively. The energies given by eq. (23) are shown in the figure.

In particular, if we had tried to continue the laddering process of eq. (27) one more time from $m_0 = -1.1$ to an $m_0 = -0.1$, we would be led to a potential of strength $(-0.1)^2 - \frac{1}{4} = -0.24$, of the opposite sign from the potentials shown, i.e., a repulsive potential, with no bound states. Therefore, the process has to stop at V_0 . No connection can exist from the problem with negative m values to the branch with positive m values, as for the θ equation for the spherical harmonics. The negative and positive m values are connected only in two special cases: if m_0

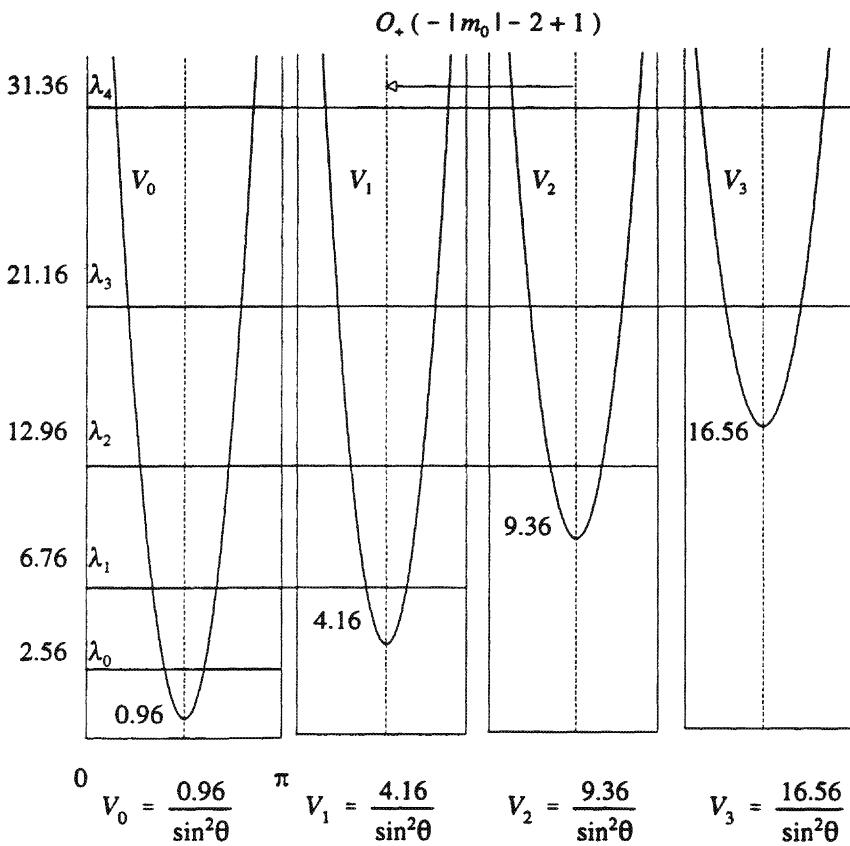


FIGURE 11.1. The family of shape-invariant $1/\sin^2 \theta$ potentials, with $m_0 = -1.1$; $m = m_{\min. \rightarrow +\infty}$.

is integer or $\frac{1}{2}$ -integer. For an arbitrary value of V_0 , it remains to be shown that the positive root, $m_0 = +\sqrt{V_0 + \frac{1}{4}}$, gives the same spectrum of eigenvalues and eigenfunctions. In the region of positive m values, $\mathcal{L}(m) = (m - \frac{1}{2})^2$ is an increasing function of m and $\lambda = \mathcal{L}(m_{\max.} + 1)$. The shape-invariant partner potentials are $V_0(\theta, m_0)$, $V_1(\theta, m_0 + 1)$, ..., $V_n(\theta, m_0 + n)$, with $m_{\max.} = m_0 = +\sqrt{V_0 + \frac{1}{4}}$ for V_0 and $m_{\max.} = m_0 + n$ for V_n , so λ_n , which is the ground-state eigenvalue for V_n and the n^{th} excited state for V_0 , is given by

$$\lambda_n = (m_0 + n + \frac{1}{2})^2 \quad \text{with } m_0 > 0, \quad (28)$$

in agreement with eq. (23). Now the ground-state eigenfunction for V_n is given by

$$O_+(m_0 + n + 1)u_{\lambda_n, m_0+n} = \left(-\frac{d}{d\theta} + (m_0 + n + \frac{1}{2})\cot\theta \right) u_{\lambda_n, m_0+n} = 0, \quad (29)$$

leading again to

$$u_{\lambda_n, m_0+n} = N_n \sin^{(m_0+n+\frac{1}{2})}(\theta), \quad (30)$$

and the n^{th} excited state for V_0 is given by

$$\begin{aligned} u_{\lambda_n, m_0} &= \mathcal{O}_-(m_0 + 1) \cdots \mathcal{O}_-(m_0 + n - 1) \mathcal{O}_-(m_0 + n) u_{\lambda_n, (m_0+n)} \\ &= \frac{\left(\frac{d}{d\theta} + (m_0 + \frac{1}{2}) \cot \theta \right) \cdots \left(\frac{d}{d\theta} + (m_0 + n - \frac{3}{2}) \cot \theta \right)}{\sqrt{[\lambda_n - (m_0 + \frac{1}{2})^2]} \cdots \sqrt{[\lambda_n - (m_0 + n - \frac{3}{2})^2]}} \\ &\times \frac{\left(\frac{d}{d\theta} + (m_0 + n - \frac{1}{2}) \cot \theta \right)}{\sqrt{[\lambda_n - (m_0 + n - \frac{1}{2})^2]}} u_{\lambda_n, (m_0+n)}. \end{aligned} \quad (31)$$

Except for an overall phase factor $(-1)^n$, this function agrees with eq. (27), so the positive branch of m values gives exactly the same results as the negative branch and does not lead to anything new.

C Soluble One-Dimensional Potential Problems

1. The Pöschl–Teller Potential.

All of the factorizable equations we have met so far lead to soluble 1-D potential problems. One of these potentials is the so-called Pöschl–Teller potential, which leads to the 1-D Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2u(x)}{dx^2} - \frac{V}{\cosh^2(x/a)} u(x) = Eu(x), \quad (32)$$

or introducing dimensionless quantities

$$\begin{aligned} z &= \frac{x}{a}, & V &= \mathcal{V} \frac{2ma^2}{\hbar^2}, & \epsilon &= E \frac{2ma^2}{\hbar^2}, \\ -\frac{d^2u(z)}{dz^2} - \frac{V}{\cosh^2 z} u(z) &= \epsilon u(z) = \lambda u(z), \end{aligned} \quad (33)$$

where the case $V > 0$ leads to an attractive potential. With

$$V = l(l+1), \quad \text{or} \quad l = -\frac{1}{2} \pm \sqrt{V + \frac{1}{4}},$$

Chapter 9 tells us

$$O_{\pm} = \mp \frac{d}{dz} + l \tanh z, \quad \text{with} \quad \mathcal{L}(l) = -l^2. \quad (34)$$

This equation corresponds to an $\mathcal{L}(l)$ of case 4 of Chapter 7 with allowed negative values of $\epsilon = \lambda$ only for positive values of $l = l_{\min.}, (l_{\min.} + 1), \dots, (l_{\min.} + n), \dots$

and for negative values of $l = l_{\max.}, (l_{\max.} - 1), \dots, (l_{\max.} - n), \dots$. If we choose the positive branch, with $l = -\frac{1}{2} + \sqrt{V + \frac{1}{4}}$,

$$l = l_{\min.} + n = -\frac{1}{2} + \sqrt{V + \frac{1}{4}}, \quad \text{so with } \epsilon = \mathcal{L}(l_{\min.}),$$

we have

$$\epsilon_n = \lambda_n = \mathcal{L}(l_{\min.}) = -(l - n)^2 = -\left(\sqrt{V + \frac{1}{4}} - (n + \frac{1}{2})\right)^2, \quad (35)$$

with shape-invariant potential partners $V_0(z, l_0), V_1(z, l_0 - 1), \dots, V_n(z, l_0 - n)$, where now $l_0 = -\frac{1}{2} + \sqrt{V + \frac{1}{4}}$. Now a maximum possible value of $n = n_{\max.}$ exists, however, for which $(l_0 - n_{\max.})$ is such that

$$(l_0 - n_{\max.})(l_0 - n_{\max.} + 1) > 0; \quad \text{but } 0 < (l_0 - n_{\max.}) < 1.$$

In that case,

$$(l_0 - (n_{\max.} + 1))(l_0 - (n_{\max.} + 1) + 1) < 0,$$

and this implies the potential $V(z, l_0 - (n_{\max.} + 1))$ is repulsive and therefore has no bound states. The condition $0 \leq (l_0 - n_{\max.}) \leq 1$ determines $n_{\max.}$ through

$$n_{\max.} + \frac{1}{2} \leq \sqrt{V + \frac{1}{4}} \leq n_{\max.} + \frac{3}{2}, \quad \text{or}$$

$$n_{\max.}(n_{\max.} + 1) \leq V \leq (n_{\max.} + 1)(n_{\max.} + 2).$$

For $0 \leq V \leq 2$, $n_{\max.} = 0$, and therefore only a single bound state with $\epsilon_0 = -(-\frac{1}{2} + \sqrt{V + \frac{1}{4}})^2$ exists, but always at least this one bound state exists, even as $V \rightarrow 0$. Note the similarity in this regard between the Pöschl–Teller potential and the square well potential with $V = -V_0$ for $|z| \leq a$, and $V = 0$ for $|z| > a$ (see section B of Chapter 4).

Finally, $u_{\lambda_n, l_{\min.}=(l_0-n)}$ is determined from

$$\begin{aligned} \frac{d}{dz} u_{\lambda_n(l_0-n)} &= -[(l_0 - n) \tanh z] u_{\lambda_n(l_0-n)} = 0, \quad \text{so} \\ u_{\lambda_n(l_0-n)} &= \frac{N_n}{(\cosh z)^{l_0-n}} = \sqrt{\frac{\Gamma(l_0 - n + 1)}{a \Gamma(\frac{1}{2}) \Gamma(l_0 - n)}} \frac{1}{(\cosh z)^{l_0-n}}, \end{aligned} \quad (36)$$

where this is the ground-state eigenfunction for the potential, $V_n(z, l_0 - n)$, with $\epsilon_n = -(\sqrt{V + \frac{1}{4}} - (n + \frac{1}{2}))^2$, which is also the energy of the n^{th} excited state for the potential, $V_0 = -V/(\cosh^2 z)$. The normalized eigenfunction for this n^{th} excited state of V_0 is again given by

$$\begin{aligned} u_{\lambda_n l_0} &= \frac{O_+(l_0)}{\sqrt{[-(l_0 - n)^2 + l_0^2]}} \cdots \frac{O_+(l_0 - n + 2)}{\sqrt{[-(l_0 - n)^2 + (l_0 - n + 2)^2]}} \\ &\times \frac{O_+(l_0 - n + 1)}{\sqrt{[-(l_0 - n)^2 + (l_0 - n + 1)^2]}} u_{\lambda_n(l_0-n)}. \end{aligned} \quad (37)$$

Finally, the negative branch of allowed l values, with $l = -\frac{1}{2} - \sqrt{V + \frac{1}{4}}$, i.e., with $l < 0$, gives no additional eigenvalues or eigenvectors. In this case, $l = l_{\max.} - n$, and $\lambda = \mathcal{L}(l_{\max.} + 1) = -(l + n + 1)^2 = -(-\sqrt{V + \frac{1}{4}} + n + \frac{1}{2})^2$, in agreement with the result of eq. (35) for the positive branch of allowed l values. Except for a possible overall phase factor, the eigenfunctions again agree with those of the other branch. We could again show this explicitly as in the previous example, but also we note: Because we are dealing with a 1-D eigenvalue problem, we do not expect degeneracies for the general ϵ_n .

The inverse $\sin^2 \theta$ potential, $V/(\sin^2 \theta)$, and the Pöschl–Teller potential, $-V/(\cosh^2 z)$, are special cases of the general factorizable case, for which the 1-D Schrödinger equation can be written as

$$\left(-\frac{d^2}{dz^2} + V(z, m) \right) u(z) = \lambda u(z), \quad \text{with}$$

$$V(z, m) = \frac{b^2(m+c)(m+c+1) + d^2 + 2bd(m+c+\frac{1}{2}) \cos b(z+p)}{\sin^2 b(z+p)} \quad (38)$$

and with

$$O_{\pm}(m) = \mp \frac{d}{dz} + (m+c)b \cot b(z+p) + \frac{d}{\sin b(z+p)},$$

$$\mathcal{L}(m) = b^2(m+c)^2, \quad (39)$$

where b, c, d , and p are arbitrary constants. For example, the Pöschl–Teller potential is obtained by setting $b = -i, c = 0, d = 0, p = (i\pi)/2$. Other specializations of this general case are listed by Infeld and Hull; see also problem 16, which treats the θ equation for the symmetric rigid rotator.

2. One-Dimensionalized Hydrogenic Potential.

The factorization of the radial equation for the hydrogen atom leads to a factorizable Schrödinger equation for a 1-D hydrogen-like potential

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dx^2} + V(x)u(x) = Eu(x), \quad \text{with} \quad V(x) = -\frac{A}{x} + \frac{B}{x^2} \quad \text{for } |x| \geq 0, \quad (40)$$

where we set $V = \infty$ for $x < 0$ and $V(x)$ has a minimum for positive values of $x = 2B/A$ if both $A > 0, B > 0$. With dimensionless quantities

$$z = \frac{x}{(\hbar^2/mA)}, \quad \epsilon = E \left(\frac{\hbar^2}{mA^2} \right), \quad l(l+1) = \frac{2m}{\hbar^2} B,$$

the Schrödinger equation becomes

$$\left(-\frac{d^2}{dz^2} - \frac{2}{z} + \frac{l(l+1)}{z^2} \right) u(z) = 2\epsilon u(z) = \lambda u(z), \quad \text{with} \quad (41)$$

$$l = -\frac{1}{2} \pm \sqrt{\frac{2mB}{\hbar^2} + \frac{1}{4}}. \quad (42)$$

The results of Chapter 10 tell us

$$O_{\pm}(l) = \mp \frac{d}{dz} + \left(\frac{l}{z} - \frac{1}{l} \right), \quad \text{with } \mathcal{L}(l) = -\frac{1}{l^2}. \quad (43)$$

From Chapter 10, we also know this equation will have bound states with $\lambda = 2\epsilon < 0$. For the branch of $\mathcal{L}(l)$, which is an increasing function of l , i.e., the positive branch with $l_0 = -\frac{1}{2} + \sqrt{(2mB)/\hbar^2 + \frac{1}{4}}$, the allowed l values range from $l_{\max.}, (l_{\max.} - 1), \dots, (l_{\max.} - n), \dots$, and $\lambda = \mathcal{L}(l_{\max.} + 1)$, so, with $\lambda_n = 2\epsilon_n$,

$$2\epsilon_n = -\frac{1}{(l_{\max.} + 1)^2} = -\frac{1}{(l + n + 1)^2} = -\frac{1}{\left[\sqrt{\frac{2mB}{\hbar^2}} + \frac{1}{4} + (n + \frac{1}{2}) \right]^2}. \quad (44)$$

The shape-invariant partner potentials are $V_0(z, l_0)$, $V_1(l_0 + 1)$, \dots , $V_n(z, l_0 + n)$. The ground-state eigenfunction of $V_n(z, l_0 + n)$, with eigenvalue ϵ_n , is given by

$$O_+(l_0 + n + 1)u_{\lambda_n(l_0+n)} = \left(-\frac{d}{dz} + \frac{(l_0 + n + 1)}{z} - \frac{1}{(l_0 + n + 1)} \right) u_{\lambda_n(l_0+n)} = 0 \quad (45)$$

leading to a normalized

$$u_{\lambda_n(l_0+n)} = \sqrt{\left[\frac{2}{(l_0 + n + 1)} \right]^{(l_0+n+3)}} \frac{1}{\Gamma(2l_0 + 2n + 3)} z^{l_0+n+1} e^{-\frac{z}{(l_0+n+1)}}. \quad (46)$$

The ground-state eigenfunction of $V_0(z, l_0)$ is obtained from this equation by setting $n = 0$. The eigenfunction of the n^{th} excited state of V_0 , with ϵ_n , is again given by

$$\begin{aligned} u_{\lambda_n l_0} &= \frac{O_-(l_0 + 1)}{\sqrt{[\lambda_n - \mathcal{L}(l_0 + 1)]}} \cdots \frac{O_-(l_0 + n - 1)}{\sqrt{[\lambda_n - \mathcal{L}(l_0 + n - 1)]}} \\ &\times \frac{O_-(l_0 + n)}{\sqrt{[\lambda_n - \mathcal{L}(l_0 + n)]}} u_{\lambda_n(l_0+n)}. \end{aligned} \quad (47)$$

For an arbitrary value of l_0 , not equal to an integer or $\frac{1}{2}$ -integer, and a fixed $l_{\max.}$, an n value will exist such that $l(l + 1) = (l_{\max.} - n)(l_{\max.} - n + 1)$ becomes a negative quantity. Because the generalized hydrogenic potential remains attractive even for this case, the value of the integer, n , can go to arbitrarily high values, and an infinite number of bound states exist. The values for $(l_0 + n)$ are positive for all positive integers n in the shape-invariant partner potentials, $V_n(z, l_0 + n)$. The action of the n stepdown operators, O_- , on $u_{\lambda_n(l_0+n)}$ produce an eigenfunction of the form, $z^{l_0+1} \mathcal{P}_n(z) e^{-\frac{z}{(l_0+n+1)}}$, where $\mathcal{P}_n(z)$ is a polynomial of degree n . This function is square-integrable over the interval, $0 \leq z \leq \infty$, for all positive integers, n . Because a second branch of allowed $\mathcal{L}(l)$ values for negative values of l exists, with $l = -\frac{1}{2} - \sqrt{2mB/\hbar^2 + \frac{1}{4}} = -(l_0 + 1)$ and $l = l_{\min.}, (l_{\min.} + 1), \dots, (l_{\min.} + n), \dots$, we again need to examine the possibility this branch would lead to new eigenvalues. For $l < 0$, $\mathcal{L}(l)$ is a decreasing function of l . Therefore, now, with $\lambda_n = 2\epsilon_n$,

$$2\epsilon_n = \mathcal{L}(l_{\min.}) = -\frac{1}{l_{\min.}^2} = -\frac{1}{(l - n)^2} = -\frac{1}{\left[-\frac{1}{2} - \sqrt{2mB/\hbar^2 + \frac{1}{4}} - n \right]^2}, \quad (48)$$

exactly the same result as that already obtained for the positive l branch. Both the eigenvalues and eigenfunctions obtained from this negative l branch, thus, do not give anything new.

3. The Morse Potential.

Another 1-D potential leading to a factorizable Schrödinger equation is the Morse potential (see Fig. 11.2),

$$V(x) = D(e^{-2(x/a)} - 2e^{-(x/a)}), \quad (49)$$

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + D(e^{-2(x/a)} - 2e^{-(x/a)}) \right] u(x) = Eu(x). \quad (50)$$

D gives the classical ionization or dissociation energy. The potential has a minimum value, $V_{\min.} = -D$, at $x = 0$. For $E \geq 0$, a continuous spectrum exists. The particle can proceed to $x \rightarrow +\infty$. With the introduction of dimensionless quantities,

$$z = \frac{x}{a}, \quad \epsilon = E \frac{2\mu a^2}{\hbar^2}, \quad \delta^2 = D \frac{2\mu a^2}{\hbar^2}, \quad \text{this function leads to}$$

$$-\frac{d^2 u}{dz^2} + (\delta^2 e^{-2z} + 2\delta(m + \frac{1}{2})e^{-z})u(z) = \epsilon u(z) = \lambda u(z), \quad (51)$$

where the parameter, m , with

$$\frac{(m + \frac{1}{2})}{\delta} = -1, \quad (52)$$

has been introduced to put the equation into factorizable form, with

$$O_{\pm}(m) = \mp \frac{d}{dz} + (\delta e^{-z} + m), \quad \text{and} \quad \mathcal{L}(m) = -m^2. \quad (53)$$

Note, $-\delta - \frac{1}{2} = -\sqrt{(2\mu a^2 D / \hbar^2)} - \frac{1}{2}$, and hence, m , is a patently negative quantity. For $m < 0$, the above $\mathcal{L}(m)$ is an increasing function of m . For bound states, with $\lambda < 0$, a maximum possible value of $m = m_{\max.}$ exists. The allowed m values are $m = m_{\max.}, (m_{\max.} - 1), \dots, (m_{\max.} - n), \dots$, with

$$\begin{aligned} \lambda_n = \epsilon_n = \mathcal{L}(m_{\max.} + 1) &= -(m + n + 1)^2 = -(-\delta + n + \frac{1}{2})^2 \\ &= -\delta^2 + 2\delta(n + \frac{1}{2}) - (n + \frac{1}{2})^2, \end{aligned} \quad (54)$$

so

$$E_n = -D + 2\sqrt{\frac{\hbar^2 D}{2\mu a^2}}(n + \frac{1}{2}) - \frac{\hbar^2}{2\mu a^2}(n + \frac{1}{2})^2. \quad (55)$$

For the case $\delta \gg 1$, the last term, quadratic in $(n + \frac{1}{2})$, will be much smaller than the linear term, and the excitation energy is that of a slightly anharmonic oscillator, with

$$E_n + D \approx \hbar\omega(n + \frac{1}{2}), \quad \text{with} \quad \hbar\omega = 2\sqrt{\frac{\hbar^2 D}{2\mu a^2}}. \quad (56)$$

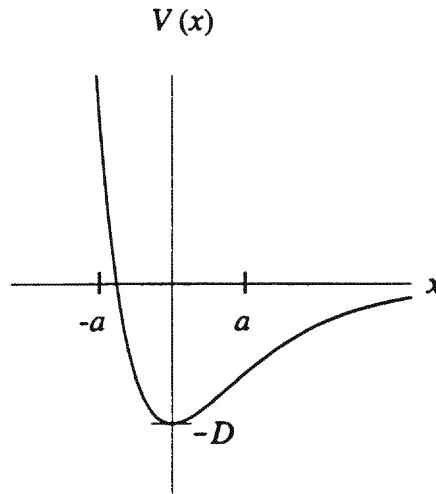


FIGURE 11.2. The Morse potential.

The shape-invariant partner potentials are $V_0(z, m_0)$, $V_1(z, m_0+1)$, \dots , $V_n(z, m_0+n)$, with $m_0 = -(\delta + \frac{1}{2})$, so

$$V_n(z, m_0+n) = (\left(\delta^2 e^{-2z} + 2\delta(-\delta + n)e^{-z} \right)). \quad (57)$$

This potential has the form shown in Fig. 11.2, with an attractive minimum, only for $n < \delta$; and the number of vibrational states is therefore limited. A maximum possible n value, n_{\max} , exists.

The ground-state eigenfunction of V_n is given by

$$O_+(m_0+n+1)u_{\lambda_n(m_0+n)} = \left[-\frac{d}{dz} + (\delta e^{-z} + (n - \delta + \frac{1}{2})) \right] u_{\lambda_n(m_0+n)} = 0, \quad (58)$$

$$u_{\lambda_n(m_0+n)} = N_n e^{-(\delta - n - \frac{1}{2})z + \delta e^{-z}}. \quad (59)$$

Successive action with the normalized step-down operators, $O_-(m)$, with $m = (m_0+n), (m_0+n-1), \dots, (m_0+1)$ yields the needed n^{th} excited-state eigenfunction of V_0 . These $u_{\lambda_n, m}$ are normalized in the interval $-\infty \leq z \leq +\infty$. Also, the $u_{\lambda_n, m}$ are normalizable only for integers n such that $n < (\delta - \frac{1}{2})$, which determines, n_{\max} .

In the actual applications, the Morse potential is used for the relative motion of the two atoms in a diatomic molecule, i.e., for the radial function of this two-body problem. In that case, therefore, μ is the reduced mass of the diatomic molecule, and $x = (r - r_e)$, where, r_e is the equilibrium value of the interatomic distance, r . Thus, the eigenfunctions *should* apply to the interval, $-(r_e/a) \leq z \leq +\infty$. For realistic parameters for most diatomic molecules, however, the Morse potential has such a large positive value at $z = -(r_e/a)$ that the Morse eigenfunctions are effectively zero for $z < -(r_e/a)$. The 1-D solutions found above for the full z -space

Molecule	$D_{\text{obs.}} \frac{1}{\hbar c}$	$(\hbar^2/2\mu a^2)_{\text{obs.}} \frac{1}{\hbar c}$	δ	$n_{\text{max.}}$	$(\hbar\omega)_{\text{obs.}} \frac{1}{\hbar c}$
H_2	$38,276 \text{ cm}^{-1}$	118 cm^{-1}	18.0	17	4395 cm^{-1}
HCl	$37,257 \text{ cm}^{-1}$	52.05 cm^{-1}	26.7	26	2990 cm^{-1}
O_2	$41,758 \text{ cm}^{-1}$	12.07 cm^{-1}	58.8	58	1580 cm^{-1}

are therefore a good approximation for most diatomic molecules. The parameters D , $(\hbar^2/2\mu a^2)$, and δ are shown for a few molecules in the table provided here. The $D_{\text{obs.}}$ and $(\hbar^2/2\mu a^2)_{\text{obs.}}$ have been extracted from the observed vibrational spectra, [G. Herzberg; *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*, D. van Nostrand (1950)]. The $\hbar\omega$ predicted by the Morse-potential energy relation, eq. (55), has the values 4128 cm^{-1} for H_2 , 2728 cm^{-1} for HCl , and 1407 cm^{-1} for O_2 in reasonable agreement with the values extracted from the observed spectra. (Molecular spectroscopists in general give (energy/hc) in wavenumbers, cm^{-1} .)

4. The Rosen–Morse Potential.

A similar potential is the Rosen–Morse potential, which leads to the 1-D Schrödinger equation

$$-\frac{\hbar^2}{2\mu} \frac{d^2u}{dx^2} + \left(-\frac{V_1}{\cosh^2(x/a)} + 2V_2 \tanh(\frac{x}{a}) \right) u(x) = Eu(x). \quad (60)$$

With dimensionless quantities,

$$z = \frac{x}{a}, \quad \epsilon = E \frac{2\mu a^2}{\hbar^2}, \quad m(m+1) = V_1 \frac{2\mu a^2}{\hbar^2}, \quad q = V_2 \frac{2\mu a^2}{\hbar^2},$$

this equation leads to

$$-\frac{d^2u}{dz^2} + \left(-\frac{m(m+1)}{\cosh^2 z} + 2q \tanh z \right) u(z) = \epsilon u(z). \quad (61)$$

This potential has an attractive well with a minimum at z_0 , given by

$$\tanh z_0 = -\frac{V_2}{V_1} = -\frac{q}{m(m+1)}, \quad (62)$$

which has a solution only for

$$|q/m(m+1)| < 1. \quad (63)$$

The equation is factorizable, with

$$O_{\pm}(m) = \left(\mp \frac{d}{dz} + m \tanh z + \frac{q}{m} \right), \quad \text{and} \quad \mathcal{L}(m) = -m^2 - \frac{q^2}{m^2}. \quad (64)$$

Choosing the branch of $\mathcal{L}(m)$ with positive values of m , this $\mathcal{L}(m)$ belongs to case 4. The maximum of the function $\mathcal{L}(m)$ occurs at $m = \sqrt{|q|}$, where $\mathcal{L}(m)$ has the value $-2|q|$, which is also the ionization or dissociation value of $V(z)$. Thus, bound states will exist if $\epsilon < -2|q|$, and the requirement $[\lambda - \mathcal{L}(m)] \geq 0$, together with the requirement of eq. (63) leads to an allowed branch of m values with $m > \sqrt{|q|}$, where $\mathcal{L}(m)$ is a decreasing function of m , so $m = m_{\min.}, (m_{\min.} + 1), \dots, (m_{\min.} +$

n), . . . , with

$$\begin{aligned}\epsilon_n = \lambda_n = \mathcal{L}(m_{\min.}) &= -(m-n)^2 - \frac{q^2}{(m-n)^2} \\ &= -\left(\sqrt{\frac{2\mu a^2 V_1}{\hbar^2} + \frac{1}{4}} - (n + \frac{1}{2})\right)^2 - \frac{q^2}{\left(\sqrt{\frac{2\mu a^2 V_1}{\hbar^2} + \frac{1}{4}} - (n + \frac{1}{2})\right)^2}. \quad (65)\end{aligned}$$

The shape-invariant partner potentials are $V_0(z, m_0)$, $V_1(z, m_0-1)$, . . . , $V_n(z, m_0-n)$, with $m_0 = -\frac{1}{2} + \sqrt{(2\mu a^2 V_1/\hbar^2) + \frac{1}{4}}$. The ground-state eigenfunction of $V(z, m_0-n)$ is determined by

$$\begin{aligned}\left(\frac{d}{dz} + (m_0 - n) \tanh z + \frac{q}{(m_0 - n)}\right) u_{\lambda_n(m_0-n)} &= 0, \\ u_{\lambda_n(m_0-n)} &= N_n \frac{1}{(\cosh z)^{(m_0-n)}} e^{-\frac{q}{(m_0-n)}z}, \quad (66)\end{aligned}$$

and the eigenfunction of the n^{th} excited state of V_0 is obtained from this function by the action of n operators $\mathcal{O}_+(m)$ with m running from $(m_0 - n + 1)$ to m_0 . Again, a maximum n value exists beyond which the potential $V(z, m_0 - n)$ ceases to have an attractive minimum with bound states and square-integrable bound-state eigenfunctions, so V_0 again has only a finite number of bound states.

5. The one-dimensional harmonic oscillator revisited.

The 1-D harmonic oscillator Schrödinger equation

$$\left(-\frac{d^2}{dx^2} + x^2\right) u(x) = 2\epsilon u(x), \quad (67)$$

with dimensionless, x and ϵ , is factorizable, with

$$O_{\pm} = \left(\mp \frac{d}{dx} + x\right). \quad (68)$$

The only parameter, however, is the energy, ϵ , itself, and the factors, O_{\pm} , are not functions of ϵ . Now,

$$\begin{aligned}\text{I} \quad O_+ O_- u(x) &= (2\epsilon - 1)u(x) = [-1 + 2\epsilon]u(x), \\ \text{II} \quad O_- O_+ u(x) &= (2\epsilon + 1)u(x) = [-1 + 2(\epsilon + 1)]u(x), \quad (69)\end{aligned}$$

are to be compared with

$$\begin{aligned}\text{I} \quad O_+ O_- u_{\lambda m} &= [\lambda - \mathcal{L}(m)]u_{\lambda m}, \\ \text{II} \quad O_- O_+ u_{\lambda m} &= [\lambda - \mathcal{L}(m + 1)]u_{\lambda m}. \quad (70)\end{aligned}$$

Therefore, λ has the single-fixed eigenvalue, $\lambda = -1$, and the parameter, m , is replaced by ϵ , with $\mathcal{L}(\epsilon) = -2\epsilon$. Because $\mathcal{L}(\epsilon)$ is a decreasing function of ϵ , an $\epsilon_{\min.}$ exists, with

$$\lambda = -1 = \mathcal{L}(\epsilon_{\min.}) = -2\epsilon_{\min.}, \quad \text{so } \epsilon_{\min.} = \frac{1}{2}. \quad (71)$$

The allowed values of ϵ are $\epsilon = \epsilon_{\min.}, (\epsilon_{\min.} + 1), \dots, (\epsilon_{\min.} + n) = (\frac{1}{2} + n), \dots$. Therefore, $\epsilon_n = (n + \frac{1}{2})$. The starting eigenfunction is obtained from

$$\begin{aligned} O_- u_{-1, \epsilon_{\min.}} &= \left(\frac{d}{dx} + x \right) u_{-1, \epsilon_{\min.}} = 0, \\ u_{-1, \epsilon_{\min.}} &= \frac{1}{\pi^{\frac{1}{4}}} e^{-\frac{1}{2}x^2}. \end{aligned} \quad (72)$$

The excited-state eigenfunctions are obtained with the normalized step-up operators

$$O_+(n+1) = \frac{\left(-\frac{d}{dx} + x\right)}{\sqrt{[-1 + 2\epsilon_{(n+1)}]}} = \frac{\left(-\frac{d}{dx} + x\right)}{\sqrt{2(n+1)}},$$

so

$$u_{-1, \epsilon_n}(x) = \frac{1}{\sqrt{2^n n! \sqrt{\pi}}} \left(-\frac{d}{dx} + x\right)^n e^{-\frac{1}{2}x^2}. \quad (73)$$

Using the identities

$$\left(-\frac{d}{dx} + x\right) = e^{\frac{1}{2}x^2} \left[e^{-\frac{1}{2}x^2} \left(-\frac{d}{dx} + x\right) e^{\frac{1}{2}x^2} \right] e^{-\frac{1}{2}x^2} = e^{\frac{1}{2}x^2} \left[-\frac{d}{dx}\right] e^{-\frac{1}{2}x^2}, \quad (74)$$

the normalized n^{th} eigenfunction becomes

$$\begin{aligned} u_{-1, \epsilon_n}(x) &= \frac{1}{\sqrt{2^n n! \sqrt{\pi}}} e^{\frac{1}{2}x^2} \left(-\frac{d}{dx}\right)^n e^{-\frac{1}{2}x^2} e^{-\frac{1}{2}x^2} \\ &= \frac{e^{-\frac{1}{2}x^2}}{\sqrt{2^n n! \sqrt{\pi}}} \left[e^{x^2} \left(-\frac{d}{dx}\right)^n e^{-x^2} \right] = \frac{e^{-\frac{1}{2}x^2} H_n(x)}{\sqrt{2^n n! \sqrt{\pi}}}, \end{aligned} \quad (75)$$

where we have used the Rodriguez-type definition of the Hermite polynomial, $H_n(x)$, [see eq. (75) of Chapter 4].

Finally, the radial equation for the 3-D harmonic oscillator can also be solved by the factorization method. For details, see problem 15.

Altogether, Infeld and Hull list 31 generalizations or specializations of the Pöschl–Teller, hydrogenic, Morse, Rosen–Morse, 1-D harmonic oscillator, or 3-D harmonic oscillator Schrödinger equations, which lead to eigenvalues and eigenfunctions in analytic form, where the eigenfunctions correspond to many of the well-known functions of classical analysis. The question now arises: Do additional potentials exist for which the 1-D Schrödinger problem can be solved exactly? This question will be partially answered in the next chapter.

Problems

- 14. (a)** Find the eigenvalues, ϵ_n , and the normalized eigenfunctions for all of the bound states of a Pöschl–Teller potential with dimensionless

$$V(z) = -\frac{V_0}{\cosh^2 z}, \quad \text{with } V_0 = 7.2.$$

(b) A particle of mass μ moves in one dimension subject to the Schrödinger equation

$$-\frac{\hbar^2}{2\mu a^2} \left(-\frac{d^2}{dz^2} + \frac{m(m+1)}{\sinh^2 z} - 2\nu \coth z \right) u(z) = Eu(z),$$

where z is a dimensionless variable, restricted to $z \geq 0$, and m and ν are dimensionless potential constants. Find the conditions that must be satisfied by these constants, so the potential has an attractive minimum for $z > 0$, and find an expression for the eigenvalues, E_n , as a function of n . Does a maximum possible value of n exist?

15. The 3-D harmonic oscillator. With $u(r) = rR(r)$, and $r = \sqrt{\hbar/m\omega_0}\rho$, $E = \hbar\omega_0\epsilon$, the radial wave equation for the 3-D harmonic oscillator (with $l = 0, 1, 2, \dots$) takes the form

$$-\frac{d^2u}{d\rho^2} + \left[\frac{l(l+1)}{\rho^2} + \rho^2 \right] u(\rho) = 2\epsilon u(\rho).$$

Show that this equation is factorizable via

$$O_{\pm}(l) = -\left(\mp \frac{d}{d\rho} + \left(\frac{l}{\rho} - \rho \right) \right),$$

but the standard λ must be interpreted as $\lambda = 2\epsilon + 2l$; so $O_{\pm}(l)$ steps both l and ϵ . Show that this equation is also factorizable via

$$\bar{O}_{\pm}(l) = \left(\mp \frac{d}{d\rho} + \left(\frac{l}{\rho} + \rho \right) \right),$$

but now with $\lambda = 2\epsilon - 2l$.

Use these results to show that

$$E = \hbar\omega_0(N + \frac{3}{2}), \quad \text{with } N = 0, 1, 2, \dots$$

and that the allowed l values for a particular, N , are

$$l = N, N-2, N-4, \dots, 0(\text{or } 1), \quad \text{for } N = \text{even (odd).}$$

Find the normalized eigenfunctions for the special states with $l = N$. Construct the four normalized step operators, which convert normalized u_{Nl} into normalized $u_{N+1,l-1}$, $u_{N-1,l+1}$, $u_{N+1,l+1}$, and $u_{N-1,l-1}$. Construct all normalized radial eigenfunctions for $N \leq 3$

Find relations giving ρu_{Nl} as a linear combination of (i) $u_{N+1,l+1}$ and $u_{N-1,l+1}$, and as a linear combination of (ii) $u_{N+1,l-1}$ and $u_{N-1,l-1}$. Use these relations to find matrix elements of the operators, $\rho \cos \theta$ and $\rho \sin \theta e^{\pm i\phi}$ in the complete 3-D oscillator basis, ψ_{Nlm} . (The u_{Nl} and $u_{N'l'}$, with $l' \neq l$, are not orthogonal to each other in ρ -space, but the full energy eigenfunctions, $u_{Nl}(\rho)Y_{lm}(\theta, \phi)$ form a complete orthogonal set.)

Find all nonzero matrix elements of the operator, ρ^2 .

Note: The above matrix elements of $\rho \cos \theta$ and $\rho \sin \theta e^{\pm i\phi}$ give the matrix elements of the dimensionless z and $(x \pm iy)$. The corresponding matrix elements

of the dimensionless p_z and $(p_x \pm ip_y)$ can be obtained by utilizing the commutator relations

$$p_z = i[H, z], \quad (p_x \pm ip_y) = i[H, (x \pm iy)],$$

together with the known matrix elements of the dimensionless H and $z, (x \pm iy)$. Use this technique to find the expressions for the nonzero matrix elements of p_z .

Solution for Problem 15

With

$$O_{\pm}(l) = -\left(\mp \frac{d}{d\rho} + \left(\frac{l}{\rho} - \rho\right)\right),$$

(where the extra overall minus sign in this definition is added merely for convenience to gain phases for the final matrix elements in best agreement with the “standard” phases for the 3-D oscillator), we have the two basic equations

$$\begin{aligned} O_+(l)O_-(l) &= -\frac{d^2}{d\rho^2} + \frac{l(l+1)}{\rho^2} + \rho^2 - (2l-1), \\ O_-(l+1)O_+(l+1) &= -\frac{d^2}{d\rho^2} + \frac{l(l+1)}{\rho^2} + \rho^2 - (2l+3). \end{aligned} \quad (1)$$

and

$$\begin{aligned} O_+(l)O_-(l)u_{\lambda l} &= [2\epsilon - (2l-1)]u_{\lambda l} = [\lambda - \mathcal{L}(l)]u_{\lambda l}, \\ O_-(l+1)O_+(l+1)u_{\lambda l} &= [2\epsilon - (2l+3)]u_{\lambda l} = [\lambda - \mathcal{L}(l+1)]u_{\lambda l}. \end{aligned} \quad (2)$$

These two equations are satisfied only if $\mathcal{L}(l+1) - \mathcal{L}(l) = 4$, and have a proper solution only if

$$\mathcal{L}(l) = 4l + c, \quad \lambda = 2\epsilon + 2l + c + 1, \quad c = \text{a constant.} \quad (3)$$

We will find it convenient to choose, $c = -1$ (this choice is quite arbitrary and will not affect final results). With this choice,

$$\mathcal{L}(l) = (4l-1), \quad \lambda = 2\epsilon + 2l. \quad (4)$$

Because our $l \geq 0$, this $\mathcal{L}(l)$ is an increasing function of l . Thus, an l_{\max} exists (to be named N), $l_{\max} = N$, with $\lambda = \mathcal{L}(l_{\max} + 1) = (4l_{\max} + 3) = (4N + 3)$, and therefore

$$2\epsilon = (2N + 3), \quad E_N = \hbar\omega_0(N + \frac{3}{2}). \quad (5)$$

The starting functions of $u_{\lambda l_{\max}}$ are given by

$$O_+(l_{\max} + 1)u_{\lambda l_{\max}}(\rho) = 0, \quad \left(\frac{d}{d\rho} - \frac{N+1}{\rho} + \rho\right)u_{\lambda N}(\rho) = 0, \quad (6)$$

where this first-order differential equation has the solution

$$u_{\lambda, l=N}(\rho) = \mathcal{N}\rho^{N+1}e^{-\frac{1}{2}\rho^2}, \quad (7)$$

with $|\mathcal{N}|^2 \int_0^\infty d\rho \rho^{2N+2} e^{-\rho^2} = \frac{1}{2} |\mathcal{N}|^2 \int_0^\infty d\eta \eta^{N+\frac{1}{2}} e^{-\eta} = \frac{1}{2} |\mathcal{N}|^2 \Gamma(N + \frac{3}{2}) = 1$.

$$\text{[Note, } \frac{1}{2}\Gamma(N + \frac{3}{2}) = \frac{1}{2}(N + \frac{1}{2})(N - \frac{1}{2}) \cdots \frac{3}{2} \frac{1}{2} \sqrt{\pi} = \frac{(2N+1)!!}{2^{N+2}} \sqrt{\pi}].$$

$O_-(l)$ changes $l \rightarrow (l-1)$, but because it keeps λ invariant, and $\lambda = 2\epsilon + 2l$, it must simultaneously raise ϵ by one unit, and hence, shifts $N \rightarrow (N+1)$. Similarly, $O_+(l+1)$ simultaneously changes $l \rightarrow (l+1)$, $N \rightarrow (N-1)$. To obtain the possible l values for a fixed N , we first examine the action of the operators

$$\bar{O}_\pm(l) = \left(\mp \frac{d}{d\rho} + \left(\frac{l}{\rho} + \rho \right) \right),$$

with

$$\begin{aligned} \bar{O}_+(l)\bar{O}_-(l)u_{\bar{\lambda}l} &= \left(-\frac{d^2}{d\rho^2} + \frac{l(l+1)}{\rho^2} + \rho^2 + (2l-1) \right) u_{\bar{\lambda}l} \\ &= (2\epsilon + 2l - 1)u_{\bar{\lambda}l} = [\bar{\lambda} - \bar{\mathcal{L}}(l)]u_{\bar{\lambda}l} \\ \bar{O}_-(l+1)\bar{O}_+(l+1)u_{\bar{\lambda}l} &= \left(-\frac{d^2}{d\rho^2} + \frac{l(l+1)}{\rho^2} + \rho^2 + (2l+3) \right) u_{\bar{\lambda}l} \\ &= (2\epsilon + 2l + 3)u_{\bar{\lambda}l} = [\bar{\lambda} - \bar{\mathcal{L}}(l+1)]u_{\bar{\lambda}l}, \end{aligned} \quad (8)$$

which can be satisfied by

$$\bar{\mathcal{L}}(l) = -(4l-1), \quad \bar{\lambda} = (2\epsilon - 2l). \quad (9)$$

$\bar{\lambda} - \bar{\mathcal{L}}(l)$ remains positive for all possible values of l , even as l is increased indefinitely. No new limits are set on l by the operators \bar{O}_\pm . Also,

$\bar{O}_-(l)$ changes $l \rightarrow (l-1)$ and simultaneously $N \rightarrow (N-1)$, and

$\bar{O}_+(l+1)$ changes $l \rightarrow (l+1)$ and simultaneously $N \rightarrow (N+1)$.

Starting with the maximum l value for a particular N , $l_{\max.} = N$, successive action with $O_-(l)$ followed by $\bar{O}_-(l-1)$, or equally well $O_-(l)$ followed by $\bar{O}_-(l-1)$, will change a state with quantum numbers, N, l to a state with quantum numbers $N, (l-2)$, skipping states with $N, (l-1)$. The four operators, O_\pm, \bar{O}_\pm , do not change the parity of $(N+l)$. For a fixed energy (fixed N), the possible l values are

$$l = N, (N-2), (N-4), \dots, 0 \text{ (or 1), for } N = \text{even (or odd).}$$

It will now be convenient to define the four step operators preserving the normalization of the u_{NL} , which will be denoted by \mathcal{O} . [Also, we will characterize the radial eigenfunctions by the quantum numbers, N, l ; that is, we will replace the λ (or $\bar{\lambda}$) with the quantum number N , which gives the energy eigenvalue, ϵ .]

$$\mathcal{O}_-(l) = \frac{O_-(l)}{\sqrt{[\lambda - \mathcal{L}(l)]}}, \quad \mathcal{O}_+(l+1) = \frac{O_+(l+1)}{\sqrt{[\lambda - \mathcal{L}(l+1)]}},$$

$$\text{with } [\lambda - \mathcal{L}(l)] = (2\epsilon + 2l) - (4l-1) = (2N+3-2l+1).$$

$$\bar{\mathcal{O}}_-(l) = \frac{\bar{\mathcal{O}}_-(l)}{\sqrt{[\bar{\lambda} - \bar{\mathcal{L}}(l)]}}, \quad \bar{\mathcal{O}}_+(l+1) = \frac{\bar{\mathcal{O}}_+(l+1)}{\sqrt{[\bar{\lambda} - \bar{\mathcal{L}}(l+1)]}},$$

with $\bar{\lambda} = [\bar{\lambda} - \bar{\mathcal{L}}(l)] = (2\epsilon - 2l) + (4l - 1) = (2N + 3 + 2l - 1)$.

Thus,

$$u_{(N+1)(l-1)} = \mathcal{O}_-(l)u_{Nl} = \frac{1}{\sqrt{2(N+2-l)}} \left(-\frac{d}{d\rho} - \frac{l}{\rho} + \rho \right) u_{Nl},$$

$$u_{(N-1)(l+1)} = \mathcal{O}_+(l+1)u_{Nl} = \frac{1}{\sqrt{2(N-l)}} \left(\frac{d}{d\rho} - \frac{(l+1)}{\rho} + \rho \right) u_{Nl},$$

$$u_{(N-1)(l-1)} = \bar{\mathcal{O}}_-(l)u_{Nl} = \frac{1}{\sqrt{2(N+1+l)}} \left(\frac{d}{d\rho} + \frac{l}{\rho} + \rho \right) u_{Nl},$$

$$u_{(N+1)(l+1)} = \bar{\mathcal{O}}_+(l+1)u_{Nl} = \frac{1}{\sqrt{2(N+3+l)}} \left(-\frac{d}{d\rho} + \frac{(l+1)}{\rho} + \rho \right) u_{Nl}.$$

Combining the first and third of these relations, we get

$$\rho u_{Nl} = \sqrt{\frac{(N+2-l)}{2}} u_{(N+1)(l-1)} + \sqrt{\frac{(N+1+l)}{2}} u_{(N-1)(l-1)}. \quad (10)$$

Similarly, combining the second and fourth relation, we get

$$\rho u_{Nl} = \sqrt{\frac{(N-l)}{2}} u_{(N-1)(l+1)} + \sqrt{\frac{(N+3+l)}{2}} u_{(N+1)(l+1)}. \quad (11)$$

If we left-multiply the first of these equations with $u_{(N+1)(l-1)}^*$ and integrate over ρ , and use the orthonormality of the u_{Nl} with the same l value, we get

$$\int_0^\infty d\rho u_{(N+1)(l-1)}^* \rho u_{Nl} = \int_0^\infty d\rho \rho^2 R_{(N+1)(l-1)}^* \rho R_{Nl} = \sqrt{\frac{(N+2-l)}{2}},$$

where we have used

$$\int_0^\infty d\rho u_{(N+1)(l-1)}^* u_{(N-1)(l-1)} = 0.$$

Both functions have the same l value, viz., $(l-1)$, and where we recall that the 1-D $u_{Nl}(\rho)$ is related to the radial function, $R_{Nl}(\rho)$, via $u_{Nl}(\rho) = \rho R_{Nl}(\rho)$, where we also recall ρ is the dimensionless radial coordinate $\rho = r_{\text{phys.}}/\sqrt{\hbar/m\omega_0}$. Finally, if we combine the dimensionless ρ with the angular functions, we get the components of the (dimensionless) vector \vec{r} : $z = \rho \cos \theta$; $(x \pm iy) = \rho \sin \theta e^{\pm i\phi}$. With the matrix elements of the angular functions given through eqs. (42)–(44) of Chapter 9, we have, e.g.,

$$\langle \psi_{(N+1)(l-1)m}, \rho \cos \theta \psi_{Nlm} \rangle = \sqrt{\frac{(N+2-l)}{2}} \sqrt{\frac{(l^2 - m^2)}{(2l+1)(2l-1)}},$$

$$\begin{aligned}\langle \psi_{(N-1)(l-1)m}, \rho \cos \theta \psi_{Nlm} \rangle &= \sqrt{\frac{(N+1+l)}{2}} \sqrt{\frac{(l^2 - m^2)}{(2l+1)(2l-1)}}, \\ \langle \psi_{(N+1)(l+1)m}, \rho \cos \theta \psi_{Nlm} \rangle &= \sqrt{\frac{(N+3+l)}{2}} \sqrt{\frac{[(l+1)^2 - m^2]}{(2l+1)(2l+3)}}, \\ \langle \psi_{(N-1)(l+1)m}, \rho \cos \theta \psi_{Nlm} \rangle &= \sqrt{\frac{(N-l)}{2}} \sqrt{\frac{[(l+1)^2 - m^2]}{(2l+1)(2l+3)}},\end{aligned}\quad (12)$$

where the similar matrix elements of $\rho \sin \theta e^{\pm i\phi}$ differ only in the l, m dependent square root factors coming from the angular parts [which now also change m to $(m \pm 1)$].

To get the matrix elements of ρ^2 , we can combine eqs. (10) and (11)

$$\begin{aligned}\rho^2 u_{Nl} &= \sqrt{\frac{(N+2-l)}{2}} \left(\sqrt{\frac{(N+2-l)}{2}} u_{Nl} + \sqrt{\frac{(N+3+l)}{2}} u_{(N+2)l} \right) \\ &\quad + \sqrt{\frac{(N+1+l)}{2}} \left(\sqrt{\frac{(N-l)}{2}} u_{(N-2)l} + \sqrt{\frac{(N+1+l)}{2}} u_{Nl} \right).\end{aligned}\quad (13)$$

This equation leads to the matrix elements

$$\begin{aligned}\langle \psi_{Nlm}, \rho^2 \psi_{Nlm} \rangle &= (N + \frac{3}{2}), \\ \langle \psi_{(N+2)lm}, \rho^2 \psi_{Nlm} \rangle &= \frac{1}{2} \sqrt{(N+2-l)(N+l+3)}, \\ \langle \psi_{(N-2)lm}, \rho^2 \psi_{Nlm} \rangle &= \frac{1}{2} \sqrt{(N-l)(N+l+1)}.\end{aligned}\quad (14)$$

Finally, to obtain matrix elements of p_z and $(p_x \pm ip_y)$, we can use the commutator relations

$$p_z = i[H, z], \quad (p_x \pm ip_y) = i[H, (x \pm iy)],$$

so, e.g.,

$$\langle \psi_{N'l'm}, p_z \psi_{Nlm} \rangle = i[(N' + \frac{3}{2}) - (N + \frac{3}{2})] \langle \psi_{N'l'm}, z \psi_{Nlm} \rangle, \quad (15)$$

giving

$$\begin{aligned}\langle \psi_{(N+1)(l-1)m}, p_z \psi_{Nlm} \rangle &= i \sqrt{\frac{(N+2-l)}{2}} \sqrt{\frac{(l^2 - m^2)}{(2l+1)(2l-1)}}, \\ \langle \psi_{(N-1)(l-1)m}, p_z \psi_{Nlm} \rangle &= -i \sqrt{\frac{(N+1+l)}{2}} \sqrt{\frac{(l^2 - m^2)}{(2l+1)(2l-1)}}, \\ \langle \psi_{(N+1)(l+1)m}, p_z \psi_{Nlm} \rangle &= i \sqrt{\frac{(N+3+l)}{2}} \sqrt{\frac{[(l+1)^2 - m^2]}{(2l+1)(2l+3)}}, \\ \langle \psi_{(N-1)(l+1)m}, p_z \psi_{Nlm} \rangle &= -i \sqrt{\frac{(N-l)}{2}} \sqrt{\frac{[(l+1)^2 - m^2]}{(2l+1)(2l+3)}}.\end{aligned}\quad (16)$$

As our last result, we shall obtain explicit expressions for the normalized radial eigenfunctions for $N \leq 3$. The functions with $l = l_{\max.} = N$ are given through

eq. (7). Functions with lower l values can be obtained with actions of \mathcal{O}_- or $\bar{\mathcal{O}}_-$:

$$u_{N=3,l=3} = \sqrt{\frac{2}{\Gamma(\frac{9}{2})}} \rho^4 e^{-\frac{1}{2}\rho^2} = \sqrt{\frac{2^5}{105\sqrt{\pi}}} \rho^4 e^{-\frac{1}{2}\rho^2},$$

$$u_{N=2,l=2} = \sqrt{\frac{2}{\Gamma(\frac{7}{2})}} \rho^3 e^{-\frac{1}{2}\rho^2} = \sqrt{\frac{2^4}{15\sqrt{\pi}}} \rho^3 e^{-\frac{1}{2}\rho^2},$$

$$u_{N=1,l=1} = \sqrt{\frac{2}{\Gamma(\frac{5}{2})}} \rho^2 e^{-\frac{1}{2}\rho^2} = \sqrt{\frac{2^3}{3\sqrt{\pi}}} \rho^2 e^{-\frac{1}{2}\rho^2},$$

$$\begin{aligned} u_{N=0,l=0} &= \sqrt{\frac{2}{\Gamma(\frac{3}{2})}} \rho e^{-\frac{1}{2}\rho^2} = \sqrt{\frac{2^2}{\sqrt{\pi}}} \rho e^{-\frac{1}{2}\rho^2}, \\ u_{N=3,l=1} &= \mathcal{O}_-(2)u_{N=2,l=2} = \frac{1}{2} \left(-\frac{d}{d\rho} - \frac{2}{\rho} + \rho \right) u_{N=2,l=2}, \end{aligned}$$

$$\begin{aligned} u_{N=2,l=0} &= \mathcal{O}_-(1)u_{N=1,l=1} = \frac{1}{2} \left(-\frac{d}{d\rho} - \frac{1}{\rho} + \rho \right) u_{N=1,l=1}, \\ &= \sqrt{\frac{2}{3\sqrt{\pi}}} (2\rho^3 - 3\rho) e^{-\frac{1}{2}\rho^2}. \end{aligned}$$

16. The symmetric top rigid rotator. In problem 5, the Schrödinger equation for the symmetric top rigid rotator, with $A = B \neq C$, led to the θ equation via the assumed form of the solution

$$\psi_{JMK}(\phi, \theta, \chi) = \frac{e^{iM\phi}}{\sqrt{2\pi}} \frac{e^{iK\chi}}{\sqrt{2\pi}} \Theta_{JMK}(\theta).$$

This θ equation is one-dimensionalized via

$$u_{JMK}(\theta) = \sqrt{\sin\theta} \Theta_{JMK}(\theta)$$

to give

$$\left(-\frac{d^2}{d\theta^2} + \frac{M^2 + K^2 - 2MK \cos\theta}{\sin^2\theta} \right) u_{\lambda MK}(\theta) = \lambda u_{\lambda MK}(\theta),$$

where

$$E = \frac{\hbar^2}{2A} (\lambda - \frac{1}{4} - K^2) + \frac{\hbar^2}{2C} K^2.$$

Show that this equation can be factorized in two ways, via

$$O_{\pm}(M) = \left(\mp \frac{d}{d\theta} + (M - \frac{1}{2}) \cot \theta - \frac{K}{\sin \theta} \right)$$

or

$$O_{\pm}(K) = \left(\mp \frac{d}{d\theta} + (K - \frac{1}{2}) \cot \theta - \frac{M}{\sin \theta} \right)$$

where $\lambda = (J + \frac{1}{2})^2$, with $J = M_{\max.} = K_{\max.}$. Assume M and K can only be integers, so J is an integer.

Convert the above to normalized M step- and K step-operators, which preserve the normalization

$$\int_0^\pi d\theta \sin \theta |\Theta_{JMK}(\theta)|^2 = 1.$$

Find the normalized $\Theta_{JJK}(\theta)$ with $M = J$, but arbitrary allowed K , and $\Theta_{JMJ}(\theta)$ with $K = J$ but arbitrary allowed M .

Find the normalized J step-operators that step $J \rightarrow (J \pm 1)$, but keep M and K fixed. These operators will require new normalization factor ratios, c_{J+1MK}/c_{JMK} , as for the corresponding spherical harmonic problem. Prove these ratios are independent of K and, hence, can be taken over from the known case with $K = 0$.

Find all nonzero matrix elements of $\cos \theta$ and $\sin \theta e^{\pm i\phi}$, $\sin \theta e^{\pm i\chi}$:

$$\langle \psi_{J'M'K'}, \cos \theta \psi_{JMK} \rangle,$$

$$\langle \psi_{J'M'K'}, \sin \theta e^{\pm i\phi} \psi_{JMK} \rangle,$$

$$\langle \psi_{J'M'K'}, \sin \theta e^{\pm i\chi} \psi_{JMK} \rangle.$$

12

The Darboux Method: Supersymmetric Partner Potentials

Even if the two partner potentials, $V(x, m)$ and $V(x, m-1)$, of the form $[k^2(x, m) \mp k'(x, m) + \mathcal{L}(m)]$ of eqs. (7) and (8) of the last chapter do *not* have the same shape, it may still be possible to say something about the eigenvalue spectrum of the partner potential if the eigenvalues of one of the potentials are known. This will be true whether or not the potentials are functions of a parameter, m . This has been known since 1882 through the work of G. Darboux; (*Comptes Rendus Acad. de Sci. (Paris)* **94**(1882)1456). This 19th century work has only recently been rediscovered by quantum theorists in connection with work in particle physics on supersymmetry. Hence, the partner potentials are known as supersymmetric partner potentials.

Suppose we have an eigenvalue problem with a potential $V_1(x)$

$$\left(-\frac{d^2}{dx^2} + V_1(x) \right) u_\lambda(x) = \left(A^\dagger A + \text{const.} \right) u_\lambda(x) = \lambda u_\lambda(x), \quad (1)$$

which is a solved problem and can be put in the form

$$\left(\left[-\frac{d}{dx} + k(x) \right] \left[\frac{d}{dx} + k(x) \right] + \text{const.} \right) u_\lambda(x) = \lambda u_\lambda(x). \quad (2)$$

Because we have no parameter, m , we have named the two operators, A , and A^\dagger ,

$$A = \left[\frac{d}{dx} + k(x) \right]; \quad A^\dagger = \left[-\frac{d}{dx} + k(x) \right]. \quad (3)$$

In addition, let $u_{\bar{\lambda}}$ be any solution of eq. (1), perhaps *not* a square-integrable solution,

$$\left(-\frac{d^2}{dx^2} + V_1(x) \right) u_{\bar{\lambda}}(x) = \bar{\lambda} u_{\bar{\lambda}}(x). \quad (4)$$

This equation is satisfied if we choose

$$k(x) = -\left(\frac{u'_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right), \quad \text{and} \quad \text{const.} = \bar{\lambda}, \quad (5)$$

because

$$A^\dagger A = -\frac{d^2}{dx^2} + \left(\frac{u'_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right)^2 + \frac{d}{dx} \left(\frac{u'_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right) = -\frac{d^2}{dx^2} + \left(\frac{u''_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right), \quad (6)$$

so

$$A^\dagger A u_{\bar{\lambda}} = -\frac{d^2 u_{\bar{\lambda}}}{dx^2} + u''_{\bar{\lambda}} = 0 = (\bar{\lambda} - \text{const.}) u_{\bar{\lambda}}(x). \quad (7)$$

Therefore, the constant in the original equation must be $\bar{\lambda}$ and the potential $V_1(x)$ is given by

$$V_1(x) = \left(\frac{u''_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right) + \bar{\lambda}. \quad (8)$$

Now, let us look at a different eigenvalue problem, with a different potential, and different eigenfunctions, but with the same eigenvalues λ

$$AA^\dagger w_\lambda(x) = (\lambda - \bar{\lambda}) w_\lambda(x). \quad (9)$$

The order of the operators, A , and A^\dagger , is reversed from that in the original equation, which was

$$A^\dagger A u_\lambda(x) = (\lambda - \bar{\lambda}) u_\lambda(x). \quad (10)$$

Now, because

$$\begin{aligned} \left(AA^\dagger + \bar{\lambda} \right) w_\lambda(x) &= \lambda w_\lambda(x) \\ &= \left[-\frac{d^2}{dx^2} + 2 \left(\frac{u'_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right)^2 - \left(\frac{u''_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right) + \bar{\lambda} \right] w_\lambda(x) \\ &= \left(-\frac{d^2}{dx^2} + V_2(x) \right) w_\lambda, \end{aligned} \quad (11)$$

we have

$$\begin{aligned} V_2(x) &= 2 \left(\frac{u'_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right)^2 - \left(\frac{u''_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right) + \bar{\lambda} \\ &= 2 \left(\frac{u'_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right)^2 + 2\bar{\lambda} - V_1(x), \end{aligned} \quad (12)$$

where problem 1, with potential $V_1(x)$, is given by

$$A^\dagger A u_\lambda = (\lambda - \bar{\lambda}) u_\lambda, \quad (13)$$

whereas problem 2, with potential $V_2(x)$, is given by

$$AA^\dagger w_\lambda = (\lambda - \bar{\lambda}) w_\lambda. \quad (14)$$

Now, acting on eq. (13) from the left with A yields

$$AA^\dagger(Au_\lambda) = (\lambda - \bar{\lambda})(Au_\lambda). \quad (15)$$

Thus, we see: If u_λ is an eigenfunction of problem 1, with eigenvalue λ , (Au_λ) is an eigenfunction of problem 2, with the same eigenvalue, λ . The question remains: Is w_λ square-integrable, if u_λ is square-integrable? To answer this question, calculate

$$\begin{aligned} \int_{-\infty}^{+\infty} dx w_\lambda^* w_\lambda &= \int_{-\infty}^{+\infty} dx (Au_\lambda)^* Au_\lambda = \int_{-\infty}^{+\infty} dx u_\lambda^* (A^\dagger A u_\lambda) \\ &= (\lambda - \bar{\lambda}) \int_{-\infty}^{+\infty} dx u_\lambda^* u_\lambda. \end{aligned} \quad (16)$$

Thus, if u_λ is square-integrable over the domain from $-\infty$ to $+\infty$ (as assumed here, or over some domain from a to b), and if the value $\bar{\lambda}$ lies below the lowest allowed eigenvalue λ of the original problem, the right-hand side is positive, and

$$w_\lambda(x) = \left[\frac{d}{dx} - \left(\frac{u'_\lambda}{u_\lambda} \right) \right] u_\lambda(x) \quad (17)$$

will also be square-integrable, even if u_λ is not. A word of caution is needed here. The above derivation required the property $A^\dagger = (A)^\dagger$, which required an integration by parts over the domain from $-\infty$ to $+\infty$. For the needed integrals to exist, the logarithmic derivative, (u'_λ/u_λ) , which arises through the function $k(x)$, must not have any infinities; i.e., the function u_λ must not have any zeros. This will be true in general if $V(x)$ has both a left and a right classical turning point, and if $\bar{\lambda}$ lies below the lowest eigenvalue λ . For the lowest possible eigenvalue, the eigenfunction u_λ will have just enough curvature away from the x -axis in the classically forbidden regions so both u_λ and its first derivative will go to zero together as $x \rightarrow \pm\infty$, as required for a square-integrable function. Moreover, the lowest allowed eigenfunction will have no zeros. For a $\bar{\lambda}$ below the lowest allowed λ , the curvature away from the x -axis in the classically forbidden regions will be too great and the function $u_\lambda(x)$ will approach ∞ for both $x \rightarrow \pm\infty$ before $u_\lambda(x)$ can reach the value zero (see Fig. 12.1). Thus, for every eigenvalue λ of the potential $V_1(x)$, a square-integrable (calculable) eigenfunction of the potential $V_2(x)$ exists. The potential $V_2(x)$, however, has an additional eigenvalue, $\bar{\lambda}$, below the lowest λ . Two candidates exist for square-integrable eigenfunctions associated with this additional eigenvalue

$$w_\lambda^{(1)} = \frac{1}{u_\lambda}, \quad w_\lambda^{(2)} = \frac{1}{u_\lambda} \int_0^x d\xi [u_\lambda(\xi)]^2. \quad (18)$$

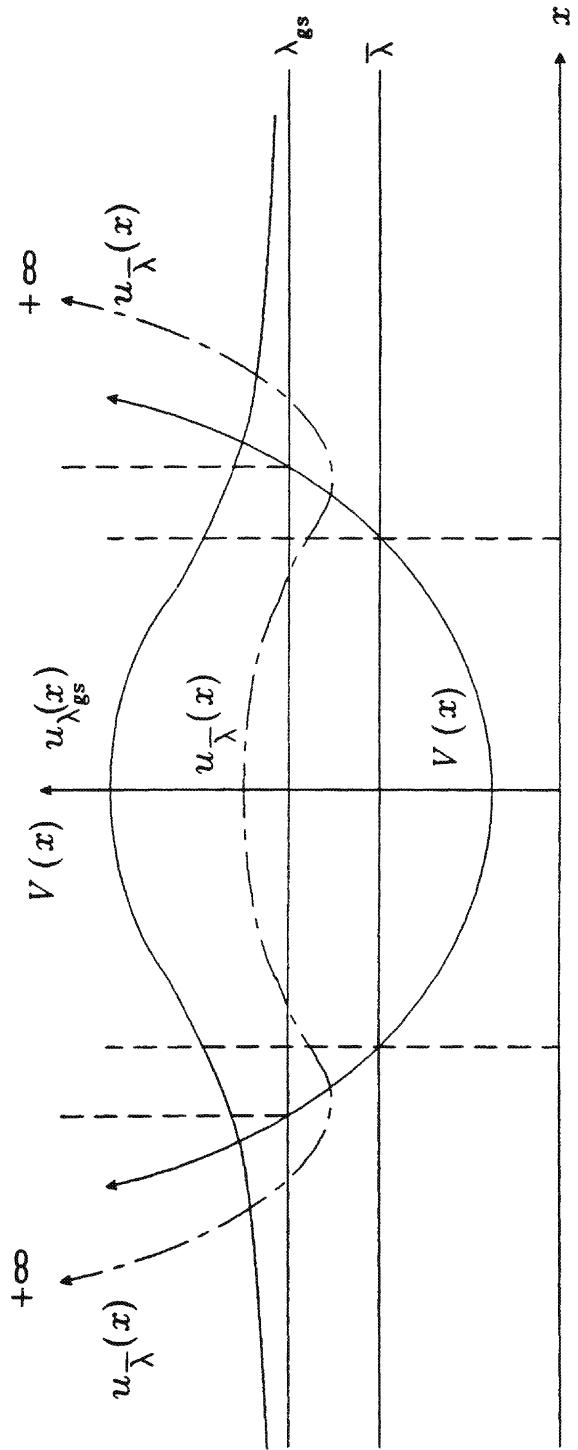


FIGURE 12.1. A $V(x)$ with a single deep minimum showing the allowed ground-state eigenfunction with $\lambda = \lambda_{gs}$ and a solution for $\bar{\lambda} < \lambda_{gs}$.

To show these equations are solutions of eq. (11) with eigenvalue $\lambda = \bar{\lambda}$, note

$$A^\dagger \left(\frac{1}{u_{\bar{\lambda}}} \right) = \left[-\frac{d}{dx} - \left(\frac{u'_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right) \right] \left(\frac{1}{u_{\bar{\lambda}}} \right) = 0. \quad (19)$$

Also,

$$\begin{aligned} AA^\dagger w_{\bar{\lambda}}^{(2)} &= A \left(-\frac{d}{dx} - \frac{u'_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right) \frac{1}{u_{\bar{\lambda}}} \int_0^x d\xi [u_{\bar{\lambda}}(\xi)]^2 \\ &= A \left[\left(\frac{u'_{\bar{\lambda}}}{(u_{\bar{\lambda}})^2} - \frac{u''_{\bar{\lambda}}}{(u_{\bar{\lambda}})^2} \right) \int_0^x d\xi [u_{\bar{\lambda}}(\xi)]^2 - \frac{1}{u_{\bar{\lambda}}} [u_{\bar{\lambda}}]^2 \right] \\ &= -Au_{\bar{\lambda}} = - \left[\frac{d}{dx} - \frac{u'_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right] u_{\bar{\lambda}} = 0. \end{aligned} \quad (20)$$

If either $w_{\bar{\lambda}}^{(1)}$ or $w_{\bar{\lambda}}^{(2)}$ are square-integrable, we have a valid eigenfunction for the additional $\bar{\lambda}$ of the spectrum. The arguments given in connection with Fig. 12.1 show the new eigenfunction, $w_{\bar{\lambda}}^{(1)} = 1/u_{\bar{\lambda}}$ will in general be square-integrable if the potential $V_1(x)$ has both left and right classical turning points, and if $\bar{\lambda} < \lambda$. Thus, we have a prescription for finding an infinite number of new potentials $V_2(x)$ with an eigenvalue spectrum given by the new $\bar{\lambda}$ and the original full spectrum of λ 's. The eigenfunctions for the new potential are given by eq. (17) and (18). This is the method of supersymmetric partner potentials.

In problem 17, we shall use the 1-D harmonic oscillator to find double minimum potentials with a known spectrum of eigenvalues and eigenfunctions. Because the process of finding a $V_2(x)$ from a $V_1(x)$ with a known spectrum can in principle be iterated, we can find a potential with a spectrum of eigenvalues such that a few low-lying eigenvalues are placed arbitrarily, but with a spectrum of higher eigenvalues of the initial $V_1(x)$.

Problems

17. Supersymmetric partner potentials. Use a solution $u_{\bar{\lambda}}(x)$ of the 1-D harmonic oscillator equation

$$-\frac{d^2 u_{\bar{\lambda}}}{dx^2} + x^2 u_{\bar{\lambda}}(x) = \bar{\lambda} u_{\bar{\lambda}}(x)$$

to find the eigenvalues and eigenfunctions for the wave equation for a particle moving in the potential $V_2(x)$, the supersymmetric partner potential, where

$$V_2(x) = 2\bar{\lambda} + 2 \left(\frac{u'_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right)^2 - V_1(x) = 2\bar{\lambda} + 2 \left(\frac{u'_{\bar{\lambda}}}{u_{\bar{\lambda}}} \right)^2 - x^2$$

in the case $u_{\bar{\lambda}}$ is an even function of x , and $\bar{\lambda} < 1$, so $u_{\bar{\lambda}}$ has no zeros. Show first that the infinite series for $u_{\bar{\lambda}}$ can be put in the form

$$u_{\bar{\lambda}}(x) = {}_1F_1\left(\frac{(1-\bar{\lambda})}{4}; \frac{1}{2}; x^2\right) e^{-\frac{1}{2}x^2},$$

where

$${}_1F_1(a; b; x^2) = \sum_{n=0}^{\infty} \frac{(a)_n}{(b)_n} \frac{x^{2n}}{n!},$$

$$\text{and } (a)_n = a(a+1)(a+2)\cdots(a+n-1), \quad (a)_0 = 1,$$

and show that

$$u'_{\bar{\lambda}} = x \left((1 - \bar{\lambda}) {}_1F_1\left(\frac{5 - \bar{\lambda}}{4}; \frac{3}{2}; x^2\right) - {}_1F_1\left(\frac{1 - \bar{\lambda}}{4}; \frac{1}{2}; x^2\right) \right) e^{-\frac{1}{2}x^2}.$$

The case with two nearly degenerate levels near $\lambda = 1$ is of particular interest. Plot the potential $V_2(x)$ together with the eigenvalue spectrum for the two cases:

$$\bar{\lambda} = 1 - \frac{1}{3}, \quad \bar{\lambda} = 1 - \frac{1}{256}.$$

Also, plot the eigenfunctions for the two lowest energy eigenvalues.

18. Find the hydrogenic expectation values of $(1/r, 1/r^2, 1/r^3)$:

(a) Use

$$\frac{dO}{dt} = \frac{i}{\hbar} [H, O] + \frac{\partial O}{\partial t}$$

to derive the quantum-mechanical form of the virial theorem, for an N -particle system, including $N = 1$:

$$\frac{1}{4} \frac{d}{dt} \langle \psi, \sum_{i=1}^N (\vec{r}_i \cdot \vec{p}_i + \vec{p}_i \cdot \vec{r}_i) \psi \rangle = \langle \psi, \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} \psi \rangle - \frac{1}{2} \langle \psi, \sum_{i=1}^N (\vec{r}_i \cdot \vec{\nabla}_i V) \psi \rangle.$$

Use this theorem to find the expectation value of $1/r$ for a state ψ_{nlm} of the hydrogen atom.

(b) Derive the Hellmann–Feynman theorem which applies to a system whose Hamiltonian is a function of a parameter, v , and states

$$\frac{\partial E_n}{\partial v} = \langle \psi_n, \frac{\partial H}{\partial v} \psi_n \rangle.$$

Use this theorem to calculate the expectation value of $1/r^2$ for a state ψ_{nlm} of the hydrogen atom. Use l as the parameter, ($l \equiv v$). The quantum number, n , depends on this parameter through $n = (n_r + l + 1)$; ($n_r = 0, 1, 2, \dots$).

(c) The radial functions, $u_{nl}(r)$, $u_{n'l'}(r)$, with $l' \neq l$, are by themselves not orthogonal to each other

$$\int_0^\infty dr u_{nl}^*(r) u_{n'l'}(r) = \int_0^\infty dr r^2 R_{nl}^*(r) R_{n'l'}(r) \neq 0,$$

but show that, with $n' = n$,

$$\int_0^\infty dr \frac{1}{r^2} u_{nl}^*(r) u_{nl'}(r) = \int_0^\infty dr R_{nl}^*(r) R_{nl'}(r) = 0, \quad \text{with } l' \neq l.$$

Hint: Use the radial equation to evaluate

$$\frac{\hbar^2}{2\mu}[l'(l'+1) - l(l+1)] \int_0^\infty dr \frac{1}{r^2} u_{nl}^* u_{nl'}.$$

Now eliminate $\frac{d}{dr}$ from the hydrogen step-up and down operators, $O_+(l+1)$, $O_-(l)$, and combine the resulting expression for $\frac{1}{r}u_{nl}(r)$ with the above to evaluate the expectation value of $1/r^3$ in the state ψ_{nlm} .

19. Commutator algebra for the hydrogen atom.

(a) Use the dimensionless angular momentum and Runge–Lenz vectors, \vec{L} and \vec{R} , as well as the dimensionless \vec{p} , \vec{r} , H , and ϵ of problem 13 to show these dimensionless operators satisfy the commutation relations

$$[L_j, L_k] = i\epsilon_{jka} L_\alpha, \quad [L_j, \mathcal{R}_k] = i\epsilon_{jka} \mathcal{R}_\alpha,$$

$$[\mathcal{R}_j, \mathcal{R}_k] = (-\vec{p}^2 + \frac{2}{r})i\epsilon_{jka} L_\alpha = (-2H)i\epsilon_{jka} L_\alpha.$$

(b) Define

$$\vec{V} = \frac{\vec{R}}{\sqrt{(-2\epsilon)}}$$

to show in the subspace of a fixed, n ,

$$[L_j, L_k] = i\epsilon_{jka} L_\alpha, \quad [L_j, V_k] = i\epsilon_{jka} V_\alpha, \quad [V_j, V_k] = i\epsilon_{jka} L_\alpha.$$

If we define

$$L_{ij} = \frac{1}{i} \left(x_i \frac{\partial}{\partial x_j} - x_j \frac{\partial}{\partial x_i} \right)$$

so $L_1 = L_{23}$; $L_2 = L_{31}$; $L_3 = L_{12}$, V_j can be defined through

$$V_j = \frac{1}{i} \left(x_j \frac{\partial}{\partial x_4} - x_4 \frac{\partial}{\partial x_j} \right).$$

Show that these operators satisfy the above commutation relations. That is, show the six operators, \vec{L} and \vec{V} can be related to the six operators, L_{ij} , with $i, j = 1, \dots, 4$, which are the angular momentum operators in an abstract 4-D space generating rotations in this abstract 4-D space, x_1, x_2, x_3, x_4 , where x_1, x_2, x_3 are our 3-D real space.

(c) Show that \vec{M} and \vec{N} , defined by

$$\vec{M} = \frac{1}{2}(\vec{L} + \vec{V}), \quad \vec{N} = \frac{1}{2}(\vec{L} - \vec{V}),$$

satisfy the commutation relations of two commuting angular momentum operators

$$[M_j, M_k] = i\epsilon_{jka} M_\alpha, \quad [N_j, N_k] = i\epsilon_{jka} N_\alpha, \quad [M_j, N_k] = 0.$$

(d) Show that

$$\vec{M}^2 - \vec{N}^2 = \frac{1}{2}((\vec{L} \cdot \vec{V}) + (\vec{V} \cdot \vec{L})) = 0, \quad \text{see Problem 13,}$$

$$2(\vec{M}^2 + \vec{N}^2) + 1 = (\vec{L}^2 + \vec{V}^2 + 1) = -\frac{1}{2\epsilon} = n^2.$$

(e) Show that the double angular momentum eigenfunctions, $\psi_{j_1 m_1 j_2 m_2}$, with

$$\vec{M}^2 \psi_{j_1 m_1 j_2 m_2} = j_1(j_1 + 1)\psi_{j_1 m_1 j_2 m_2}, \quad M_3 \psi_{j_1 m_1 j_2 m_2} = m_1 \psi_{j_1 m_1 j_2 m_2},$$

$$\vec{N}^2 \psi_{j_1 m_1 j_2 m_2} = j_2(j_2 + 1)\psi_{j_1 m_1 j_2 m_2}, \quad N_3 \psi_{j_1 m_1 j_2 m_2} = m_2 \psi_{j_1 m_1 j_2 m_2},$$

are also eigenvectors of the hydrogen atom H , provided

$$j_1 = j_2 = \frac{(n - 1)}{2}.$$

13

The Vector Space Interpretation of Quantum-Mechanical Systems

A Different “Representations” of the State of a Quantum-Mechanical System

So far, we have specified the state of a quantum-mechanical system by the wave function, $\Psi(\vec{r}, t)$, i.e., by specifying the value of the scalar function, Ψ , for all values of x , y , z , at a particular time, t . Ψ could also be specified, however, at a particular time by the infinite set of numbers, $c_n(t)$, in the expansion of $\Psi(\vec{r}, t)$ in the completee set of energy eigenfunctions of the system,

$$c_n e^{-\frac{i}{\hbar} E_n t} = \langle \psi_n, \Psi(\vec{r}, t) \rangle \equiv c_n(t), \quad (1)$$

with

$$c_n = \langle \psi_n, \Psi(\vec{r}, t = 0) \rangle = \int d\vec{r} \psi_n^*(\vec{r}) \Psi(\vec{r}, t = 0). \quad (2)$$

Alternatively, Ψ could just as well be specified by another set of numbers, a set of Fourier coefficients of some other (complete) set of generalized Fourier functions. For example, we might use the eigenfunctions of some other Hamiltonian, \bar{H} , not the Hamiltonian of *our* system, or possibly \bar{H} could be some other Hermitian operator, not a Hamiltonian. Let us assume, in particular, \bar{H} has both a discrete and a continuous spectrum, where the discrete spectrum is numbered by an index, $i = 1, 2, \dots, n$, perhaps a finite number or perhaps an infinite number, whereas the continuous eigenvalue spectrum is parameterized by a continuous variable, α , such that

$$\bar{H} u_i(\vec{r}) = E_i u_i(\vec{r}) \quad (3)$$

$$\bar{H}w_\alpha(\vec{r}) = E(\alpha)w_\alpha(\vec{r}), \quad (4)$$

where the eigenfunctions form an orthonormal set, with

$$\langle u_i, u_j \rangle = \delta_{ij}, \quad \langle u_i, w_\alpha \rangle = 0, \quad \langle w_\alpha, w_{\alpha'} \rangle = \delta(\alpha - \alpha'). \quad (5)$$

The eigenfunctions must of course also form a complete set, where the completeness relation is now

$$\sum_i u_i^*(\vec{r}') u_i(\vec{r}) + \int d\alpha w_\alpha^*(\vec{r}') w_\alpha(\vec{r}) = \delta(\vec{r}' - \vec{r}). \quad (6)$$

Now, Ψ can be expanded in terms of this complete set via

$$\Psi(\vec{r}, t) = \sum_i c_i u_i(\vec{r}) + \int d\alpha c(\alpha) w_\alpha(\vec{r}), \quad (7)$$

where the c_i and $c(\alpha)$ are given by

$$c_i = \langle u_i, \Psi \rangle = \int d\vec{r}' u_i^*(\vec{r}') \Psi(\vec{r}', t), \quad (8)$$

$$c(\alpha) = \langle w_\alpha, \Psi \rangle = \int d\vec{r}' w_\alpha^*(\vec{r}') \Psi(\vec{r}', t). \quad (9)$$

The c_i and $c(\alpha)$ are now implicitly time dependent. These c_i and $c(\alpha)$ now give us still another alternative for the description of our quantum-mechanical system.

So far, we have used Fourier expansions in a set of orthonormal functions that themselves were square-integrable functions; i.e., they were themselves part of our Hilbert space. The basis functions in the Fourier expansions, however, need not themselves be square-integrable. In fact, our original expansion in terms of ordinary Fourier plane-wave functions was of this type. The plane-wave functions (in the general notation of this chapter) are

$$u_{\vec{p}}(\vec{r}) = \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar}(\vec{p} \cdot \vec{r})}. \quad (10)$$

These functions are eigenfunctions simultaneously of the three operators $(p_x)_{\text{op.}}$, $(p_y)_{\text{op.}}$, $(p_z)_{\text{op.}}$, with eigenvalues p_x , p_y , p_z , with, e.g.,

$$\frac{\hbar}{i} \frac{\partial}{\partial x} u_{\vec{p}}(\vec{r}) = p_x u_{\vec{p}}(\vec{r}). \quad (11)$$

Because the spectrum of possible \vec{p} is continuous, the orthogonality is expressed in terms of a Dirac delta function in place of a Kronecker delta

$$\langle u_{\vec{p}'}, u_{\vec{p}} \rangle = \delta(\vec{p}' - \vec{p}), \quad (12)$$

and the completeness relation is given by

$$\int d\vec{p} u_{\vec{p}}^*(\vec{r}') u_{\vec{p}}(\vec{r}) = \delta(\vec{r}' - \vec{r}). \quad (13)$$

The Fourier expansion of Ψ is the standard Fourier one, with expansion coefficients, $\phi(\vec{p}, t)$, now the standard Fourier transform

$$\Psi(\vec{r}, t) = \int d\vec{p} \phi(\vec{p}, t) u_{\vec{p}}(\vec{r}), \quad (14)$$

with

$$\phi(\vec{p}, t) = \langle u_{\vec{p}}, \Psi \rangle. \quad (15)$$

The $\phi(\vec{p}, t)$ now give us another alternative way of specifying the state of our quantum-mechanical system.

Finally, we could even use a basis of Dirac delta functions for the generalized Fourier expansion of our Ψ , where these can be written, in analogy with the $u_{\vec{p}}$, or the ψ_n , as

$$u_{\vec{r}_0}(\vec{r}) = \delta(\vec{r} - \vec{r}_0), \quad (16)$$

where these u 's are simultaneously the eigenfunctions of the three operators x , y , z ; with eigenvalues x_0 , y_0 , z_0 . For example,

$$x u_{\vec{r}_0}(\vec{r}) = x \delta(\vec{r} - \vec{r}_0) = x_0 \delta(\vec{r} - \vec{r}_0), \quad (17)$$

where we have used the delta function relation

$$f(x)\delta(x) = f(0)\delta(x). \quad (18)$$

The orthogonality of the u 's is now given by the delta function relation

$$\int d\vec{r} u_{\vec{r}_0}^*(\vec{r}) u_{\vec{r}'_0}(\vec{r}) = \int d\vec{r} \delta(\vec{r} - \vec{r}_0) \delta(\vec{r} - \vec{r}'_0) = \delta(\vec{r}_0 - \vec{r}'_0). \quad (19)$$

The completeness relation is now given by the integral

$$\int d\vec{r}_0 u_{\vec{r}_0}^*(\vec{r}') u_{\vec{r}_0}(\vec{r}) = \int d\vec{r}_0 \delta(\vec{r}_0 - \vec{r}') \delta(\vec{r}_0 - \vec{r}) = \delta(\vec{r}' - \vec{r}). \quad (20)$$

The Fourier expansion of a ψ (let us make it time independent for simplicity), in terms of Fourier amplitudes $c_{\vec{r}_0}$, now leads to

$$\psi(\vec{r}) = \int d\vec{r}_0 c_{\vec{r}_0} u_{\vec{r}_0}(\vec{r}) = \int d\vec{r}_0 \psi(\vec{r}_0) \delta(\vec{r} - \vec{r}_0). \quad (21)$$

Now the Fourier coefficients $c_{\vec{r}_0}$, the analogs of the c_n , are just the wave functions $\psi(\vec{r}_0)$. Hence, this description of the state of our system is just the wave function description, where we specify ψ at every point x_0 , y_0 , z_0 in space time.

To summarize, we have given a number of alternative ways to give a complete description of the state of our system:

- 1) through specification of Ψ at every point in space time;
- 2) through the coefficients c_n through an expansion of Ψ in terms of the eigenfunctions of the Hamiltonian of our system;
- 3) through the coefficients, c_i and $c(\alpha)$, through an expansion of Ψ in terms of the eigenfunctions of an hermitian operator \bar{H} with both a discrete and a continuous eigenvalue spectrum;

4) through the $\phi(\vec{p}, t)$ in a standard Fourier expansion of plane waves.

There are thus many “representations” of our quantum-mechanical system. This will lead us to an introduction to the Dirac notation in the next section.

B The Dirac Notation

Many different “representations” exist that can specify the state of an atomic quantum-mechanical system, described by the wave function, $\Psi(\vec{r}, t)$. We can specify Ψ at every point in space time; we can specify it through the c_n , or through another set c_i and $c(\alpha)$, or through the $\phi(p, t)$, and so on.

Because our $\Psi(\vec{r}, t)$ belong to the space of square-integrable functions, a quantum system specified by a Ψ can be thought of as a vector in infinite-dimensional vector space. The coefficients, c_n , can be thought of as the components of this vector along a particular set of coordinate axes, similarly, for the c_i and $c(\alpha)$ for a different set of coordinate axes. In the same way, the $\phi(\vec{p}, t)$ can be thought of as the components of the state vector along the set of axes specified by the momentum values, and the $\Psi(\vec{r}, t)$ as the components of the state vector along a set of axes specified by the values of the coordinates. The vector space of our Ψ with a well-defined complex scalar product is also called a Hilbert space. Just as in ordinary finite-dimensional vector analysis, it will be convenient to specify a vector by a generic symbol, not always by its coordinates along particular axes. Dirac proposed to do this through his “ket” symbol. Thus, a state vector is specified by $|\Psi\rangle$. Because scalar products $\langle \Phi, \Psi \rangle$ are complex numbers, linear in Ψ but antilinear in Φ , with

$$\begin{aligned} \langle \Phi, (\lambda_1 \Psi_1 + \lambda_2 \Psi_2) \rangle &= \lambda_1 \langle \Phi, \Psi_1 \rangle + \lambda_2 \langle \Phi, \Psi_2 \rangle, & \text{but} \\ \langle (\lambda_1 \Phi_1 + \lambda_2 \Phi_2), \Psi \rangle &= \lambda_1^* \langle \Phi_1, \Psi \rangle + \lambda_2^* \langle \Phi_2, \Psi \rangle, \end{aligned} \quad (22)$$

where λ_1 and λ_2 are complex numbers, Dirac defines for every “ket” vector, $|\Psi\rangle$, a dual vector, the so-called “bra,” denoted by $\langle \Psi |$, where

$$\begin{aligned} |\lambda_1 \Psi_1 + \lambda_2 \Psi_2\rangle &= \lambda_1 |\Psi_1\rangle + \lambda_2 |\Psi_2\rangle, \\ \langle \lambda_1 \Psi_1 + \lambda_2 \Psi_2 | &= \lambda_1^* \langle \Psi_1 | + \lambda_2^* \langle \Psi_2 |. \end{aligned} \quad (23)$$

The “bra” vector then permits us to write the scalar product of two vectors in terms of a “bracket”

$$\langle \Phi, \Psi \rangle \equiv \langle \Phi | \Psi \rangle. \quad (24)$$

In the new language, the Hilbert space is an infinite-dimensional vector space of all vectors $|\Psi\rangle$ with a finite norm,

$$\langle \Psi | \Psi \rangle = \text{finite real positive number.}$$

Because we are dealing with an infinite-dimensional vector space, we will also insist on the absolute convergence of expansions, such as

$$\Psi_N = \sum_{n=0}^N c_n \psi_n \quad \text{as } N \rightarrow \infty.$$

A linear operator, O , acting on a “ket,” $|\Psi\rangle$, converts this into a new “ket,” $|\Psi'\rangle = O|\Psi\rangle$, with a dual “bra,” given by $\langle\Psi'| = \langle\Psi|O^\dagger$, so

$$\langle\Phi|\Psi'\rangle = \langle\Phi|O|\Psi\rangle = \langle\Psi|O^\dagger|\Phi\rangle^*. \quad (25)$$

$\langle\Phi|\Psi\rangle$ is a number, usually a complex number.

In this new language, an operator can be written as, e.g.,

$$|\Phi\rangle\langle\Lambda| \quad (26)$$

because

$$|\Phi\rangle\langle\Lambda|\Psi\rangle = (\text{a complex number})|\Phi\rangle; \quad (27)$$

that is, the operator $|\Phi\rangle\langle\Lambda|$, acting on the vector $|\Psi\rangle$, converts it into a new vector $|\Phi\rangle$, multiplied by the complex number $\langle\Lambda|\Psi\rangle$.

A very important type of operator is the projection operator, which projects an arbitrary state vector, $|\Psi\rangle$, onto a basis vector, such as $|\psi_n\rangle$. We will assume that $|\psi_n\rangle$ is normalized such that

$$\langle\psi_n|\psi_n\rangle = 1. \quad (28)$$

Then,

$$P_n = |\psi_n\rangle\langle\psi_n|. \quad (29)$$

Note,

$$P_n^2 = |\psi_n\rangle\langle\psi_n|\psi_n\rangle\langle\psi_n| = |\psi_n\rangle\langle\psi_n| = P_n, \quad \text{via } \langle\psi_n|\psi_n\rangle = 1. \quad (30)$$

Once we have projected the arbitrary vector onto the n^{th} basis vector, projecting once more will not alter this result, so $P_n^2 = P_n$.

The completeness relation for the functions ψ_n can be translated into the “closure” relation in Dirac notation

$$\sum_n |\psi_n\rangle\langle\psi_n| = 1. \quad (31)$$

If the n^{th} energy eigenvalue is degenerate, i.e., if g_n independent eigenfunctions $\psi_n^{(i)}$ with $i = 1, 2, \dots, g_n$ exist (assuming we have orthonormalized the states with the same n , viz., $\langle\psi_n^{(i)}|\psi_n^{(j)}\rangle = \delta_{ij}$), it may be useful to define a projection operator

$$P_n = \sum_{i=1}^{i=g_n} |\psi_n^{(i)}\rangle\langle\psi_n^{(i)}| \quad (32)$$

that projects onto the subspace of states with definite energy E_n . Now the closure relation (completeness condition) becomes

$$\sum_n \sum_{i=1}^{i=g_n} |\psi_n^{(i)}\rangle \langle \psi_n^{(i)}| = 1. \quad (33)$$

For simplicity, let us for the moment assume no degeneracies exist. Then, P_n acting on an arbitrary state vector $|\Psi\rangle$ yields

$$P_n |\Psi\rangle = |\psi_n\rangle \langle \psi_n| \Psi \rangle = |\psi_n\rangle c_n, \quad (34)$$

or, using the closure relation, an arbitrary state vector, $|\Psi\rangle$, can be expanded in terms of base vectors, $|\psi_n\rangle$,

$$|\Psi\rangle = 1|\Psi\rangle = \sum_n |\psi_n\rangle \langle \psi_n| \Psi \rangle = \sum_n |\psi_n\rangle c_n. \quad (35)$$

This equation is the analog in the infinite-dimensional Hilbert space of the expansion of a vector, \vec{V} , in ordinary vector analysis in terms of base vectors, \vec{e}_i (unit vectors along the i^{th} direction),

$$\vec{V} = \sum_i \vec{e}_i V_i. \quad (36)$$

If we use some of the other representations introduced in the previous section, we can construct similar projection operators and similar projections. In a basis of eigenvectors of the operator, \overline{H} , with

$$\overline{H}|u_i\rangle = E_i|u_i\rangle, \quad \overline{H}|w_\alpha\rangle = E(\alpha)|w_\alpha\rangle. \quad (37)$$

The closure relation is given by

$$\sum_i |u_i\rangle \langle u_i| + \int d\alpha |w_\alpha\rangle \langle w_\alpha| = 1, \quad (38)$$

and a state vector $|\Psi\rangle$ can be expanded in this basis by

$$|\Psi\rangle = 1|\Psi\rangle = \sum_i |u_i\rangle \langle u_i| \Psi \rangle + \int d\alpha |w_\alpha\rangle \langle w_\alpha| \Psi \rangle = \sum_i |u_i\rangle c_i + \int d\alpha |w_\alpha\rangle c(\alpha). \quad (39)$$

Similarly, in the basis of eigenvectors of the momentum operator, \vec{p} ,

$$|\Psi\rangle = \int d\vec{p} |u_{\vec{p}}\rangle \langle u_{\vec{p}}| \Psi \rangle = \int d\vec{p} |u_{\vec{p}}\rangle \phi(\vec{p}, t). \quad (40)$$

Finally, in the basis of eigenvectors of the position operator, \vec{r} ,

$$|\Psi\rangle = \int d\vec{r}_0 |u_{\vec{r}_0}\rangle \langle u_{\vec{r}_0}| \Psi \rangle. \quad (41)$$

The projection onto the base vector $|u_{\vec{r}_0}\rangle$ is now just the Schrödinger wave function, $\langle u_{\vec{r}_0}|\Psi\rangle = \psi(\vec{r}_0)$, where we have used the orthonormality of the $u_{\vec{r}_0}$, eq. (19).

In all of the above examples, we have expanded ket vectors in terms of ket base vectors. We could of course have done the same with the bra versions of the

vectors. For example, multiplying with the unit operator from the right,

$$\langle \Psi | = \sum_n \langle \Psi | \psi_n \rangle \langle \psi_n | = \sum_n c_n^* \langle \psi_n |. \quad (42)$$

Finally, operators can be represented through their matrix elements via

$$O = 1O1 = \sum_{n,m} |\psi_n\rangle\langle\psi_n| O |\psi_m\rangle\langle\psi_m| = \sum_{n,m} |\psi_n\rangle\langle\psi_m| (O)_{nm}, \quad (43)$$

$$O|\Psi\rangle = \sum_{n,m} |\psi_n\rangle\langle\psi_n| O |\psi_m\rangle\langle\psi_m| |\Psi\rangle = \sum_{n,m} |\psi_n\rangle O_{nm} c_m = |\Psi'\rangle = \sum_n |\psi_n\rangle c'_n, \quad (44)$$

so

$$c'_n = \sum_m O_{nm} c_m. \quad (45)$$

C Notational Abbreviations

Often, we shall abbreviate the ket $|\psi_n\rangle$ simply by $|n\rangle$. If we have a one-degree of freedom problem, a single quantum number n , associated with the eigenvalue E_n , is sufficient to specify the ket. For a particle moving in three dimensions, three quantum numbers would be needed. For example, for a single particle (without spin) moving in a 3-D harmonic oscillator well, the ket would be specified by $|n_1 n_2 n_3\rangle$. For a single particle with spin moving in a central potential $V(r)$, the specification $|nlm_l m_s\rangle$ would be natural. Thus, we abbreviate

$$|\psi_n\rangle \quad \rightarrow \quad |nlm_l m_s\rangle. \quad (46)$$

Similarly, for the momentum representation

$$|u_{\vec{p}}\rangle \quad \rightarrow \quad |\vec{p}\rangle = |p_x p_y p_z\rangle, \quad (47)$$

and, in the coordinate representation

$$|u_{\vec{r}_0}\rangle \quad \rightarrow \quad |\vec{r}_0\rangle = |x_0 y_0 z_0\rangle. \quad (48)$$

14

The Angular Momentum Eigenvalue Problem (Revisited)

A Simultaneous Eigenvectors of Commuting Hermitian Operators

So far, we have solved the angular momentum eigenvalue problem very specifically in the coordinate representation for the case of the orbital angular momentum eigenfunctions, the well-known spherical harmonics. Let us look at this problem once more from a much more general point of view, which can be taken over for *any* angular momentum problem, or even more generally for any problem involving three hermitian operators with the same commutation relations as the L_x , L_y , and L_z . We want to solve the problem of finding the simultaneous eigenvalues and eigenvectors of the two (commuting) operators $\vec{L} \cdot \vec{L}$, and L_z . We will now write the eigenequations in the new language

$$(\vec{L} \cdot \vec{L})|\lambda m\rangle = \lambda|\lambda m\rangle$$
$$L_z|\lambda m\rangle = m|\lambda m\rangle, \quad (1)$$

where we have purposely used the Dirac notation for the eigenvectors, so no implication is made as to a choice of representation.

The problem of finding the simultaneous eigenvectors of a pair (or more generally a number) of commuting hermitian operators is a very general one, because the complete specification of a base vector for an n -degree of freedom problem will in general involve n quantum numbers, associated with the eigenvalues of n commuting, hermitian operators. Let us first look at the case with $n = 2$. Let us first prove a theorem as follows.

Theorem: Two hermitian operators A and B have the same set of eigenvectors if and only if they commute.

First, assume the set of vectors $|\alpha\rangle$ are eigenvectors of both A and B :

$$\begin{aligned} A|\alpha\rangle &= a_\alpha|\alpha\rangle, \\ B|\alpha\rangle &= b_\alpha|\alpha\rangle. \end{aligned} \quad (2)$$

Now, let $[A, B] = (AB - BA)$ act on an arbitrary state vector $|\psi\rangle$ of our vector space. We shall assume the states $|\alpha\rangle$ form a complete set, and also note that a particular $|\alpha\rangle$ may require more than one label for a complete specification, so α may be a shorthand for two labels. Then, with

$$\sum_{\alpha} |\alpha\rangle\langle\alpha| = 1 \quad (3)$$

in the subspace in which A , and B act, we can project an arbitrary state vector $|\psi\rangle$ onto the $|\alpha\rangle$ basis to get

$$(AB - BA)|\psi\rangle = \sum_{\alpha} (AB - BA)|\alpha\rangle\langle\alpha|\psi\rangle = \sum_{\alpha} (a_\alpha b_\alpha - b_\alpha a_\alpha)|\alpha\rangle\langle\alpha|\psi\rangle = 0, \quad (4)$$

because the a_α and b_α are ordinary real numbers.

Conversely, if the $|\alpha\rangle$ are eigenvectors of the operator A , and if $[A, B] = 0$,

$$\begin{aligned} (AB - BA)|\psi\rangle &= 0 \\ &= (AB - BA)\sum_{\alpha} |\alpha\rangle\langle\alpha|\psi\rangle \\ &= \sum_{\alpha} (A - a_\alpha)B|\alpha\rangle\langle\alpha|\psi\rangle \\ &= \sum_{\alpha, \alpha'} (A - a_\alpha)|\alpha'\rangle\langle\alpha'|B|\alpha\rangle\langle\alpha|\psi\rangle \\ &= \sum_{\alpha, \alpha'} (a_{\alpha'} - a_\alpha)\langle\alpha'|B|\alpha\rangle\langle\alpha|\psi\rangle. \end{aligned} \quad (5)$$

Because $|\psi\rangle$ is an arbitrary vector and the $|\alpha\rangle$ are assumed to form a basis for the subspace of our vector space, we must have, for each pair of basis states $|\alpha\rangle$, $|\alpha'\rangle$,

$$(a_{\alpha'} - a_\alpha)\langle\alpha'|B|\alpha\rangle = 0. \quad (6)$$

Hence,

$$\langle\alpha'|B|\alpha\rangle = 0, \quad \text{if } a_{\alpha'} \neq a_\alpha. \quad (7)$$

If the eigenvalues a_α have no degeneracies, i.e., if but a single eigenvector associated with each a_α exists, the matrix of B is diagonal in the $|\alpha\rangle$ basis, and $\langle\alpha'|B|\alpha\rangle = \delta_{\alpha, \alpha'} b_\alpha$. The more common situation, however, is one in which degeneracies associated with the eigenvalues of A exist. For example, if $A = \vec{L}^2$, $(2l + 1)$ eigenvectors associated with each eigenvalue of A exist. Then, with

$$A|\alpha^{(i)}\rangle = a_\alpha|\alpha^{(i)}\rangle, \quad \text{with } i = 1, 2, \dots g_{a_\alpha}, \quad (8)$$

$$\langle\alpha'^{(j)}|B|\alpha^{(i)}\rangle = \delta_{\alpha, \alpha'}\langle\alpha^{(j)}|B|\alpha^{(i)}\rangle. \quad (9)$$

In this case, it is still possible to take a linear combination of the $|\alpha^{(i)}\rangle$, with the same eigenvalue, a_α of the operator A , to make the matrix of the operator B diagonal in this g_{a_α} -dimensional subspace. To specify the basis completely, we then need the simultaneous eigenvalues of both operators A and B .

B The Angular Momentum Algebra

With this introduction, let us look at the eigenvalue problem of eq. (1) for the operators L_z , and \vec{L}^2 , built from the three (dimensionless) operators, L_x , L_y , L_z , where these satisfy the commutation relations

$$[L_x, L_y] = iL_z, \quad \text{and cyclically,} \quad \text{or} \quad [L_j, L_k] = i\epsilon_{jkl}L_l. \quad (10)$$

Our results will depend only on these commutation relations. Hence, other operators with these same commutation relations will also be interesting. The other angular momentum example involves the three components of the spin operator, S_x , S_y , S_z . In the case of the orbital angular momentum operator, we were able to write the operators in terms of functions of θ , ϕ , $\frac{\partial}{\partial\theta}$, and $\frac{\partial}{\partial\phi}$, i.e., in terms of explicit functions of the orbital coordinates. In the case of the electron, and other fundamental particles, we know nothing about the intrinsic or internal coordinates of such particles. In 1924, G. E. Uhlenbeck and S. Goudsmit had a picture in their mind of an electron that was like a little rotating sphere, but to the best of our ability to measure anything today to many significant figures, the electron is still a point particle (with no observable internal structure). Hence, we cannot relate the spin operators to internal “angles.” In the case of a rotating molecule, we can write the rotational, internal angular momentum in terms of three Euler angles and their partial derivatives (as we shall see). Even though we know nothing about the internal structure of an electron, however, it will be reasonable to assume the three components of \vec{S} obey the same commutation relations as the three components of \vec{L} :

$$[S_j, S_k] = i\epsilon_{jkl}S_l. \quad (11)$$

In addition, because the spin-degree of freedom will involve only internal or intrinsic degrees of freedom of the electron, it will be natural to assume all components of \vec{S} commute with all components of \vec{L} . With this additional relation, the three components of \vec{J} , the total angular momentum, with

$$\vec{J} = \vec{L} + \vec{S}, \quad (12)$$

will also have the basic commutation relations of angular momentum

$$[J_j, J_k] = i\epsilon_{jkl}J_l. \quad (13)$$

Still other operators exist, which may not be at all the three components of an angular momentum, but have the same commutation relations. For example, the

three operators

$$\begin{aligned} M_1 &= \frac{1}{4}[(p_x^2 + x^2) - (p_y^2 + y^2)], \\ M_2 &= \frac{1}{2}(p_x p_y + xy), \\ M_3 &= \frac{1}{2}(xp_y - yp_x), \end{aligned} \quad (14)$$

where x and p_x are dimensionless coordinate and momenta, with x and y measured in appropriate length units, such that $[p_j, x_k] = -i\delta_{jk}$. From these commutation relations, it follows that

$$[M_j, M_k] = i\epsilon_{jkl}M_l. \quad (15)$$

Because we shall prove the eigenvalues of M_3 (like those of S_z , or J_z) can only be either integers or $\frac{1}{2}$ -integers, and because $M_3 = \frac{1}{2}L_z$, we now have the proof that the orbital angular momentum quantum number m must be an integer. (It cannot be a $\frac{1}{2}$ -integer, as the corresponding m quantum number of an arbitrary “spin.”) The operators M_j of eq. (14), which are single-particle operators, can be generalized to operators for a many-body system by summing over N particle indices, e.g.,

$$M_3 = \frac{1}{2} \sum_{n=1}^{n=N} \left(x_n p_{y_n} - y_n p_{x_n} \right). \quad (16)$$

Thus, the result can be generalized to the m quantum number of an N -body system.

C General Angular Momenta

Let us consider the generic operators J_x , J_y , J_z . Again, we define

$$J_{\pm} = (J_x \pm i J_y), \quad J_0 = J_z. \quad (17)$$

The commutation relations translate to

$$[J_0, J_+] = +J_+, \quad [J_0, J_-] = -J_-, \quad [J_+, J_-] = 2J_0. \quad (18)$$

It will be useful to rewrite \vec{J}^2 in various ways

$$\begin{aligned} \vec{J}^2 &= \frac{1}{2}(J_x + i J_y)(J_x - i J_y) + \frac{1}{2}(J_x - i J_y)(J_x + i J_y) + J_z^2 \\ &= \frac{1}{2}(J_+ J_- + J_- J_+) + J_0^2 \\ &= J_- J_+ + J_0^2 + J_0 \\ &= J_+ J_- + J_0^2 - J_0, \end{aligned} \quad (19)$$

where we have used $[J_+, J_-] = 2J_0$ to write the operator in two basic forms. Now, let us assume $|\lambda m\rangle$ is simultaneously an eigenvector of \vec{J}^2 and J_0 , with eigenvalues λ and m , respectively, where these are (so far) arbitrary real numbers:

$$\vec{J}^2 |\lambda m\rangle = \lambda |\lambda m\rangle,$$

$$J_0|\lambda m\rangle = m|\lambda m\rangle. \quad (20)$$

Acting on these two equations from the left with the operator J_+ and using the commutation relations, $[J_+, \vec{J}^2] = 0$ and $[J_+, J_0] = -J_+$, we get

$$\begin{aligned} \vec{J}^2\left(J_+|\lambda m\rangle\right) &= \lambda\left(J_+|\lambda m\rangle\right), \\ J_0\left(J_+|\lambda m\rangle\right) &= (m+1)\left(J_+|\lambda m\rangle\right). \end{aligned} \quad (21)$$

Similarly, acting on both equations from the left with J_- , we get

$$\begin{aligned} \vec{J}^2\left(J_-|\lambda m\rangle\right) &= \lambda\left(J_-|\lambda m\rangle\right), \\ J_0\left(J_-|\lambda m\rangle\right) &= (m-1)\left(J_-|\lambda m\rangle\right). \end{aligned} \quad (22)$$

Thus, if $|\lambda m\rangle$ is an eigenvector of \vec{J}^2 and J_0 with eigenvalues λ and m , two possibilities exist. Either $(J_+|\lambda m\rangle)$ is an eigenvector of \vec{J}^2 and J_0 , with eigenvalues λ and $(m+1)$, or $J_+|\lambda m\rangle = 0$. Similarly, either $(J_-|\lambda m\rangle)$ is an eigenvector of \vec{J}^2 and J_0 , with eigenvalues λ and $(m-1)$, or $J_-|\lambda m\rangle = 0$.

Let us assume the first possibility for the operator J_+ . Using eq. (19), let us evaluate the diagonal matrix element of $J_- J_+$ for the eigenstate $|\lambda m\rangle$

$$\begin{aligned} \langle\lambda m|J_- J_+|\lambda m\rangle &= \langle\lambda m|(\vec{J}^2 - J_0^2 - J_0)|\lambda m\rangle = [\lambda - m(m+1)]\langle\lambda m|\lambda m\rangle \\ &= \sum_{\lambda',m'} \langle\lambda m|J_-|\lambda' m'\rangle \langle\lambda' m'|J_+|\lambda m\rangle \\ &= \sum_{\lambda',m'} \langle\lambda' m'|J_+^\dagger|\lambda m\rangle^* \langle\lambda' m'|J_+|\lambda m\rangle = \sum_{\lambda',m'} |\langle\lambda' m'|J_+|\lambda m\rangle|^2 \\ &= [\lambda - m(m+1)]. \end{aligned} \quad (23)$$

The state $J_+|\lambda m\rangle$ can exist if $\lambda > m(m+1)$. In that case, we could act with J_+ to make the new state with $(m+1)$ and calculate the diagonal matrix element in the state $|\lambda(m+1)\rangle$. Moreover, we could repeat this process to ladder our way up to a state with $(m+n)$, but the same λ , so

$$\sum_{\lambda',m'} |\langle\lambda' m'|J_+|\lambda(m+n)\rangle|^2 = [\lambda - (m+n)(m+n+1)]. \quad (24)$$

An integer n will then be large enough that the negative quantity $-(m+n)(m+n+1)$ will overwhelm the positive λ , and we will have a patently positive quantity on the left-hand side of the equation equal to a negative quantity on the right. Therefore, the assumption that $\langle\lambda m|\lambda m\rangle = 1$ for the starting value of m must have been wrong. If the starting value of m is such that the ladder process has an upper bound, however, we must come to a maximum value of m , such that $(m+n) = m_{\max}$, with

$$J_+|\lambda m_{\max}\rangle = 0, \quad (25)$$

and, hence,

$$\lambda = m_{\max}(m_{\max} + 1). \quad (26)$$

Similarly, using the last form of eq. (19), $J_+ J_- = (\vec{J}^2 - J_0^2 + J_0)$, we arrive in the same way at the result

$$\langle \lambda m | J_+ J_- | \lambda m \rangle = \sum_{\lambda'' m''} |\langle \lambda'' m'' | J_- | \lambda m \rangle|^2 = [\lambda - m(m-1)]. \quad (27)$$

Now, we can repeat the step-down process and step-down m until it would become such a large negative number, so the negative quantity $-m(m-1) = -|m|(|m|+1)$ would overwhelm the positive λ . Thus, again the step-down ladder must quit at a value $m = m_{\min}$ for which

$$J_- |\lambda m_{\min} \rangle = 0, \quad (28)$$

and

$$\lambda = m_{\min}(m_{\min} - 1). \quad (29)$$

Hence,

$$\lambda = m_{\max}(m_{\max} + 1) = m_{\min}(m_{\min} - 1), \quad (30)$$

leading to $m_{\min.} = +\frac{1}{2} \pm \sqrt{(m_{\max.} + \frac{1}{2})^2}$, so $m_{\min.} = -m_{\max.}$. The other root, $m_{\min.} = (m_{\max.} + 1)$, is of course meaningless. Let us now name $m_{\max.} = j$. Because now $(m_{\max.} - m_{\min.}) = 2m_{\max.} = 2j = \text{integer}$, the quantum number j can only be an integer or a $\frac{1}{2}$ -integer; with

$$\lambda = j(j+1), \quad \text{where } m = +j, (j-1), \dots, -j. \quad (31)$$

In addition, because the operators J_{\pm} do not change the eigenvalue λ , the sums over λ' or λ'' in eqs. (24) and (27) collapse to the single value λ . Also, if the eigenvectors are such that the state $|\lambda m_{\max.}\rangle$ is nondegenerate, the state $\langle J_- | \lambda m_{\max.} \rangle$ will also be nondegenerate; similarly for states with even lower m values. Then, the sum over m' in eq. (23) and m'' in eq. (27) collapses to a single value. Thus, replacing the label λ with the quantum number j ,

$$|\langle j(m+1) | J_+ | jm \rangle|^2 = [j(j+1) - m(m+1)], \quad (32)$$

$$|\langle j(m-1) | J_- | jm \rangle|^2 = [j(j+1) - m(m-1)]. \quad (33)$$

Choosing the matrix elements themselves to be real, we get

$$\langle j(m+1) | J_+ | jm \rangle = \sqrt{(j-m)(j+m+1)}, \quad (34)$$

$$\langle j(m-1) | J_- | jm \rangle = \sqrt{(j+m)(j-m+1)}, \quad (35)$$

and, with $J_x = \frac{1}{2}(J_+ + J_-)$, $J_y = \frac{i}{2}(J_- - J_+)$,

$$\begin{aligned} \langle jm' | J_x | jm \rangle &= \frac{1}{2}(\delta_{m'(m+1)}\sqrt{(j-m)(j+m+1)} + \delta_{m'(m-1)}\sqrt{(j+m)(j-m+1)}), \\ \langle jm' | J_y | jm \rangle &= \frac{1}{2}(-i\delta_{m'(m+1)}\sqrt{(j-m)(j+m+1)} + i\delta_{m'(m-1)}\sqrt{(j+m)(j-m+1)}), \\ \langle jm | J_z | jm \rangle &= m. \end{aligned} \quad (36)$$

For $j = \frac{1}{2}$, these matrices are very simple 2×2 matrices with rows and columns labeled by $m = +\frac{1}{2}, m = -\frac{1}{2}$, in that order. It is convenient to factor out the factor $\frac{1}{2}$, and to define the operator $\vec{\sigma}$, via

$$\vec{J} = \frac{1}{2} \vec{\sigma}, \quad (37)$$

where the matrices have the simple form

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (38)$$

These equations are the famous Pauli spin-matrices. They satisfy

$$\sigma_j \sigma_k = i \epsilon_{j k \alpha} \sigma_\alpha + \delta_{jk}. \quad (39)$$

As a final small exercise, let us calculate ΔJ_x for an angular momentum system is in a definite angular momentum eigenstate $|jm\rangle$. We note

$$\langle jm|J_x|jm\rangle = 0, \quad (40)$$

so the expectation value of this perpendicular component of \vec{J} is zero in the eigenstate with definite value of J_z . Also,

$$\begin{aligned} \langle jm|J_x^2|jm\rangle &= \sum_{m'=(m\pm 1)} \langle jm|J_x|jm'\rangle \langle jm'|J_x|jm\rangle \\ &= \sum_{m'=(m\pm 1)} |\langle jm'|J_x|jm\rangle|^2 \\ &= \frac{1}{4} ([j(j+1) - m(m+1)] + [j(j+1) - m(m-1)]) \\ &= \frac{1}{2} [j(j+1) - m^2]. \end{aligned} \quad (41)$$

Furthermore, the diagonal matrix elements of J_y and J_y^2 have the same values as those for the x component. Thus, converting now to physical components with angular momentum in units of \hbar ,

$$\Delta J_x = \Delta J_y = \hbar \sqrt{\frac{j(j+1) - m^2}{2}}, \quad (42)$$

in the state $|jm\rangle$ for which J_z has the precise value $\hbar m$, so $\Delta J_z = 0$. This is illustrated with the semiclassical vector model in which the vector \vec{J} , now of length $\hbar\sqrt{j(j+1)}$, is pictured to precess about its z-component with precise value $\hbar m$, which is less than $\hbar\sqrt{j(j+1)}$ even in the state with $m = j$. Also, for $j = \frac{1}{2}, m = \pm\frac{1}{2}$, we have $\Delta J_x = \Delta J_y = \frac{1}{2}\hbar$, the minimum quantum-mechanical uncertainty.

Final Remark: With our choice of phase for eqs. (34) and (35), we have made the matrix elements of J_y pure imaginary, and the matrix elements for J_x real. This is the standard angular momentum phase convention. All three components, however, are of course equivalent. We could, e.g., have used a basis in which J_x is diagonal, J_y real and off-diagonal, and J_z pure imaginary and off-diagonal.

15

Rigid Rotators: Molecular Rotational Spectra

A The Diatomic Molecule Rigid Rotator

For a rotating molecule the angular momentum, associated with the rotation of this “nearly rigid” body can be expressed in terms of Euler angles and their partial derivatives. Hence, this may be a good first example. Consider the simplest case: a diatomic molecule, e.g., the HCl molecule with one hydrogen and one Chlorine nucleus and $1 + 17$ electrons. The full 20-body problem is extremely complicated, but at very low energies no excitations associated with the electron degrees of freedom will come into play. The electron cloud binds the two atomic nuclei into a nearly rigid structure. The position of the diatomic molecule in 3-D space can be described by a radial coordinate, r , giving the distance between the H and Cl nuclei, and two angles, θ , and ϕ , giving the orientation in space of the molecule axis, or H–Cl line. The wave function can be written as $\psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi)$. The electron cloud gives rise to a potential, $V(r)$, with a deep (nearly parabolic) well with a minimum at $r = r_e$, where this is the equilibrium distance between the two atomic nuclei. The radial problem is associated with the vibrational motion of the molecule, a nearly harmonic oscillator motion to good first approximation. The energy associated with this vibration, $\hbar\omega_0$, is approximately 30 times that associated with the lower rotational excitations. Thus, at sufficiently low energies, we can replace the radial coordinate with its constant equilibrium value, r_e , and the Hamiltonian collapses to

$$H = -\frac{\hbar^2}{2I_e} \left(\frac{\partial^2}{\partial\theta^2} + \cot\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right) = \frac{\hbar^2}{2\mu r_e^2} \vec{L}^2, \quad (1)$$

with corresponding Schrödinger equation

$$\frac{\hbar^2}{2\mu r_e^2} \vec{L}^2 Y_{lm}(\theta, \phi) = E Y_{lm}(\theta, \phi) = \frac{\hbar^2}{2\mu r_e^2} l(l+1) Y_{lm}(\theta, \phi). \quad (2)$$

Here, μ is the H-Cl reduced mass, and I_e is the moment of inertia about an axis perpendicular to the molecular axis, through the center of mass of the system. The energies are

$$E_l = \frac{\hbar^2}{2\mu r_e^2} l(l+1). \quad (3)$$

The eigenfunctions are the standard spherical harmonics. Each level is $(2l+1)$ -fold degenerate, because the energy does not depend on m .

B The Polyatomic Molecule Rigid Rotator

For a polyatomic molecule, such as H_2O , with an isosceles triangle equilibrium structure, the rotational Hamiltonian is more complicated. We now need three Euler angles to specify the orientation in space of the nearly rigid molecule: two angles, θ and ϕ , to give the direction of the triangle's symmetry axis, and a third angle, χ , to describe the "spinning" of the two H atoms about this symmetry axis. Again, assuming the energies to be considered are so low vibrational excitations can be neglected, we can replace the coordinates of the atomic nuclei by their (constant) equilibrium values and are led to the rigid rotator Hamiltonian

$$H = \frac{1}{2A} P_{x'}^2 + \frac{1}{2B} P_y^2 + \frac{1}{2C} P_{z'}^2, \quad (4)$$

where $P_{z'}$ is the component of the rotational angular momentum vector along the z' , body-fixed principal axis, the H_2O symmetry axis; similarly, the x' and y' axes can be taken as the remaining principal axes, one perpendicular to the plane of the triangle, the other lying in the triangle plane, all going through the center of mass of the molecule. The constants A, B, C are the three principal moments of inertia in the equilibrium configuration: $I_{xx} = A, I_{yy} = B, I_{zz} = C$. The principal or primed axes components of the rotational angular momentum vector, \vec{P} , must be translated to operator form to write the above Hamiltonian in quantum-mechanical form. Using the techniques of problem 5, these components are [converting from the physical angular momentum components of eq. (4) to dimensionless ones, e.g., $(P_{z'})_{\text{phys.}} = \hbar P_{z'}$],

$$\begin{aligned} P_{x'} &= \frac{1}{i} \left(\frac{\sin \chi}{\sin \theta} \frac{\partial}{\partial \phi} + \cos \chi \frac{\partial}{\partial \theta} - \sin \chi \cot \theta \frac{\partial}{\partial \chi} \right), \\ P_{y'} &= \frac{1}{i} \left(\frac{\cos \chi}{\sin \theta} \frac{\partial}{\partial \phi} - \sin \chi \frac{\partial}{\partial \theta} - \cos \chi \cot \theta \frac{\partial}{\partial \chi} \right), \\ P_{z'} &= \frac{1}{i} \frac{\partial}{\partial \chi}, \end{aligned} \quad (5)$$

with

$$\vec{P}^2 = -\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\left[\frac{\partial^2}{\partial\phi^2} - 2\cos\theta\frac{\partial^2}{\partial\phi\partial\chi} + \cos^2\theta\frac{\partial^2}{\partial\chi^2}\right] + \frac{\partial^2}{\partial\chi^2}\right). \quad (6)$$

We can of course also write the space-fixed, x , y , and z components of the rotational angular momentum in this operator form. The component of greatest interest to us is the space-fixed z -component

$$P_z = \frac{1}{i}\frac{\partial}{\partial\phi}. \quad (7)$$

The three operators P_z , $P_{z'}$, and \vec{P}^2 , form a set of three commuting operators. In addition, straightforward calculation gives the commutator algebra of the three body-fixed or principal axis components of the rotational angular momentum operator

$$[P_{x'}, P_y] = -iP_{z'}, \quad [P_{y'}, P_z] = -iP_{x'}, \quad [P_{z'}, P_{x'}] = -iP_{y'}. \quad (8)$$

Note the minus signs! These signs are the complex conjugates of the standard angular momentum commutators. If we had taken the space-fixed components P_x , P_y , and P_z , we would have been led to the standard angular momentum commutator algebra. In translating the standard results to their complex conjugates (needed for the primed components), we must merely interchange P'_+ and P'_- , where now

$$P'_+ = (P_{x'} + iP_{y'}), \quad P'_- = (P_{x'} - iP_{y'}). \quad (9)$$

Now

$$[P_{z'}, P'_+] = -P'_-, \quad [P_{z'}, P'_-] = +P'_+. \quad (10)$$

(Note the difference in sign compared with the standard angular momentum algebra!) Also, now, the simultaneous eigenvectors of the three commuting operators, P_z , $P_{z'}$, and \vec{P}^2 , will yield a complete basis of the subspace of our Hilbert space, corresponding to the three rotational degrees of freedom. (We need three quantum numbers, and three commuting, hermitian operators.) The needed eigenvector equations are

$$\begin{aligned} \vec{P}^2|JMK\rangle &= \lambda|JMK\rangle = J(J+1)|JMK\rangle, \\ P_z|JMK\rangle &= M|JMK\rangle, \\ P_{z'}|JMK\rangle &= K|JMK\rangle, \end{aligned} \quad (11)$$

where the commutator algebra of the unprimed angular momentum components leads to $M_{\max} = -M_{\min} = J$, and the commutator algebra of the primed angular momentum components leads to $K_{\max} = -K_{\min} = J$, where $\lambda = J(J+1)$. Because we are dealing with orbital degrees of freedom of a many-body system, the quantum numbers, J , M , K must all be integers, with $M = J, (J-1), \dots, -J$, and, similarly, $K = J, (J-1), \dots, -J$. (We use capital letters for the J , M , K quantum numbers according to the usual convention by which capital letters are used for many-body systems.)

We will now write the rigid rotator Hamiltonian for the asymmetric top with $A \neq B \neq C$ (valid for the H_2O molecule), by first introducing the energy constants

$$a = \frac{\hbar^2}{2A}, \quad b = \frac{\hbar^2}{2B}, \quad c = \frac{\hbar^2}{2C}. \quad (12)$$

$$\begin{aligned} H = aP_{x'}^2 + bP_{y'}^2 + cP_{z'}^2 &= \frac{1}{2}(a+b)(P_{x'}^2 + P_{y'}^2) + \frac{1}{2}(a-b)(P_{x'}^2 - P_{y'}^2) + cP_{z'}^2 \\ &= \frac{1}{2}(a+b)(\vec{P}^2 - P_z^2) + \frac{1}{4}(a-b)(P'_+P'_+ + P'_-P'_-) + cP_z^2. \end{aligned} \quad (13)$$

In the $|JMK\rangle$ basis, the nonzero matrix elements of the primed components of \vec{P} are

$$\begin{aligned} \langle JM(K+1)|P'_-|JMK\rangle &= \sqrt{(J-K)(J+K+1)}, \\ \langle JM(K-1)|P'_+|JMK\rangle &= \sqrt{(J+K)(J-K+1)}, \\ \langle JMK|P'_{z'}|JMK\rangle &= K. \end{aligned} \quad (14)$$

(P'_- is now a K step-up operator, and P'_+ is a K step-down operator. This results because the commutation relations of the primed components of the rotational angular-momentum operators are the complex conjugates of the standard ones.) The Hamiltonian is not diagonal in the $|JMK\rangle$ basis. In this basis, the diagonal matrix elements of the Hamiltonian are

$$\langle JMK|H|JMK\rangle = \frac{1}{2}(a+b)(J(J+1) - K^2) + cK^2. \quad (15)$$

With $a \neq b$, off-diagonal terms exist. For the special case of a symmetric rotator, with $a = b$, however, these terms vanish, and the $|JMK\rangle$ are eigenstates of this symmetric rotator. The rotational energies are

$$E_{JK} = \frac{1}{2}(a+b)(J(J+1) - K^2) + cK^2. \quad (16)$$

For the asymmetric rotator, with $a \neq b$, we need the matrix elements

$$\begin{aligned} \langle JMK'|P'_-P'_-|JMK\rangle &= \delta_{K'(K+2)}\sqrt{(J-K)(J-K-1)(J+K+1)(J+K+2)}, \\ \langle JMK'|P'_+P'_+|JMK\rangle &= \delta_{K'(K-2)}\sqrt{(J+K)(J+K-1)(J-K+1)(J-K+2)}. \end{aligned} \quad (17)$$

When multiplied by $(a-b)/4$, these give the nonzero off-diagonal matrix elements. To get the energy eigenvectors, we now need to make a transformation from the $|JMK\rangle$ basis to a basis of the type $|JME_\alpha\rangle$, where these base vectors are simultaneously eigenvectors of the three commuting operators, \vec{P}^2 , P_z , and H , with

$$\begin{aligned} \vec{P}^2|JME_\alpha\rangle &= J(J+1)|JME_\alpha\rangle, \\ P_z|JME_\alpha\rangle &= M|JME_\alpha\rangle, \\ H|JME_\alpha\rangle &= E_\alpha|JME_\alpha\rangle, \end{aligned} \quad (18)$$

where α is a label that simply orders the energy eigenvalues for a particular $J M$. To find the energy eigenvalues and eigenvectors, we need to make a transformation from the $|JMK\rangle$ basis to the $|JME_\alpha\rangle$ basis:

$$|JME_\alpha\rangle = \sum_{K=-J}^{K=+J} |JMK\rangle \langle JMK|JME_\alpha\rangle = \sum_{K=-J}^{K=+J} c_K(E_\alpha) |JMK\rangle. \quad (19)$$

If we substitute this linear combination of the $|JMK\rangle$ into the energy eigenequation

$$H|JME_\alpha\rangle = E_\alpha|JME_\alpha\rangle, \quad (20)$$

we get

$$\sum_K H|JMK\rangle \langle JMK|JME_\alpha\rangle = E_\alpha|JME_\alpha\rangle. \quad (21)$$

Taking the scalar product of this with a particular $\langle JMK'|$, i.e., with left-multiplication by the bra for a particular value of K' , we get

$$\sum_K \langle JMK'|H|JMK\rangle \langle JMK|JME_\alpha\rangle = E_\alpha \langle JMK'|JME_\alpha\rangle. \quad (22)$$

If we use the shorthand notation

$$\langle JMK'|H|JMK\rangle = H_{K'K}, \quad c_K = \langle JMK|JME_\alpha\rangle, \quad (23)$$

the above equation can be written as

$$\sum_K H_{K'K} c_K = E_\alpha c_{K'}, \quad \text{or} \quad \sum_K (H_{K'K} - E_\alpha \delta_{K'K}) c_K = 0. \quad (24)$$

The H submatrix for a particular J , and some fixed M , has been abbreviated by its matrix elements $H_{K'K}$, where the common quantum numbers, J and M , have been suppressed. [From eqs. (15) and (17), these matrix elements are functions only of J and K and are completely independent of M .] Eq. (24) is a set of $(2J + 1)$ linear equations in the unknown coefficients, c_K , with $K' = +J, +(J - 1), \dots, -J$. These linear equations have solutions for the c_K if/only if the determinant of the coefficients is zero:

$$\det|H_{K'K} - E_\alpha \delta_{K'K}| = 0. \quad (25)$$

This determinantal relation leads to a polynomial in the unknown E_α of degree $(2J + 1)$, which must be set equal to zero, leading to $(2J + 1)$ roots E_α , with $\alpha = 1, 2, \dots, (2J + 1)$.

For example, for $J = 1$, the linear equations are

$$\begin{aligned} (H_{+1+1} - E)c_{+1} + H_{+10}c_0 + H_{+1-1}c_{-1} &= 0, \\ H_{0+1}c_{+1} + (H_{00} - E)c_0 + H_{0-1}c_{-1} &= 0, \\ H_{-1+1}c_{+1} + H_{-10}c_0 + (H_{-1-1} - E)c_{-1} &= 0, \end{aligned} \quad (26)$$

with the determinantal relation

$$\begin{vmatrix} (H_{+1+1} - E) & H_{+10} & H_{+1-1}, \\ H_{0+1} & (H_{00} - E) & H_{0-1}, \\ H_{-1+1} & H_{-10} & (H_{-1-1} - E) \end{vmatrix} = 0.$$

The Hamiltonian matrix for $J = 1$ follows from eqs. (15) and (17). The $J = 1$ matrix is

$$\langle JMK'|(H - E)|JMK\rangle =$$

	$K = +1$	$K = 0$	$K = -1$
$K = +1$	$\left(\frac{a+b}{2} + c - E\right)$	0	$\frac{a-b}{2}$
$K = 0$	0	$(a + b - E)$	0
$K = -1$	$\frac{a-b}{2}$	0	$\left(\frac{a+b}{2} + c - E\right)$

where it would have been advantageous to rearrange the columns and rows (taking first all even K values, followed by all odd K values), because the matrix elements of H are nonzero only for $\Delta K = \pm 2$. The determinant of the $(H - E)$ matrix will then always factor into two subdeterminants. For $J = 1$, the determinantal relation leads to the requirement

$$\left[(a + b - E)\right] \left[\left(\frac{a+b}{2} + c - E\right)^2 - \left(\frac{a-b}{2}\right)^2\right] = 0, \quad (27)$$

with the three roots

$$\begin{aligned} E_1 &= (a + b), \\ E_2 &= \left(\frac{a+b}{2} + c\right) + \left(\frac{a-b}{2}\right) = (a + c), \\ E_3 &= \left(\frac{a+b}{2} + c\right) - \left(\frac{a-b}{2}\right) = (b + c). \end{aligned} \quad (28)$$

For $E = E_1 = (a + b)$, the allowed c 's are given by $c_{+1} = c_{-1} = 0, c_0 = 1$. For $E = E_2$ or $E = E_3$, we must have $c_0 = 0$, and the remaining c 's follow from the equations

$$\begin{aligned} \left(\frac{a+b}{2} + c - E\right)c_{-1} + \left(\frac{a-b}{2}\right)c_{+1} &= 0 \\ \left(\frac{a-b}{2}\right)c_{-1} + \left(\frac{a+b}{2} + c - E\right)c_{+1} &= 0 \end{aligned} \quad (29)$$

For $E = E_2 = (a + c)$, these equations have the solution $c_{-1} = c_{+1} = \sqrt{\frac{1}{2}}$. Conversely, for $E = E_3 = (b + c)$, these equations lead to $-c_{-1} = c_{+1} = \sqrt{\frac{1}{2}}$. We have normalized the solutions such that $\sum_K |c_K|^2 = 1$.

Thus, the energy eigenvalues and eigenvectors of the asymmetric rotator, with $J = 1$ are

$$\begin{aligned} E_1 &= (a + b), & |J = 1 M E_1\rangle &= |J = 1 M K = 0\rangle, \\ \text{and for } & & & \\ E_2 &= (a + c), & \text{and } E_3 &= (b + c), \\ |J = 1 M E_2\rangle &= \frac{1}{\sqrt{2}}(|J = 1 M K = +1\rangle + |J = 1 M K = -1\rangle), \\ |J = 1 M E_3\rangle &= \frac{1}{\sqrt{2}}(|J = 1 M K = +1\rangle - |J = 1 M K = -1\rangle). \end{aligned} \quad (30)$$

For arbitrary J , we are led to a $(2J + 1) \times (2J + 1)$ determinantal problem. The $(2J + 1)$ roots of eq. (24) will give us the eigenvalues E_α and the eigenvectors for arbitrary J . The energies are independent of M . All states are therefore still $(2J + 1)$ -fold degenerate. This degeneracy can be lifted only by an external field. For the H_2O molecule, which has a permanent electric dipole moment directed along its symmetry axis, the degeneracy could be removed if the molecule is placed in an external electric field (Stark effect).

In condensed-matter physics, effective Hamiltonians of the type of eq. (13) are often useful. These may be functions, e.g., of the spin operators of an impurity ion and have the general form

$$H = aS_x^2 + bS_y^2 + cS_z^2 + d(S_xS_y + S_yS_x) + e(S_xS_z + S_zS_x) + f(S_yS_z + S_zS_y). \quad (31)$$

The combinations, such as $(S_xS_y + S_yS_x)$, are hermitian. Problems of this type can be solved by the techniques illustrated in this section by the asymmetric rotator.

Problems

- 20.** Find the allowed energies for the $J = 2$ states of the asymmetric rigid rotator with Hamiltonian

$$H = aP_{x'}^2 + bP_{y'}^2 + cP_{z'}^2 = \frac{1}{2}(a+b)(\vec{P}^2 - P_{z'}^2) + \frac{1}{4}(a-b)(P'_+P'_+ + P'_-P'_-) + cP_{z'}^2$$

as functions of a, b, c . Find the eigenvectors of these states as linear combinations of the $|JMK\rangle$; i.e., find the coefficients, c_K , for the allowed $J = 2$ states in the expansions

$$|JME_\alpha\rangle = \sum_K c_K^{(\alpha)} |JMK\rangle.$$

- 21.** For the asymmetric rigid rotator of problem 20, show from the symmetry of the Hamiltonian, H , the eigenvectors split into four classes of the form

$$|JME_\alpha\rangle_{\pm,e(o)} = \sum_K \frac{1}{\sqrt{2}} (|JMK\rangle \pm |JM-K\rangle),$$

where the $e(o)$ states involve a sum over even or odd K values only. Using this $e+, e-, o+, o-$ basis, show the 7×7 matrix of the Hamiltonian matrix for $J = 3$ factors into three 2×2 submatrices and one 1×1 submatrix, and find the allowed energies for $J = 3$ as functions of a, b, c .

- 22.** An impurity ion with a spin, $S = \frac{3}{2}$, is imbedded in a magnetic crystal and is subject to the local effective Hamiltonian

$$H = a(S_xS_y + S_yS_x) + bS_z^2,$$

where S_x, S_y, S_z are the three components of the spin operator and a and b are constants. Find the Hamiltonian matrix in the basis, $|SM_S\rangle$, where M_S is the eigenvalue of S_z . Find the energy eigenvalues, E_α , and the energy eigenvectors as linear combinations of the $|SM_S\rangle$.

16

Transformation Theory

A General

In our example of the diagonalization of the asymmetric rotator Hamiltonian in the last chapter, we encountered a very special case of a very general problem in quantum theory, the transformation from one basis in Hilbert space to another. In our example, it was a transformation from the $|JMK\rangle$ basis to the $|JME_\alpha\rangle$ basis, involving two different complete sets of commuting operators to specify the two different bases. In our specific example of the $J = 1$ energy eigenstates, the transformation was a very simple one, in a 3-D subspace of the asymmetric rotator subspace of the full Hilbert space of our problem, and thus it involved a 3×3 transformation.

For a general state vector, $|\psi\rangle$, in the asymmetric rotator subspace of the Hilbert space of the polyatomic molecule system, we could use either the representation

$$|\psi\rangle = \sum_{JMK} |JMK\rangle \langle JMK| \psi \rangle \quad (1)$$

or the representation

$$|\psi\rangle = \sum_{JM\alpha} |JM\alpha\rangle \langle JM\alpha| \psi \rangle, \quad (2)$$

where we have used the abbreviation α for E_α , and

$$\langle JM\alpha| \psi \rangle = \sum_K \langle JM\alpha| JMK \rangle \langle JMK| \psi \rangle, \quad (3)$$

and

$$\langle JMK|\psi\rangle = \sum_{\alpha} \langle JMK|JM\alpha\rangle \langle JM\alpha|\psi\rangle. \quad (4)$$

Here, eqs. (1) and (2) are the analogs in Hilbert space of the relations in ordinary n -dimensional vector space that give the specification of a vector \vec{V} in terms of the components along a set of axes defined by unit vectors \vec{e}_i , or in terms of components along a set of \vec{e}'_{α} , which are unit vectors along a set of rotated coordinate axes.

$$\vec{V} = \sum_k \vec{e}_k V_k, \quad (5)$$

$$\vec{V} = \sum_{\alpha} \vec{e}'_{\alpha} V'_{\alpha}, \quad (6)$$

with

$$V'_{\alpha} = \sum_k O_{\alpha k} V_k, \quad \text{where} \quad O_{\alpha k} = \vec{e}'_{\alpha} \cdot \vec{e}_k. \quad (7)$$

The inverse gives

$$V_k = \sum_{\alpha} (O^{-1})_{k\alpha} V'_{\alpha}, \quad \text{with} \quad (O^{-1})_{k\alpha} = O_{\alpha k}, \quad (8)$$

showing the orthogonal character of the transformation matrix, i.e., the $O_{\alpha k}$ satisfy the orthogonality relations

$$\sum_k O_{\alpha k} O_{\beta k} = \delta_{\alpha\beta}, \quad \sum_{\alpha} O_{\alpha k} O_{\alpha j} = \delta_{kj}. \quad (9)$$

Now, eqs. (3) and (4) are the analogs in Hilbert space of the ordinary vector relations, eqs. (7) and (8). If we name $\langle JM\alpha|\psi\rangle \equiv c'_{\alpha}$ and $\langle JMK|\psi\rangle \equiv c_K$,

$$\begin{aligned} c'_{\alpha} &= \sum_K \langle JM\alpha|JMK\rangle c_K = \sum_K U_{\alpha K} c_K, \\ c_K &= \sum_{\alpha} \langle JMK|JM\alpha\rangle c'_{\alpha} = \sum_{\alpha} (U^{-1})_{K\alpha} c'_{\alpha}, \end{aligned} \quad (10)$$

where now

$$(U^{-1})_{K\alpha} = \langle JMK|JM\alpha\rangle = \langle JM\alpha|JMK\rangle^* = U_{\alpha K}^*. \quad (11)$$

That is, the transformation is now unitary, rather than just orthogonal. The U matrix elements satisfy the unitary conditions

$$\sum_K U_{\alpha K} U_{\beta K}^* = \delta_{\alpha\beta}, \quad \sum_{\alpha} U_{\alpha K} U_{\alpha K'}^* = \delta_{KK'}. \quad (12)$$

Now, the inverse matrix is the complex conjugate of the transposed matrix. We can also think of the U , not as a matrix, but as an operator, where

$$U = \sum_{\alpha, K} |JM\alpha\rangle \langle JM\alpha|JMK\rangle \langle JMK|. \quad (13)$$

That is, U is the operator converting a $|JMK\rangle$ into a $|JM\alpha\rangle$ and multiplying it by the complex number $U_{\alpha K}$. Similarly,

$$U^{-1} = \sum_{K,\alpha} |JMK\rangle\langle JMK| |JM\alpha\rangle\langle JM\alpha|, \quad (14)$$

where now

$$U^{-1} = U^\dagger. \quad (15)$$

For the very specific case of the $J = 1$ states of the asymmetric rotator, using the ordering of energies of eqs. (28)–(30) of Chapter 15 for the index α , we have

$$U = \langle \alpha | K \rangle = \begin{matrix} & \begin{matrix} K = +1 & K = 0 & K = -1 \end{matrix} \\ \begin{matrix} \alpha = 1 \\ \alpha = 2 \\ \alpha = 3 \end{matrix} & \left(\begin{array}{ccc} 0 & 1 & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{array} \right) \end{matrix}$$

and

$$U^\dagger = \langle K | \alpha \rangle = \begin{matrix} & \begin{matrix} \alpha = 1 & \alpha = 2 & \alpha = 3 \end{matrix} \\ \begin{matrix} K = +1 \\ K = 0 \\ K = -1 \end{matrix} & \left(\begin{array}{ccc} 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ 1 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{array} \right) \end{matrix}.$$

Combining this with the matrix, $H_{KK'}$ of Chapter 15, we can see by straightforward matrix multiplication that

$$\sum_{K,K'} \langle \alpha' | K' \rangle \langle K' | H | K \rangle \langle K | \alpha \rangle = \langle \alpha' | H | \alpha \rangle, \quad (16)$$

or, in matrix form,

$$\sum_{K,K'} U_{\alpha' K'} H_{K' K} (U^\dagger)_{K \alpha} = H_{\alpha' \alpha} = E_\alpha \delta_{\alpha' \alpha}. \quad (17)$$

B Note on Generators of Unitary Operators and the Transformation $UHU^\dagger = H'$

A unitary operator, U , can be generated by a hermitian operator, $G = G^\dagger$, by exponentiation

$$U = e^{i\epsilon G}, \quad (18)$$

where ϵ is a real finite number and the operator G is called the generator of the unitary transformation. To prove the unitary character of U , consider first an infinitesimal transformation, with $\epsilon = \epsilon_0 \ll 1$, so

$$U = 1 + i\epsilon_0 G, \quad U^\dagger = 1 - i\epsilon_0 G, \quad (19)$$

so

$$UU^\dagger = (1 + i\epsilon_0 G)(1 - i\epsilon_0 G) = 1 + \text{Order}(\epsilon_0^2) = 1. \quad (20)$$

To convert this to a transformation with a finite ϵ , write the exponential in the limiting form

$$\begin{aligned} e^{i\epsilon G} &= \lim_{N \rightarrow \infty} \left(1 + i\frac{\epsilon}{N}G\right)^N \\ &= \lim_{N \rightarrow \infty} \sum_k \frac{(i\epsilon)^k}{N^k} \frac{G^k}{k!} \frac{N!}{(N-k)!} = \sum_k \frac{(i\epsilon)^k}{k!} G^k. \end{aligned} \quad (21)$$

To prove the product of N factors $(1 + i\frac{\epsilon}{N}G)$ is unitary, we still need to show the product of two unitary operators is unitary

$$\begin{aligned} (U_1 U_2)^\dagger &= U_2^\dagger U_1^\dagger \\ &= (U_1 U_2)^{-1} = U_2^{-1} U_1^{-1} = U_2^\dagger U_1^\dagger \end{aligned} \quad (22)$$

if $U_1^{-1} = U_1^\dagger$ and $U_2^{-1} = U_2^\dagger$. Finally, it will be very useful to have a series expansion in powers of ϵ of the transformed Hamiltonian, $H' = UHU^\dagger$,

$$\begin{aligned} H' &= e^{i\epsilon G} H e^{-i\epsilon G} = \left(1 + i\epsilon G + \frac{(i\epsilon)^2}{2!} G^2 + \dots\right) H \left(1 - i\epsilon G + \frac{(-i\epsilon)^2}{2!} G^2 + \dots\right) \\ &= H + i\epsilon [G, H] + \frac{(i\epsilon)^2}{2!} [G, [G, H]] \\ &\quad + \dots + \frac{(i\epsilon)^n}{n!} [G, [G, [G, \dots [G, H]]]]_n + \dots \end{aligned} \quad (23)$$

where we have used $(G^2 H - 2GHG + HG^2) = [G, [G, H]]$ for the second term. The n^{th} term, involving n commutators, can be seen to follow from the $(n-1)^{\text{th}}$ term from the Taylor expansion in ϵ ,

$$f(\epsilon) = e^{i\epsilon G} H e^{-i\epsilon G} = \sum_n \frac{\epsilon^n}{n!} \left(\frac{d^n f(\epsilon)}{d\epsilon^n} \right)_{\epsilon=0}, \quad (24)$$

where

$$\frac{df(\epsilon)}{d\epsilon} = e^{i\epsilon G} i[G, H] e^{-i\epsilon G},$$

and with

$$\begin{aligned} \frac{d^{(n-1)} f(\epsilon)}{d\epsilon^{(n-1)}} &= e^{i\epsilon G} i^{n-1} [G, [G, \dots [G, H]]]_{n-1} e^{-i\epsilon G}, \\ \frac{d^n f(\epsilon)}{d\epsilon^n} &= iG \frac{d^{(n-1)} f(\epsilon)}{d\epsilon^{(n-1)}} - i \frac{d^{(n-1)} f(\epsilon)}{d\epsilon^{(n-1)}} G = i[G, \frac{d^{(n-1)} f(\epsilon)}{d\epsilon^{(n-1)}}]. \end{aligned} \quad (25)$$

This expansion in multiple commutators of G with H is particularly useful, if (1) the n^{th} commutator is zero for a relatively small n ; (2) if H and H' differ only by a small term (perturbation theory), so the infinite series can, in good approximation, be terminated after a few terms; or (3) if the n^{th} commutator is so simple the series can be summed.

Another Example: Successive Polarization Filters for Beams of Spin $s = \frac{1}{2}$ Particles

So far, our first example of a unitary transformation from one basis to another involved a finite-dimensional unitary submatrix. Let us consider one more example of this type, an even simpler example involving spin $s = \frac{1}{2}$ particles, hence, a 2×2 -dimensional transformation. Suppose we have a beam of spin $s = \frac{1}{2}$ particles. They can be prepared, so all are in a state of definite spin orientation, say, with $m_s = +\frac{1}{2}$, or with $m_s = -\frac{1}{2}$, along some specific z -direction in 3-D space by passing the beam through a polarization filter. The historically first such filter is that employed by Stern and Gerlach involving a set of three magnets, with nonuniform magnetic fields, placed in succession along the beam line, so a set of baffles can eliminate the particles with one of the two spin orientations. Other types of sophisticated polarization filters exist. (For a reference to modern polarization filters, see, e.g., *Polarized Beams and Polarized Gas Targets*, Hans Paetz gen. Schieck and Lutz Sydow, eds. World Scientific, 1996). We will assume the filter is perfect and prepares particles in a pure state of very definite m_s along a specific z -direction. Suppose the first such filter is followed with a second filter, identical to the first, but now with its new z' axis oriented along some new direction, given by polar and azimuth angles, θ and ϕ , relative to the original x , y , z axes, and set for some definite m'_s along the new direction. What fraction of the $s = \frac{1}{2}$ -particles will pass through the second filter?

The first filter prepares particles in eigenstates $|m = \pm \frac{1}{2}\rangle$, which are eigenstates of \vec{S}^2 and S_z :

$$\vec{S}^2 |\frac{1}{2}m\rangle = \frac{3}{4} |\frac{1}{2}m\rangle, \quad S_z |\frac{1}{2}m\rangle = m |\frac{1}{2}m\rangle. \quad (1)$$

The second filter passes particles in the eigenstates $|\alpha = \pm \frac{1}{2}\rangle$, which are eigenstates of \vec{S}^2 and $S_{z'}$:

$$\vec{S}^2 |\frac{1}{2}\alpha\rangle = \frac{3}{4} |\frac{1}{2}\alpha\rangle, \quad S_{z'} |\frac{1}{2}\alpha\rangle = \alpha |\frac{1}{2}\alpha\rangle. \quad (2)$$

The answer to our problem is as follows: The probability a particle in the beam with definite $|\frac{1}{2}m\rangle$ will pass through the second filter set to pass a specific $|\frac{1}{2}\alpha\rangle$ is

$$P(m, \alpha) = |\langle \frac{1}{2}\alpha | \frac{1}{2}m \rangle|^2, \quad (3)$$

so we need to calculate the transformation coefficient $\langle \frac{1}{2}\alpha | \frac{1}{2}m \rangle = U_{\alpha m}$. It will be advantageous to switch to the operator $\vec{\sigma}$, via $\vec{S} = \frac{1}{2}\vec{\sigma}$, and to omit the common s quantum number of $\frac{1}{2}$ in all equations. Here, $\vec{\sigma}$ is the Pauli spin operator, whose components $\sigma_x, \sigma_y, \sigma_z$ lead to the three Pauli spin matrices, we have already met through eq. (38) of Chapter 14. Thus,

$$\sigma_z |m\rangle = \lambda_m |m\rangle, \quad \sigma_z |\alpha\rangle = \lambda_\alpha |\alpha\rangle, \quad (4)$$

with $\lambda_m = \pm 1$ for states with $m = \pm \frac{1}{2}$, and $\lambda_\alpha = \pm 1$ for states with $\alpha = \pm \frac{1}{2}$. Now, we shall rewrite the relation $\sigma_z |\alpha\rangle = \lambda_\alpha |\alpha\rangle$ as

$$\sum_m \sigma_z |m\rangle \langle m | \alpha \rangle = \lambda_\alpha |\alpha\rangle. \quad (5)$$

Left-multiplying by a specific $\langle m'|$ leads to

$$\sum_m \langle m' | \sigma_z | m \rangle \langle m | \alpha \rangle = \lambda_\alpha \langle m' | \alpha \rangle. \quad (6)$$

Now we can express σ_z in terms of the original x, y, z components of $\vec{\sigma}$

$$\sigma_z' = \sin \theta \cos \phi \sigma_x + \sin \theta \sin \phi \sigma_y + \cos \theta \sigma_z, \quad (7)$$

and use the 2×2 matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ +i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} +1 & 0 \\ 0 & -1 \end{pmatrix},$$

to evaluate

$$\langle m' | \sigma_z' | m \rangle = \begin{pmatrix} \cos \theta & \sin \theta e^{-i\phi} \\ \sin \theta e^{i\phi} & -\cos \theta \end{pmatrix}.$$

Then, eq. (6) can be rewritten in matrix form, where we shall also use the shorthand notation $\langle m | \alpha \rangle = c_\pm$ for c_m with $m = \pm \frac{1}{2}$,

$$\begin{pmatrix} \cos \theta & \sin \theta e^{-i\phi} \\ \sin \theta e^{i\phi} & -\cos \theta \end{pmatrix} \begin{pmatrix} c_+ \\ c_- \end{pmatrix} = \lambda_\alpha \begin{pmatrix} c_+ \\ c_- \end{pmatrix},$$

leading to the two linear equations

$$\begin{aligned} (\cos \theta - \lambda_\alpha) c_+ + \sin \theta e^{-i\phi} c_- &= 0, \\ \sin \theta e^{i\phi} c_+ - (\cos \theta + \lambda_\alpha) c_- &= 0. \end{aligned} \quad (8)$$

For $\lambda_\alpha = +1$, these equations lead to

$$\frac{c_+}{c_-} = \frac{\sin \theta e^{-i\phi}}{(1 - \cos \theta)} = \frac{(1 + \cos \theta)}{\sin \theta e^{i\phi}} = \frac{\cos(\frac{\theta}{2})e^{-i\frac{\phi}{2}}}{\sin(\frac{\theta}{2})e^{+i\frac{\phi}{2}}}, \quad (9)$$

so, for $\lambda = +1$:

$$c_+ = \cos(\frac{\theta}{2})e^{-i\frac{\phi}{2}}, \quad c_- = \sin(\frac{\theta}{2})e^{+i\frac{\phi}{2}}, \quad (10)$$

where the undetermined normalization factor has been chosen, so $\sum_m |c_m|^2 = 1$. These two numbers give us the first column of the unitary 2×2 matrix $\langle m|\alpha\rangle$, with $\alpha = +\frac{1}{2}$. In the same way, putting $\lambda_\alpha = -1$, we get the second column of the $\langle m|\alpha\rangle$ matrix with $\alpha = -\frac{1}{2}$ to give

$$\langle m|\alpha\rangle = \begin{pmatrix} \cos(\frac{\theta}{2})e^{-i\frac{\phi}{2}} & -\sin(\frac{\theta}{2})e^{-i\frac{\phi}{2}} \\ \sin(\frac{\theta}{2})e^{i\frac{\phi}{2}} & \cos(\frac{\theta}{2})e^{i\frac{\phi}{2}} \end{pmatrix}.$$

In our notation, this is the matrix for U^\dagger , viz., $U_{m\alpha}^\dagger$. To obtain the matrix for U , $\langle \alpha|m\rangle = U_{\alpha m}$, we need to transpose and complex conjugate the above matrix to get

$$\langle \alpha|m\rangle = \begin{pmatrix} \cos(\frac{\theta}{2})e^{+i\frac{\phi}{2}} & \sin(\frac{\theta}{2})e^{-i\frac{\phi}{2}} \\ -\sin(\frac{\theta}{2})e^{i\frac{\phi}{2}} & \cos(\frac{\theta}{2})e^{-i\frac{\phi}{2}} \end{pmatrix}.$$

Finally, this U matrix can be written as

$$U = \begin{pmatrix} \cos \frac{\theta}{2} & \sin \frac{\theta}{2} \\ -\sin \frac{\theta}{2} & \cos \frac{\theta}{2} \end{pmatrix} \begin{pmatrix} e^{i\frac{\phi}{2}} & 0 \\ 0 & e^{-i\frac{\phi}{2}} \end{pmatrix} = e^{i\frac{\theta}{2}\sigma_x} e^{i\frac{\phi}{2}\sigma_z}.$$

The last operator form of this unitary transformation follows, for the z component, from

$$\mathbf{1} = \sigma_z^2 = \sigma_z^4 = \cdots = \sigma_z^{2n},$$

$$\sigma_z = \sigma_z^3 = \sigma_z^5 = \cdots = \sigma_z^{2n+1}, \quad (11)$$

and, for the y component, from the similar relation

$$\mathbf{1} = \sigma_y^2 = \sigma_y^4 = \cdots = \sigma_y^{2n},$$

$$\sigma_y = \sigma_y^3 = \sigma_y^5 = \cdots = \sigma_y^{2n+1}, \quad (12)$$

so

$$\begin{aligned} e^{i\frac{\theta}{2}\sigma_x} &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \left(1 - \left(\frac{\theta}{2}\right)^2 \frac{1}{2!} + \left(\frac{\theta}{2}\right)^4 \frac{1}{4!} + \cdots \right) \\ &\quad + i \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \left(\left(\frac{\theta}{2}\right) - \left(\frac{\theta}{2}\right)^3 \frac{1}{3!} + \left(\frac{\theta}{2}\right)^5 \frac{1}{5!} + \cdots \right). \end{aligned}$$

Finally, U^\dagger can be written in similar operator form as

$$U^\dagger = e^{-i\frac{\phi}{2}\sigma_z} e^{-i\frac{\theta}{2}\sigma_x}. \quad (13)$$

Also, note the appearance of the half-angles, associated with the $s = \frac{1}{2}$ character of the particles. Thus, e.g., if both polarization filters are set for the spin-projection $m = +\frac{1}{2}$, the fraction of the incoming particles that will pass through the second filter is

$$P(m = +\frac{1}{2}, \alpha = +\frac{1}{2}) = \cos^2(\frac{\theta}{2}). \quad (14)$$

18

Transformation Theory for Systems with Continuous Spectra

So far, we have studied transformations from one basis to another only for basis vectors that are the eigenvectors of a set of commuting hermitian operators whose spectra are discrete. Moreover, we have studied finite-dimensional subspaces of these vector spaces, so our unitary transformation matrices were finite-dimensional. Commuting operators, however, such as the operators x , y , z or the operators p_x , p_y , p_z exist with continuous spectra. Still other operators have both discrete and continuous spectra. We need to study the transformation theory for the base vectors of this type. In particular, the coordinate and momentum representations are of great importance.

In the coordinate representation, we project state vectors $|\psi\rangle$ onto the base vectors $|\vec{r}_0\rangle$ that are simultaneous eigenvectors of the three operators x , y , z ,

$$x|\vec{r}_0\rangle = x_0|\vec{r}_0\rangle, \quad y|\vec{r}_0\rangle = y_0|\vec{r}_0\rangle, \quad z|\vec{r}_0\rangle = z_0|\vec{r}_0\rangle. \quad (1)$$

The spectrum is continuous, so the orthogonality relation is given by a Dirac delta function

$$\langle\vec{r}'_0|\vec{r}_0\rangle = \delta(\vec{r}'_0 - \vec{r}_0), \quad (2)$$

and the completeness condition is given by the closure relation

$$\int d\vec{r}_0 |\vec{r}_0\rangle \langle\vec{r}_0| = 1, \quad (3)$$

so

$$|\psi\rangle = \int d\vec{r}_0 |\vec{r}_0\rangle \langle\vec{r}_0|\psi\rangle, \quad (4)$$

and

$$O|\psi\rangle = \int \int d\vec{r}'_0 d\vec{r}_0 |\vec{r}'_0\rangle \langle \vec{r}'_0| O |\vec{r}_0\rangle \langle \vec{r}_0| \psi\rangle. \quad (5)$$

Now, if the operator, O , is a function of the coordinate operators x, y, z , only,

$$\text{with } O = F(x, y, z), \quad \langle \vec{r}'_0 | O | \vec{r}_0 \rangle = F(x_0, y_0, z_0) \delta(\vec{r}'_0 - \vec{r}_0), \quad (6)$$

so

$$\langle \psi_1 | O | \psi_2 \rangle = \int d\vec{r}_0 \psi_1^*(\vec{r}_0) F(x_0, y_0, z_0) \psi_2(\vec{r}_0). \quad (7)$$

If, on the other hand, an operator, O , is a function of the momentum operators p_x, p_y, p_z , it will be useful to transform to the momentum representation, with base vectors that are the eigenvectors of the momentum operators

$$p_x |\vec{p}_0\rangle = p_{x_0} |\vec{p}_0\rangle, \quad p_y |\vec{p}_0\rangle = p_{y_0} |\vec{p}_0\rangle, \quad p_z |\vec{p}_0\rangle = p_{z_0} |\vec{p}_0\rangle. \quad (8)$$

We shall be particularly interested in the unitary transformation matrix $\langle \vec{p}_0 | \vec{r}_0 \rangle$. We could, of course, use Fourier integral analysis, from which we know the result. Let us, however, rederive this transformation matrix to learn how to deal with base vectors with continuous spectra. It will, in particular, be useful to introduce a unitary operator, the translation operator, which will serve our purpose.

A The Translation Operator

Consider the operator

$$U = e^{-\frac{i}{\hbar} \vec{c} \cdot \vec{p}} = U(\vec{c}), \quad (9)$$

where $\vec{c} = (c_1, c_2, c_3)$ and the c_j are ordinary numbers, so-called “c-numbers,” the components of \vec{p} are operators. We then have the commutator relations

$$[x, U] = -\frac{\hbar}{i} \frac{\partial U}{\partial p_x} = c_1 U, \quad (10)$$

with similar equations for the commutators $[y, U], [z, U]$. These relations lead to

$$xU|\vec{r}_0\rangle = (Ux + c_1 U)|\vec{r}_0\rangle = (x_0 + c_1)U|\vec{r}_0\rangle. \quad (11)$$

Thus, the new eigenvector obtained by acting with U on $|\vec{r}_0\rangle$ is an eigenvector of the operator, x , with eigenvalue $(x_0 + c_1)$, similarly, for the y and z components. Therefore,

$$U(\vec{c})|\vec{r}_0\rangle = |\vec{r}_0 + \vec{c}\rangle, \quad (12)$$

or

$$U(\vec{r}_0)|0\rangle = |\vec{r}_0\rangle. \quad (13)$$

We see the translation character of the operator U . The translation operator, $U = e^{-\frac{i}{\hbar} \vec{c} \cdot \vec{p}}$, can be regarded from two points of view as follows.

(1) Passive point of view. Action on base vectors. From this point of view, of eq. (12), the operator $U(\vec{c})$ acts on a base vector $|\vec{r}_0\rangle$ and converts it to a new base vector $|\vec{r}_0 + \vec{c}\rangle$, but the physical system is not translated. This process is illustrated by Fig. 18.1(a), where the physical system is illustrated by the maximum in its probability density at $x = a$. By shifting the origin of the coordinate system to the left a distance c_1 , the maximum of the probability density lies at $a + c_1$ in the translated coordinate system.

(2) Active point of view. Action on the physical system. In this point of view, the coordinate axes remain fixed, but the physical system is translated by the action of the operator $U(\vec{c})$ from its original position given by a vector \vec{a} to a new position described by the vector $\vec{a} + \vec{c}$. Now, we let U act on the original state vector $|\psi\rangle$ to make a new, translated, state vector $|\psi'\rangle$

$$U(\vec{c})|\psi\rangle = |\psi'\rangle, \quad (14)$$

so the original probability amplitude function $\psi(\vec{r})$ is shifted to a new probability amplitude function $\psi'(\vec{r})$, with

$$\begin{aligned} \psi'(\vec{r}) &= \langle \vec{r} | \psi' \rangle = \langle \vec{r} | U(\vec{c}) | \psi \rangle = \langle \psi | U^\dagger | \vec{r} \rangle^* \\ &= \langle \psi | e^{+\frac{i}{\hbar} \vec{c} \cdot \vec{p}} | \vec{r} \rangle^* = \langle \psi | \vec{r} - \vec{c} \rangle^* = \langle \vec{r} - \vec{c} | \psi \rangle = \psi(\vec{r} - \vec{c}). \end{aligned} \quad (15)$$

Now, if the original $\psi(\vec{r})$ had a maximum at $\vec{r} = \vec{a}$, the translated $\psi'(\vec{r}) = \psi(\vec{r} - \vec{c})$ will have a maximum at $(\vec{r} - \vec{c}) = \vec{a}$, or at $\vec{r} = (\vec{a} + \vec{c})$; i.e., the physical system has been translated along the positive direction of the vector \vec{c} . This process is illustrated in Fig. 18.1(b).

B Coordinate Representation Matrix Elements of p_x

Having discovered the properties of the translation operator, $U(\vec{c})$, we shall now use it to calculate the matrix elements of p_x in the coordinate representation, $\langle \vec{r}'_0 | p_x | \vec{r}_0 \rangle$.

In the relation

$$\langle \vec{r}'_0 | U(\vec{c}) | \vec{r}_0 \rangle = \langle \vec{r}'_0 | \vec{r}_0 + \vec{c} \rangle, \quad (16)$$

consider a vector $\vec{c} = \vec{\epsilon} = (\epsilon, 0, 0)$, where ϵ is an infinitesimal, $\epsilon \ll 1$, so eq. (16) becomes, retaining only first-order quantities in ϵ ,

$$\begin{aligned} \langle \vec{r}'_0 | (1 - \frac{i\epsilon}{\hbar} p_x) | \vec{r}_0 \rangle &= \delta(\vec{r}'_0 - \vec{r}_0) - \frac{i\epsilon}{\hbar} \langle \vec{r}'_0 | p_x | \vec{r}_0 \rangle \\ &= \langle \vec{r}'_0 | \vec{r}_0 + \vec{\epsilon} \rangle = \delta(\vec{r}'_0 - \vec{r}_0 - \vec{\epsilon}) = \delta(\vec{r}'_0 - \vec{r}_0) - \epsilon \left[\frac{\partial}{\partial x} \delta(\vec{r}) \right]_{\vec{r}=\vec{r}'_0-\vec{r}_0}, \end{aligned} \quad (17)$$

so

$$\langle \vec{r}'_0 | p_x | \vec{r}_0 \rangle = \frac{\hbar}{i} \left[\frac{\partial}{\partial x} \delta(\vec{r}) \right]_{\vec{r}=\vec{r}'_0-\vec{r}_0}$$

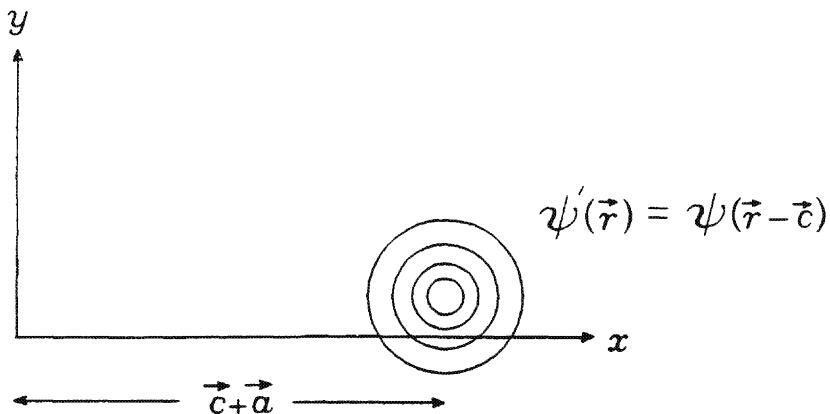
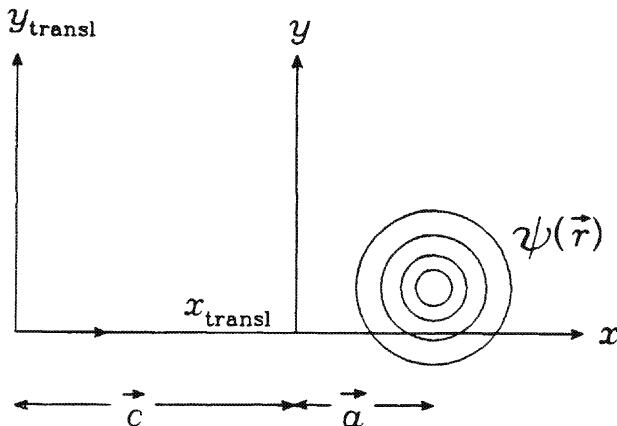


FIGURE 18.1. The translation operator. (a) Passive point of view. (b) Active point of view.

$$= \frac{\hbar}{i} \frac{\partial}{\partial x'_0} \delta(\vec{r}'_0 - \vec{r}_0) = -\frac{\hbar}{i} \frac{\partial}{\partial x_0} \delta(\vec{r}'_0 - \vec{r}_0). \quad (18)$$

Note, in particular, the minus sign in the last entry. The Dirac delta function is an even function of its argument, but its derivative is an odd function. We are now in a position to calculate the quantity $\langle \psi_1 | p_x | \psi_2 \rangle$ by the use of the coordinate representation. Projecting the states $|\psi_2\rangle$, and similarly $|\psi_1\rangle$, onto their coordinate-

space base vectors

$$\begin{aligned}
\langle \psi_1 | p_x | \psi_2 \rangle &= \int d\vec{r}'_0 \int d\vec{r}_0 \langle \psi_1 | \vec{r}'_0 \rangle \langle \vec{r}'_0 | p_x | \vec{r}_0 \rangle \langle \vec{r}_0 | \psi_2 \rangle \\
&= \int d\vec{r}'_0 \psi_1^*(\vec{r}'_0) \int d\vec{r}_0 \left(-\frac{\hbar}{i} \frac{\partial}{\partial x_0} \delta(\vec{r}'_0 - \vec{r}_0) \right) \psi_2(\vec{r}_0) \\
&= -\frac{\hbar}{i} \int d\vec{r}'_0 \psi_1^*(\vec{r}'_0) \left[\int dy_0 \int dz_0 \delta(\vec{r}'_0 - \vec{r}_0) \psi_2(\vec{r}_0) \right]_{x_0=-\infty}^{x_0=+\infty} \\
&\quad + \frac{\hbar}{i} \int d\vec{r}'_0 \psi_1^*(\vec{r}'_0) \int d\vec{r}_0 \delta(\vec{r}'_0 - \vec{r}_0) \frac{\partial}{\partial x_0} \psi_2(\vec{r}_0) \\
&= \int d\vec{r}'_0 \psi_1^*(\vec{r}'_0) \frac{\hbar}{i} \frac{\partial}{\partial x'_0} \psi_2(\vec{r}'_0). \tag{19}
\end{aligned}$$

This relation is of course just our previous result. (As always, the integrated term in the integration by parts has the value zero at the limits $x_0 = \pm\infty$.)

C Calculation of the Transformation Matrix $\langle \vec{r}_0 | \vec{p}_0 \rangle$

From the known matrix elements of p_x in the coordinate representation, we can now also calculate the unitary matrix $\langle \vec{p}_0 | \vec{r}_0 \rangle$ or its inverse $\langle \vec{r}_0 | \vec{p}_0 \rangle$. We shall proceed as in Chapters 16–17. From the eigenvector equations

$$p_x |\vec{p}_0\rangle = p_{0_x} |\vec{p}_0\rangle, \quad p_y |\vec{p}_0\rangle = p_{0_y} |\vec{p}_0\rangle, \quad p_z |\vec{p}_0\rangle = p_{0_z} |\vec{p}_0\rangle, \tag{20}$$

we get, e.g.,

$$\int d\vec{r}_0 p_x |\vec{r}_0\rangle \langle \vec{r}_0 | \vec{p}_0 \rangle = p_{0_x} |\vec{p}_0\rangle, \tag{21}$$

which is the exact analog of eq. (5) of Chapter 17, except the unit operator in the form $\sum_m |m\rangle \langle m|$ has been replaced by the unit operator in the form $\int d\vec{r}_0 |\vec{r}_0\rangle \langle \vec{r}_0|$. As in that case, left-multiplying with a specific $\langle \vec{r}'_0 |$ now leads to

$$\int d\vec{r}_0 \langle \vec{r}'_0 | p_x |\vec{r}_0\rangle \langle \vec{r}_0 | \vec{p}_0 \rangle = p_{0_x} \langle \vec{r}'_0 | \vec{p}_0 \rangle. \tag{22}$$

Using the result of eq. (18), this relation leads, with an integration by parts, to

$$\begin{aligned}
&- \frac{\hbar}{i} \int d\vec{r}_0 \left(\frac{\partial}{\partial x_0} \delta(\vec{r}'_0 - \vec{r}_0) \right) \langle \vec{r}_0 | \vec{p}_0 \rangle \\
&= + \frac{\hbar}{i} \int d\vec{r}_0 \delta(\vec{r}'_0 - \vec{r}_0) \left(\frac{\partial}{\partial x_0} \langle \vec{r}_0 | \vec{p}_0 \rangle \right) \\
&= + \frac{\hbar}{i} \frac{\partial}{\partial x'_0} \left(\langle \vec{r}'_0 | \vec{p}_0 \rangle \right) \\
&= p_{0_x} \langle \vec{r}'_0 | \vec{p}_0 \rangle. \tag{23}
\end{aligned}$$

Assuming we can factor the scalar product

$$\langle \vec{r}'_0 | \vec{p}_0 \rangle = \langle x'_0 | p_{0_x} \rangle \langle y'_0 | p_{0_y} \rangle \langle z'_0 | p_{0_z} \rangle, \tag{24}$$

the equation for $\langle x'_0 | p_{0_x} \rangle$ becomes an ordinary differential equation

$$\frac{\hbar}{i} \frac{d}{dx'_0} \langle x'_0 | p_{0_x} \rangle = p_{0_x} \langle x'_0 | p_{0_x} \rangle. \quad (25)$$

This equation can be integrated at once to yield

$$\langle x'_0 | p_{0_x} \rangle = \text{const.} e^{+\frac{i}{\hbar} x'_0 p_{0_x}}, \quad (26)$$

with similar results for $\langle y'_0 | p_{0_y} \rangle$ and $\langle z'_0 | p_{0_z} \rangle$, to give

$$\langle \vec{r}'_0 | \vec{p}_0 \rangle = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} e^{\frac{i}{\hbar} \vec{r}'_0 \cdot \vec{p}_0}, \quad (27)$$

where the integration constant has been chosen to satisfy the Dirac delta function orthonormality

$$\langle \vec{p}'_0 | \vec{p}_0 \rangle = \int d\vec{r}_0 \langle p'_0 | \vec{r}_0 \rangle \langle \vec{r}_0 | \vec{p}_0 \rangle = \frac{1}{(2\pi\hbar)^3} \int d\vec{r}_0 e^{\frac{i}{\hbar} \vec{r}_0 \cdot (\vec{p}_0 - \vec{p}'_0)} = \delta(\vec{p}'_0 - \vec{p}_0). \quad (28)$$

The results for $\langle \vec{r}_0 | \vec{p}_0 \rangle$ and $\langle \vec{p}_0 | \vec{r}_0 \rangle$ are of course well known from Fourier analysis. We have rederived them here to show how they can be derived from transformation theory.

19

Time-Dependence of State Vectors, Algebraic Techniques, Coherent States

Before examining the time-dependence of state vectors it will be useful to recapitulate and summarize the postulates of quantum theory.

A Recapitulation: The Postulates of Quantum Theory

I. The state of a physical system is specified by a vector, $|\psi\rangle$, of the infinite-dimensional Hilbert space. (We assume $\langle\psi|\psi\rangle = 1$.)

II. Every physically observable quantity is described by a hermitian operator, A .

III. The only possible result of the actual measurement of this physically observable quantity is one of the eigenvalues of the corresponding operator, A . (a) If a_n is a nondegenerate eigenvalue of A (part of the discrete spectrum of A), with

$$A|\alpha_n\rangle = a_n|\alpha_n\rangle, \quad \text{with } \langle\alpha_n|\alpha_n\rangle = 1, \quad (1)$$

the probability a measurement of the physical observable, A , of the system specified by the state $|\psi\rangle$ will yield the value a_n is given by

$$P(a_n) = |\langle\alpha_n|\psi\rangle|^2. \quad (2)$$

(b) If a_m is a degenerate eigenvalue of A (again part of the discrete spectrum of A), with

$$A|\alpha_m^{(i)}\rangle = a_m|\alpha_m^{(i)}\rangle, \quad \text{with } i = 1, 2, \dots, g_{a_m}, \quad (3)$$