Introduction to Quantum Mechanics

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Fundamental Equations

Schrödinger equation:

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi$$

Time independent Schrödinger equation:

$$H\psi = E\psi, \qquad \Psi = \psi e^{-iEt/\hbar}$$

Standard Hamiltonian:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V$$

Time dependence of an expectation value:

$$\frac{d\langle Q\rangle}{dt} = \frac{i}{\hbar}\langle[H,Q]\rangle + \left\langle\frac{\partial Q}{\partial t}\right\rangle$$

Generalized uncertainty principle:

$$\sigma_A\sigma_B \geq \left|\frac{1}{2i}\langle[A,B]\rangle\right|^2$$

Heisenberg uncertainty principle:

$$\sigma_x\sigma_p \geq \hbar/2$$

Canonical commutator:

$$[x,p] = i\hbar$$

Angular momentum:

$$[L_x,L_y] = i\hbar L_z, \quad [L_y,L_z] = i\hbar L_x, \quad [L_z,L_x] = i\hbar L_y$$

Pauli matrices:

$$\sigma_x = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \quad \sigma_y = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}, \quad \sigma_z = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

Fundamental Constants

Planck's constant :	$\hbar$	=	1.05457×10^{-34} J s
Speed of light :	c	=	2.99792×10^{8} m/s
Mass of electron :	m_e	=	9.10939×10^{-31} kg
Mass of proton :	m_p	=	1.67262×10^{-27} kg
Charge of electron :	$-e$	=	-1.60218×10^{-19} C
Permittivity of space :	ϵ_0	=	8.85419×10^{-12} C^2/J m
Boltzmann constant :	k_B	=	1.38066×10^{-23} J/K

Hydrogen Atom

Fine structure constant :	α	=	$e^2/4\pi\epsilon_0\hbar c$	=	$1/137.036$
Bohr radius :	a	=	$4\pi\epsilon_0\hbar^2/m_e e^2 = \hbar/\alpha m_e c$	=	5.29177×10^{-11} m
Bohr energies :	E_n	=	E_1/n^2 $(n = 1, 2, 3, \ldots)$		
Ground state energy :	$-E_1$	=	$m_e e^4/2(4\pi\epsilon_0)^2\hbar^2 = \alpha^2 m_e c^2/2$	=	13.6057 eV
Wave function :	ψ_0	=	$\frac{1}{\sqrt{\pi a^3}} e^{-r/a}$		
Rydberg formula :	$\frac{1}{\lambda}$	=	$R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$		
Rydberg constant :	R	=	$-E_1/2\pi\hbar c$	=	1.09737×10^{7} /m

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PREFACE

Unlike Newton's mechanics, or Maxwell's electrodynamics, or Einstein's relativity, quantum theory was not created—or even definitively packaged—by one individual, and it retains to this day some of the scars of its exhilirating but traumatic youth. There is no general consensus as to what its fundamental principles are, how it should be taught, or what it really "means." Every competent physicist can "do" quantum mechanics, but the stories we tell ourselves about what we are doing are as various as the tales of Scheherazade, and almost as implausible. Richard Feynman (one of its greatest practitioners) remarked, "I think I can safely say that nobody understands quantum mechanics."

The purpose of this book is to teach you how to *do* quantum mechanics. Apart from some essential background in Chapter 1, the deeper quasi-philosophical questions are saved for the end. I do not believe one can intelligently discuss what quantum mechanics *means* until one has a firm sense of what quantum mechanics *does*. But if you absolutely cannot wait, by all means read the Afterword immediately following Chapter 1.

Not only is quantum theory conceptually rich, it is also technically difficult, and exact solutions to all but the most artificial textbook examples are few and far between. It is therefore essential to develop special techniques for attacking more realistic problems. Accordingly, this book is divided into two parts[1]; Part I covers the basic theory, and Part II assembles an arsenal of approximation schemes, with illustrative applications. Although it is important to keep the two parts logically separate, it is not necessary to study the material in the order presented here. Some instructors, for example, may wish to treat time-independent perturbation theory immediately after Chapter 2.

[1]This structure was inspired by David Park's classic text *Introduction to the Quantum Theory*, 3rd ed., (New York: McGraw-Hill, 1992).

This book is intended for a one-semester or one-year course at the junior or senior level. A one-semester course will have to concentrate mainly on Part I; a full-year course should have room for supplementary material beyond Part II. The reader must be familiar with the rudiments of linear algebra, complex numbers, and calculus up through partial derivatives; some acquaintance with Fourier analysis and the Dirac delta function would help. Elementary classical mechanics is essential, of course, and a little electrodynamics would be useful in places. As always, the more physics and math you know the easier it will be, and the more you will get out of your study. But I would like to emphasize that quantum mechanics is not, in my view, something that flows smoothly and naturally from earlier theories. On the contrary, it represents an abrupt and revolutionary departure from classical ideas, calling forth a wholly new and radically counterintuitive way of thinking about the world. That, indeed, is what makes it such a fascinating subject.

At first glance, this book may strike you as forbiddingly mathematical. We encounter Legendre, Hermite, and Laguerre polynomials, spherical harmonics, Bessel, Neumann, and Hankel functions, Airy functions, and even the Riemann Zeta function —not to mention Fourier transforms, Hilbert spaces, Hermitian operators, Clebsch-Gordan coefficients, and Lagrange multipliers. Is all this baggage really necessary? Perhaps not, but physics is like carpentry: Using the right tool makes the job *easier*, not more difficult, and teaching quantum mechanics without the appropriate mathematical equipment is like asking the student to dig a foundation with a screwdriver. (On the other hand, it can be tedious and diverting if the instructor feels obliged to give elaborate lessons on the proper use of each tool. My own instinct is to hand the students shovels and tell them to start digging. They may develop blisters at first, but I still think this is the most efficient and exciting way to learn.) At any rate, I can assure you that there is no *deep* mathematics in this book, and if you run into something unfamiliar, and you don't find my explanation adequate, by all means *ask* someone about it, or look it up. There are many good books on mathematical methods—I particularly recommend Mary Boas, *Mathematical Methods in the Physical Sciences*, 2nd ed., Wiley, New York (1983), and George Arfken, *Mathematical Methods for Physicists*, 3rd ed., Academic Press, Orlando (1985). But whatever you do, don't let the mathematics—which, for us, is only a tool—interfere with the physics.

Several readers have noted that there are fewer worked examples in this book than is customary, and that some important material is relegated to the problems. This is no accident. I don't believe you can learn quantum mechanics without doing many exercises for yourself. Instructors should, of course, go over as many problems in class as time allows, but students should be warned that this is not a subject about which *any*one has natural intuitions—you're developing a whole new set of muscles here, and there is simply no substitute for calisthenics. Mark Semon suggested that I offer a "Michelin Guide" to the problems, with varying numbers of stars to indicate the level of difficulty and importance. This seemed like a good idea (though, like the quality of a restaurant, the significance of a problem is partly a matter of taste); I have adopted the following rating scheme:

* an essential problem that every reader should study;

** a somewhat more difficult or more peripheral problem;

*** an unusually challenging problem that may take over an hour.

(No stars at all means fast food: OK if you're hungry, but not very nourishing.) Most of the one-star problems appear at the end of the relevant section; most of the three-star problems are at the end of the chapter. A solution manual is available (to instructors only) from the publisher.

I have benefited from the comments and advice of many colleagues, who suggested problems, read early drafts, or used a preliminary version in their courses. I would like to thank in particular Burt Brody (Bard College), Ash Carter (Drew University), Peter Collings (Swarthmore College), Jeff Dunham (Middlebury College), Greg Elliott (University of Puget Sound), Larry Hunter (Amherst College), Mark Semon (Bates College), Stavros Theodorakis (University of Cyprus), Dan Velleman (Amherst College), and all my colleagues at Reed College.

Finally, I wish to thank David Park and John Rasmussen (and their publishers) for permission to reproduce Figure 8.6, which is taken from Park's *Introduction to the Quantum Theory* (footnote 1), adapted from I. Perlman and J. O. Rasmussen, "Alpha Radioactivity," in *Encyclopedia of Physics*, vol. **42**, Springer-Verlag, 1957.

PART I

THEORY

CHAPTER 1

THE WAVE FUNCTION

1.1 THE SCHRÖDINGER EQUATION

Imagine a particle of mass m, constrained to move along the x-axis, subject to some specified force $F(x, t)$ (Figure 1.1). The program of *classical* mechanics is to determine the position of the particle at any given time: $x(t)$. Once we know that, we can figure out the velocity ($v = dx/dt$), the momentum ($p = mv$), the kinetic energy ($T = (1/2)mv^2$), or any other dynamical variable of interest. And how do we go about determining $x(t)$? We apply Newton's second law: $F = ma$. (For conservative systems—the only kind we shall consider, and, fortunately, the only kind that *occur* at the microscopic level—the force can be expressed as the derivative of a potential energy function,[1] $F = -\partial V/\partial x$, and Newton's law reads $m\,d^2x/dt^2 = -\partial V/\partial x$.) This, together with appropriate initial conditions (typically the position and velocity at $t = 0$), determines $x(t)$.

Quantum mechanics approaches this same problem quite differently. In this case what we're looking for is the **wave function**, $\Psi(x, t)$, of the particle, and we get it by solving the **Schrödinger equation**:

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi. \qquad [1.1]$$

[1] Magnetic forces are an exception, but let's not worry about them just yet. By the way, we shall assume throughout this book that the motion is nonrelativistic ($v \ll c$).

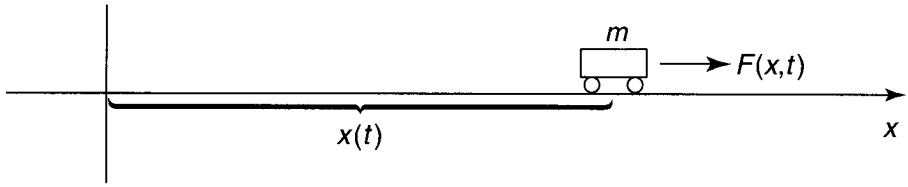

Figure 1.1: A "particle" constrained to move in one dimension under the influence of a specified force.

Here i is the square root of -1, and $\hbar$ is Planck's constant—or rather, his original constant (h) divided by 2π:

$$\hbar = \frac{h}{2\pi} = 1.054573 \times 10^{-34} \text{J s}. \qquad [1.2]$$

The Schrödinger equation plays a role logically analogous to Newton's second law: Given suitable initial conditions [typically, $\Psi(x, 0)$], the Schrödinger equation determines $\Psi(x, t)$ for all future time, just as, in classical mechanics, Newton's law determines $x(t)$ for all future time.

1.2 THE STATISTICAL INTERPRETATION

But what exactly *is* this "wave function", and what does it do for you once you've *got* it? After all, a particle, by its nature, is localized at a point, whereas the wave function (as its name suggests) is spread out in space (it's a function of x, for any given time t). How can such an object be said to describe the state of a *particle*? The answer is provided by Born's **statistical interpretation** of the wave function, which says that $|\Psi(x, t)|^2$ gives the *probability* of finding the particle at point x, at time t—or, more precisely,[2]

$$|\Psi(x, t)|^2\, dx = \left\{ \begin{array}{l} \text{probability of finding the particle} \\ \text{between } x \text{ and } (x + dx), \text{ at time } t. \end{array} \right\} \qquad [1.3]$$

For the wave function in Figure 1.2, you would be quite likely to find the particle in the vicinity of point A, and relatively unlikely to find it near point B.

The statistical interpretation introduces a kind of **indeterminacy** into quantum mechanics, for even if you know everything the theory has to tell you about the

[2]The wave function itself is complex, but $|\Psi|^2 = \Psi^*\Psi$ (where Ψ^* is the complex conjugate of Ψ) is real and nonnegative—as a probability, of course, must be.

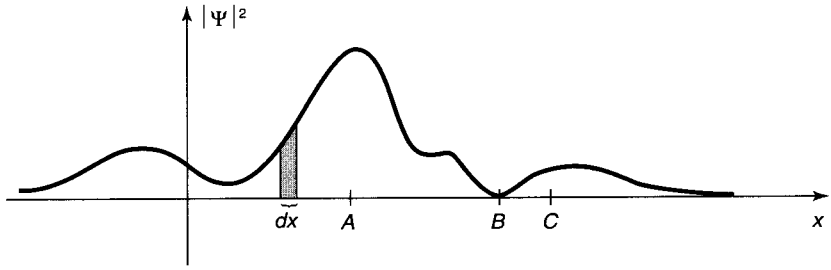

Figure 1.2: A typical wave function. The particle would be relatively likely to be found near A, and unlikely to be found near B. The shaded area represents the probability of finding the particle in the range dx.

particle (to wit: its wave function), you cannot predict with certainty the outcome of a simple experiment to measure its position—all quantum mechanics has to offer is *statistical* information about the *possible* results. This indeterminacy has been profoundly disturbing to physicists and philosophers alike. Is it a peculiarity of nature, a deficiency in the theory, a fault in the measuring apparatus, or *what*?

Suppose I *do* measure the position of the particle, and I find it to be at the point C. Question: Where was the particle just *before* I made the measurement? There are three plausible answers to this question, and they serve to characterize the main schools of thought regarding quantum indeterminacy:

1. The **realist** position: *The particle was at C.* This certainly seems like a sensible response, and it is the one Einstein advocated. Note, however, that if this is true then quantum mechanics is an **incomplete** theory, since the particle *really was* at C, and yet quantum mechanics was unable to tell us so. To the realist, indeterminacy is not a fact of nature, but a reflection of our ignorance. As d'Espagnat put it, "the position of the particle was never indeterminate, but was merely unknown to the experimenter."[3] Evidently Ψ is not the whole story—some additional information (known as a **hidden variable**) is needed to provide a complete description of the particle.

2. The **orthodox** position: *The particle wasn't really anywhere.* It was the act of measurement that forced the particle to "take a stand" (though how and why it decided on the point C we dare not ask). Jordan said it most starkly: "Observations not only *disturb* what is to be measured, they *produce* it. . . . We *compel* [the particle] to assume a definite position."[4] This view (the so-called **Copenhagen interpretation**) is associated with Bohr and his followers. Among physicists it has always been the

[3]Bernard d'Espagnat, *The Quantum Theory and Reality*, Scientific American, Nov. 1979 (Vol. 241), p. 165.

[4]Quoted in a lovely article by N. David Mermin, *Is the moon there when nobody looks?*, Physics Today, April 1985, p. 38.

most widely accepted position. Note, however, that if it is correct there is something very peculiar about the act of measurement—something that over half a century of debate has done precious little to illuminate.

3. The **agnostic** position: *Refuse to answer.* This is not quite as silly as it sounds—after all, what sense can there be in making assertions about the status of a particle *before* a measurement, when the only way of knowing whether you were right is precisely to conduct a measurement, in which case what you get is no longer "before the measurement"? It is metaphysics (in the perjorative sense of the word) to worry about something that cannot, by its nature, be tested. Pauli said, "One should no more rack one's brain about the problem of whether something one cannot know anything about exists all the same, than about the ancient question of how many angels are able to sit on the point of a needle."[5] For decades this was the "fall-back" position of most physicists: They'd try to sell you answer 2, but if you were persistent they'd switch to 3 and terminate the conversation.

Until fairly recently, all three positions (realist, orthodox, and agnostic) had their partisans. But in 1964 John Bell astonished the physics community by showing that it makes an *observable* difference if the particle had a precise (though unknown) position prior to the measurement. Bell's discovery effectively eliminated agnosticism as a viable option, and made it an *experimental* question whether 1 or 2 is the correct choice. I'll return to this story at the end of the book, when you will be in a better position to appreciate Bell's theorem; for now, suffice it to say that the experiments have confirmed decisively the orthodox interpretation[6]: A particle simply does not have a precise position prior to measurement, any more than the ripples on a pond do; it is the measurement process that insists on one particular number, and thereby in a sense *creates* the specific result, limited only by the statistical weighting imposed by the wave function.

But what if I made a *second* measurement, immediately after the first? Would I get C again, or does the act of measurement cough up some completely new number each time? On this question everyone is in agreement: A repeated measurement (on the same particle) must return the same value. Indeed, it would be tough to prove that the particle was really found at C in the first instance if this could not be confirmed by immediate repetition of the measurement. How does the orthodox interpretation account for the fact that the second measurement is bound to give the value C? Evidently the first measurement radically alters the wave function, so that it is now sharply peaked about C (Figure 1.3). We say that the wave function **collapses** upon measurement, to a spike at the point C (Ψ soon spreads out again, in accordance with the Schrödinger equation, so the second measurement must be made quickly). There

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[5]Quoted by Mermin (previous footnote), p. 40.

[6]This statement is a little too strong: There remain a few theoretical and experimental loopholes, some of which I shall discuss in the Afterword. And there exist other formulations (such as the **many worlds** interpretation) that do not fit cleanly into any of my three categories. But I think it is wise, at least from a pedagogical point of view, to adopt a clear and coherent platform at this stage, and worry about the alternatives later.

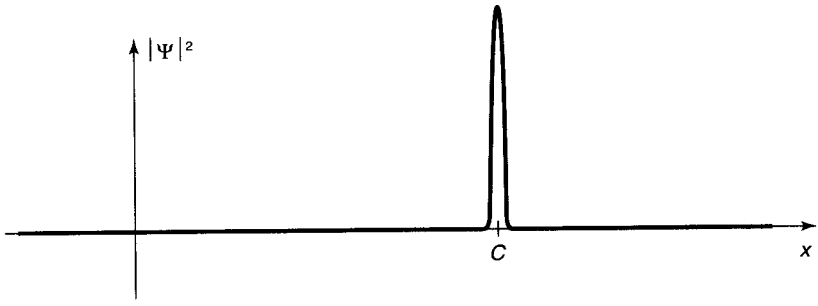

Figure 1.3: Collapse of the wave function: graph of $|\Psi|^2$ immediately after a measurement has found the particle at point C.

are, then, two entirely distinct kinds of physical processes: "ordinary" ones, in which the wave function evolves in a leisurely fashion under the Schrödinger equation, and "measurements", in which Ψ suddenly and discontinuously collapses.[7]

1.3 PROBABILITY

Because of the statistical interpretation, **probability** plays a central role in quantum mechanics, so I digress now for a brief discussion of the theory of probability. It is mainly a question of introducing some notation and terminology, and I shall do it in the context of a simple example.

Imagine a room containing 14 people, whose ages are as follows:

one person aged 14
one person aged 15
three people aged 16
two people aged 22
two people aged 24
five people aged 25.

If we let $N(j)$ represent the number of people of age j, then

[7]The role of measurement in quantum mechanics is so critical and so bizarre that you may well be wondering what precisely *constitutes* a measurement. Does it have to do with the interaction between a microscopic (quantum) system and a macroscopic (classical) measuring apparatus (as Bohr insisted), or is it characterized by the leaving of a permanent "record" (as Heisenberg claimed), or does it involve the intervention of a conscious "observer" (as Wigner proposed)? I'll return to this thorny issue in the Afterword; for the moment let's take the naive view: A measurement is the kind of thing that a scientist does in the laboratory, with rulers, stopwatches, Geiger counters, and so on.

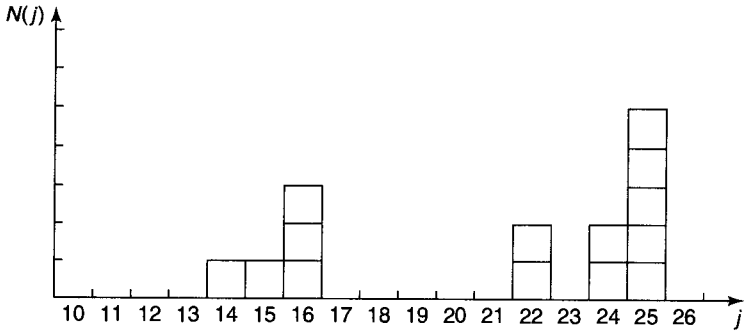

Figure 1.4: Histogram showing the number of people, $N(j)$, with age j, for the example in Section 1.3.

$$N(14) = 1$$
$$N(15) = 1$$
$$N(16) = 3$$
$$N(22) = 2$$
$$N(24) = 2$$
$$N(25) = 5$$

while $N(17)$, for instance, is zero. The *total* number of people in the room is

$$N = \sum_{j=0}^{\infty} N(j). \qquad [1.4]$$

(In this instance, of course, $N = 14$.) Figure 1.4 is a histogram of the data. The following are some questions one might ask about this distribution.

Question 1. If you selected one individual at random from this group, what is the **probability** that this person's age would be 15? *Answer:* One chance in 14, since there are 14 possible choices, all equally likely, of whom only one has this particular age. If $P(j)$ is the probability of getting age j, then $P(14) = 1/14$, $P(15) = 1/14$, $P(16) = 3/14$, and so on. In general,

$$P(j) = \frac{N(j)}{N}. \qquad [1.5]$$

Notice that the probability of getting *either* 14 *or* 15 is the *sum* of the individual probabilities (in this case, 1/7). In particular, the sum of *all* the probabilities is 1—you're *certain* to get *some* age:

$$\sum_{j=1}^{\infty} P(j) = 1. \qquad [1.6]$$

Question 2. What is the **most probable** age? *Answer:* 25, obviously; five people share this age, whereas at most three have any other age. In general, the most probable j is the j for which $P(j)$ is a maximum.

Question 3. What is the **median** age? *Answer:* 23, for 7 people are younger than 23, and 7 are older. (In general, the median is that value of j such that the probability of getting a larger result is the same as the probability of getting a smaller result.)

Question 4. What is the **average** (or **mean**) age? *Answer:*

$$\frac{(14) + (15) + 3(16) + 2(22) + 2(24) + 5(25)}{14} = \frac{294}{14} = 21.$$

In general, the average value of j (which we shall write thus: $\langle j \rangle$) is given by

$$\langle j \rangle = \frac{\sum jN(j)}{N} = \sum_{j=0}^{\infty} jP(j). \qquad [1.7]$$

Notice that there need not be anyone with the average age or the median age—in this example nobody happens to be 21 or 23. In quantum mechanics the average is usually the quantity of interest; in that context it has come to be called the **expectation value**. It's a misleading term, since it suggests that this is the outcome you would be most likely to get if you made a single measurement (*that* would be the *most probable value*, not the average value)—but I'm afraid we're stuck with it.

Question 5. What is the average of the *squares* of the ages? *Answer:* You could get $14^2 = 196$, with probability 1/14, or $15^2 = 225$, with probability 1/14, or $16^2 = 256$, with probability 3/14, and so on. The average, then, is

$$\langle j^2 \rangle = \sum_{j=0}^{\infty} j^2 P(j). \qquad [1.8]$$

In general, the average value of some *function* of j is given by

$$\langle f(j) \rangle = \sum_{j=0}^{\infty} f(j)P(j). \qquad [1.9]$$

(Equations 1.6, 1.7, and 1.8 are, if you like, special cases of this formula.) *Beware:* The average of the squares ($\langle j^2 \rangle$) is *not* ordinarily equal to the square of the average ($\langle j \rangle^2$). For instance, if the room contains just two babies, aged 1 and 3, then $\langle x^2 \rangle = 5$, but $\langle x \rangle^2 = 4$.

Now, there is a conspicuous difference between the two histograms in Figure 1.5, even though they have the same median, the same average, the same most probable value, and the same number of elements: The first is sharply peaked about the average value, whereas the second is broad and flat. (The first might represent the age profile for students in a big-city classroom, and the second the pupils in a one-room schoolhouse.) We need a numerical measure of the amount of "spread" in a

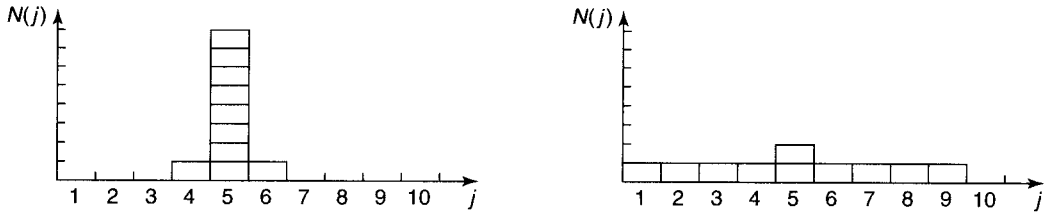

Figure 1.5: Two histograms with the same median, same average, and same most probable value, but different standard deviations.

distribution, with respect to the average. The most obvious way to do this would be to find out how far each individual deviates from the average,

$$\Delta j = j - \langle j \rangle, \tag{1.10}$$

and compute the average of Δj. Trouble is, of course, that you get *zero*, since, by the nature of the average, Δj is as often negative as positive:

$$\langle \Delta j \rangle = \sum (j - \langle j \rangle) P(j) = \sum j P(j) - \langle j \rangle \sum P(j)$$
$$= \langle j \rangle - \langle j \rangle = 0.$$

(Note that $\langle j \rangle$ is constant—it does not change as you go from one member of the sample to another—so it can be taken outside the summation.) To avoid this irritating problem, you might decide to average the *absolute value* of Δj. But absolute values are nasty to work with; instead, we get around the sign problem by *squaring* before averaging:

$$\sigma^2 \equiv \langle (\Delta j)^2 \rangle. \tag{1.11}$$

This quantity is known as the **variance** of the distribution; σ itself (the square root of the average of the square of the deviation from the average—gulp!) is called the **standard deviation**. The latter is the customary measure of the spread about $\langle j \rangle$.

There is a useful little theorem involving standard deviations:

$$\sigma^2 = \langle (\Delta j)^2 \rangle = \sum (\Delta j)^2 P(j) = \sum (j - \langle j \rangle)^2 P(j)$$
$$= \sum (j^2 - 2j\langle j \rangle + \langle j \rangle^2) P(j)$$
$$= \sum j^2 P(j) - 2\langle j \rangle \sum j P(j) + \langle j \rangle^2 \sum P(j)$$
$$= \langle j^2 \rangle - 2\langle j \rangle \langle j \rangle + \langle j \rangle^2,$$

or

$$\sigma^2 = \langle j^2 \rangle - \langle j \rangle^2. \tag{1.12}$$

Equation 1.12 provides a faster method for computing σ: Simply calculate $\langle j^2 \rangle$ and $\langle j \rangle^2$, and subtract. Incidentally, I warned you a moment ago that $\langle j^2 \rangle$ is not, in general,

equal to $\langle j \rangle^2$. Since σ^2 is plainly nonnegative (from its definition in Equation 1.11), Equation 1.12 implies that

$$\langle j^2 \rangle \geq \langle j \rangle^2, \qquad [1.13]$$

and the two are equal only when $\sigma = 0$, which is to say, for distributions with no spread at all (every member having the same value).

So far, I have assumed that we are dealing with a *discrete* variable—that is, one that can take on only certain isolated values (in the example, j had to be an integer, since I gave ages only in years). But it is simple enough to generalize to *continuous* distributions. If I select a random person off the street, the probability that her age is *precisely* 16 years, 4 hours, 27 minutes, and 3.3333 seconds is *zero*. The only sensible thing to speak about is the probability that her age lies in some *interval*—say, between 16 years, and 16 years plus one day. If the interval is sufficiently short, this probability is proportional to the length of the interval. For example, the chance that her age is between 16 and 16 plus *two* days is presumably twice the probability that it is between 16 and 16 plus *one* day. (Unless, I suppose, there was some extraordinary baby boom 16 years ago, on exactly those days—in which case we have chosen an interval too long for the rule to apply. If the baby boom lasted six hours, we'll take intervals of a second or less, to be on the safe side. Technically, we're talking about infinitesimal intervals.) Thus

$$\left\{ \begin{array}{l} \text{probability that individual (chosen at random)} \\ \text{lies between } x \text{ and } (x + dx) \end{array} \right\} = \rho(x)\, dx. \qquad [1.14]$$

The proportionality factor, $\rho(x)$, is often loosely called "the probability of getting x," but this is sloppy language; a better term is **probability density**. The probability that x lies between a and b (a *finite* interval) is given by the integral of $\rho(x)$:

$$P_{ab} = \int_a^b \rho(x)\, dx, \qquad [1.15]$$

and the rules we deduced for discrete distributions translate in the obvious way:

$$\int_{-\infty}^{+\infty} \rho(x)\, dx = 1, \qquad [1.16]$$

$$\langle x \rangle = \int_{-\infty}^{+\infty} x\rho(x)\, dx, \qquad [1.17]$$

$$\langle f(x) \rangle = \int_{-\infty}^{+\infty} f(x)\rho(x)\, dx, \qquad [1.18]$$

$$\sigma^2 \equiv \langle (\Delta x)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2. \qquad [1.19]$$

***Problem 1.1** For the distribution of ages in the example in Section 1.3,

(a) Compute $\langle j^2 \rangle$ and $\langle j \rangle^2$.

(b) Determine Δj for each j, and use Equation 1.11 to compute the standard deviation.

(c) Use your results in (a) and (b) to check Equation 1.12.

Problem 1.2 Consider the first 25 digits in the decimal expansion of π (3, 1, 4, 1, 5, 9, ...).

(a) If you selected one number at random from this set, what are the probabilities of getting each of the 10 digits?

(b) What is the most probable digit? What is the median digit? What is the average value?

(c) Find the standard deviation for this distribution.

Problem 1.3 The needle on a broken car speedometer is free to swing, and bounces perfectly off the pins at either end, so that if you give it a flick it is equally likely to come to rest at any angle between 0 and π.

(a) What is the probability density, $\rho(\theta)$? [$\rho(\theta)\, d\theta$ is the probability that the needle will come to rest between θ and $(\theta + d\theta)$.] Graph $\rho(\theta)$ as a function of θ, from $-\pi/2$ to $3\pi/2$. (Of course, part of this interval is excluded, so ρ is zero there.) Make sure that the total probability is 1.

(b) Compute $\langle \theta \rangle$, $\langle \theta^2 \rangle$, and σ for this distribution.

(c) Compute $\langle \sin\theta \rangle$, $\langle \cos\theta \rangle$, and $\langle \cos^2\theta \rangle$.

Problem 1.4 We consider the same device as the previous problem, but this time we are interested in the x-coordinate of the needle point—that is, the "shadow", or "projection", of the needle on the horizontal line.

(a) What is the probability density $\rho(x)$? [$\rho(x)\, dx$ is the probability that the projection lies between x and $(x + dx)$.] Graph $\rho(x)$ as a function of x, from $-2r$ to $+2r$, where r is the length of the needle. Make sure the total probability is 1. [*Hint*: You know (from Problem 1.3) the probability that θ is in a given range; the question is, what interval dx corresponds to the interval $d\theta$?]

(b) Compute $\langle x \rangle$, $\langle x^2 \rangle$, and σ for this distribution. Explain how you could have obtained these results from part (c) of Problem 1.3.

****Problem 1.5** A needle of length l is dropped at random onto a sheet of paper ruled with parallel lines a distance l apart. What is the probability that the needle will cross a line? [*Hint*: Refer to Problem 1.4.]

***Problem 1.6** Consider the **Gaussian** distribution

$$\rho(x) = Ae^{-\lambda(x-a)^2},$$

where A, a, and λ are constants. (Look up any integrals you need.)

(a) Use Equation 1.16 to determine A.

(b) Find $\langle x \rangle$, $\langle x^2 \rangle$, and σ.

(c) Sketch the graph of $\rho(x)$.

1.4 NORMALIZATION

We return now to the statistical interpretation of the wave function (Equation 1.3), which says that $|\Psi(x, t)|^2$ is the probability density for finding the particle at point x, at time t. It follows (Equation 1.16) that the integral of $|\Psi|^2$ must be 1 (the particle's got to be *some*where):

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 \, dx = 1. \qquad [1.20]$$

Without this, the statistical interpretation would be nonsense.

However, this requirement should disturb you: After all, the wave function is supposed to be determined by the Schrödinger equation—we can't impose an extraneous condition on Ψ without checking that the two are consistent. A glance at Equation 1.1 reveals that if $\Psi(x, t)$ is a solution, so too is $A\Psi(x, t)$, where A is any (complex) constant. What we must do, then, is pick this undetermined multiplicative factor so as to ensure that Equation 1.20 is satisfied. This process is called **normalizing** the wave function. For some solutions to the Schrödinger equation, the integral is *infinite*; in that case *no* multiplicative factor is going to make it 1. The same goes for the trivial solution $\Psi = 0$. Such **non-normalizable** solutions cannot represent particles, and must be rejected. Physically realizable states correspond to the "square-integrable" solutions to Schrödinger's equation.[8]

[8] Evidently $\Psi(x, t)$ must go to zero faster than $1/\sqrt{|x|}$, as $|x| \to \infty$. Incidentally, normalization only fixes the *modulus* of A; the *phase* remains undetermined. However, as we shall see, the latter carries no physical significance anyway.

But wait a minute! Suppose I have normalized the wave function at time $t = 0$. How do I know that it will *stay* normalized, as time goes on and Ψ evolves? (You can't keep *re*normalizing the wave function, for then A becomes a function of t, and you no longer have a solution to the Schrödinger equation.) Fortunately, the Schrödinger equation has the property that it automatically preserves the normalization of the wave function—without this crucial feature the Schrödinger equation would be incompatible with the statistical interpretation, and the whole theory would crumble. So we'd better pause for a careful proof of this point:

$$\frac{d}{dt}\int_{-\infty}^{+\infty}|\Psi(x,t)|^2\,dx = \int_{-\infty}^{+\infty}\frac{\partial}{\partial t}|\Psi(x,t)|^2\,dx. \qquad [1.21]$$

[Note that the integral is a function only of t, so I use a total derivative (d/dt) in the first term, but the integrand is a function of x as well as t, so it's a partial derivative ($\partial/\partial t$) in the second one.] By the product rule,

$$\frac{\partial}{\partial t}|\Psi|^2 = \frac{\partial}{\partial t}(\Psi^*\Psi) = \Psi^*\frac{\partial\Psi}{\partial t} + \frac{\partial\Psi^*}{\partial t}\Psi \qquad [1.22]$$

Now the Schrödinger equation says that

$$\frac{\partial\Psi}{\partial t} = \frac{i\hbar}{2m}\frac{\partial^2\Psi}{\partial x^2} - \frac{i}{\hbar}V\Psi, \qquad [1.23]$$

and hence also (taking the complex conjugate of Equation 1.23)

$$\frac{\partial\Psi^*}{\partial t} = -\frac{i\hbar}{2m}\frac{\partial^2\Psi^*}{\partial x^2} + \frac{i}{\hbar}V\Psi^*, \qquad [1.24]$$

so

$$\frac{\partial}{\partial t}|\Psi|^2 = \frac{i\hbar}{2m}\left(\Psi^*\frac{\partial^2\Psi}{\partial x^2} - \frac{\partial^2\Psi^*}{\partial x^2}\Psi\right) = \frac{\partial}{\partial x}\left[\frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)\right]. \qquad [1.25]$$

The integral (Equation 1.21) can now be evaluated explicitly:

$$\frac{d}{dt}\int_{-\infty}^{+\infty}|\Psi(x,t)|^2\,dx = \frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)\Bigg|_{-\infty}^{+\infty}. \qquad [1.26]$$

But $\Psi(x,t)$ must go to zero as x goes to ($\pm$) infinity—otherwise the wave function would not be normalizable. It follows that

$$\frac{d}{dt}\int_{-\infty}^{+\infty}|\Psi(x,t)|^2\,dx = 0, \qquad [1.27]$$

and hence that the integral on the left is *constant* (independent of time); if Ψ is normalized at $t = 0$, it *stays* normalized for all future time. QED

Problem 1.7 At time $t = 0$ a particle is represented by the wave function

$$\Psi(x,0) = \begin{cases} Ax/a, & \text{if } 0 \le x \le a, \\ A(b-x)/(b-a), & \text{if } a \le x \le b, \\ 0, & \text{otherwise,} \end{cases}$$

where A, a, and b are constants.

(a) Normalize Ψ (that is, find A in terms of a and b).

(b) Sketch $\Psi(x,0)$ as a function of x.

(c) Where is the particle most likely to be found, at $t = 0$?

(d) What is the probability of finding the particle to the left of a? Check your result in the limiting cases $b = a$ and $b = 2a$.

(e) What is the expectation value of x?

***Problem 1.8** Consider the wave function

$$\Psi(x,t) = Ae^{-\lambda|x|}e^{-i\omega t},$$

where A, λ, and ω are positive real constants. [We'll see in Chapter 2 what potential (V) actually produces such a wave function.]

(a) Normalize Ψ.

(b) Determine the expectation values of x and x^2.

(c) Find the standard deviation of x. Sketch the graph of $|\Psi|^2$, as a function of x, and mark the points $(\langle x\rangle + \sigma)$ and $(\langle x\rangle - \sigma)$ to illustrate the sense in which σ represents the "spread" in x. What is the probability that the particle would be found outside this range?

Problem 1.9 Let $P_{ab}(t)$ be the probability of finding the particle in the range $(a < x < b)$, at time t.

(a) Show that

$$\frac{dP_{ab}}{dt} = J(a,t) - J(b,t)$$

where

$$J(x,t) \equiv \frac{i\hbar}{2m}\left(\Psi\frac{\partial\Psi^*}{\partial x} - \Psi^*\frac{\partial\Psi}{\partial x}\right).$$

What are the units of $J(x,t)$? [J is called the **probability current**, because it tells you the rate at which probability is "flowing" past the point x. If $P_{ab}(t)$ is increasing, then more probability is flowing into the region at one end than flows out at the other.]

(b) Find the probability current for the wave function in the previous problem. (This is not a very pithy example, I'm afraid; we'll encounter some more substantial ones in due course.)

****Problem 1.10** Suppose you wanted to describe an **unstable particle** that spontaneously disintegrates with a "lifetime" τ. In that case the total probability of finding the particle somewhere should *not* be constant, but should decrease at (say) an exponential rate:

$$P(t) \equiv \int_{-\infty}^{+\infty} |\Psi(x,t)|^2\, dx = e^{-t/\tau}.$$

A crude way of achieving this result is as follows. In Equation 1.24 we tacitly assumed that V (the potential energy) is *real.* That is certainly reasonable, but it leads to the **conservation of probability** enshrined in Equation 1.27. What if we assign to V an imaginary part:

$$V = V_0 - i\Gamma,$$

where V_0 is the true potential energy and Γ is a positive real constant?

(a) Show that (in place of Equation 1.27) we now get

$$\frac{dP}{dt} = -\frac{2\Gamma}{\hbar} P.$$

(b) Solve for $P(t)$, and find the lifetime of the particle in terms of Γ.

1.5 MOMENTUM

For a particle in state Ψ, the expectation value of x is

$$\langle x \rangle = \int_{-\infty}^{+\infty} x |\Psi(x,t)|^2\, dx. \qquad [1.28]$$

What exactly does this mean? It emphatically does *not* mean that if you measure the position of one particle over and over again, $\int x|\Psi|^2 dx$ is the average of the results you'll get. On the contrary, the first measurement (whose outcome is indeterminate) will collapse the wave function to a spike at the value actually obtained, and the subsequent measurements (if they're performed quickly) will simply repeat that same result. Rather, $\langle x \rangle$ is the average of measurements performed on particles *all in the state* Ψ, which means that either you must find some way of returning the particle to its original state after each measurement, or else you prepare a whole ensemble of particles, each in the same state Ψ, and measure the positions of all of them: $\langle x \rangle$ is the

average of *these* results. [I like to picture a row of bottles on a shelf, each containing a particle in the state Ψ (relative to the center of the bottle). A graduate student with a ruler is assigned to each bottle, and at a signal they all measure the positions of their respective particles. We then construct a histogram of the results, which should match $|\Psi|^2$, and compute the average, which should agree with $\langle x \rangle$. (Of course, since we're only using a finite sample, we can't expect perfect agreement, but the more bottles we use, the closer we ought to come.)] In short, the expectation value is the average of repeated measurements on an ensemble of identically prepared systems, *not* the average of repeated measurements on one and the same system.

Now, as time goes on, $\langle x \rangle$ will change (because of the time dependence of Ψ), and we might be interested in knowing how fast it moves. Referring to Equations 1.25 and 1.28, we see that[9]

$$\frac{d\langle x \rangle}{dt} = \int x \frac{\partial}{\partial t} |\Psi|^2 \, dx = \frac{i\hbar}{2m} \int x \frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx. \quad [1.29]$$

This expression can be simplified using integration by parts[10]:

$$\frac{d\langle x \rangle}{dt} = -\frac{i\hbar}{2m} \int \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx. \quad [1.30]$$

[I used the fact that $\partial x / \partial x = 1$, and threw away the boundary term, on the ground that Ψ goes to zero at ($\pm$) infinity.] Performing another integration by parts on the second term, we conclude that

$$\frac{d\langle x \rangle}{dt} = -\frac{i\hbar}{m} \int \Psi^* \frac{\partial \Psi}{\partial x} \, dx. \quad [1.31]$$

What are we to make of this result? Note that we're talking about the "velocity" of the *expectation* value of x, which is not the same thing as the velocity of the *particle*. Nothing we have seen so far would enable us to calculate the velocity of a particle—it's not even clear what velocity *means* in quantum mechanics. If the particle doesn't have a determinate position (prior to measurement), neither does it have a well-defined velocity. All we could reasonably ask for is the *probability* of getting a particular value. We'll see in Chapter 3 how to construct the probability density for velocity,

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[9] To keep things from getting too cluttered, I suppress the limits of integration when they are $\pm\infty$.

[10] The product rule says that

$$\frac{d}{dx}(fg) = f\frac{dg}{dx} + \frac{df}{dx}g,$$

from which it follows that

$$\int_a^b f\frac{dg}{dx}\,dx = -\int_a^b \frac{df}{dx} g\,dx + fg\Big|_a^b.$$

Under the integral sign, then, you can peel a derivative off one factor in a product and slap it onto the other one—it'll cost you a minus sign, and you'll pick up a boundary term.

given Ψ; for our present purposes it will suffice to postulate that the *expectation value of the velocity is equal to the time derivative of the expectation value of position*:

$$\langle v \rangle = \frac{d\langle x \rangle}{dt}. \tag{1.32}$$

Equation 1.31 tells us, then, how to calculate $\langle v \rangle$ directly from Ψ.

Actually, it is customary to work with momentum ($p = mv$), rather than velocity:

$$\boxed{\langle p \rangle = m\frac{d\langle x \rangle}{dt} = -i\hbar \int \left(\Psi^* \frac{\partial \Psi}{\partial x} \right) dx.} \tag{1.33}$$

Let me write the expressions for $\langle x \rangle$ and $\langle p \rangle$ in a more suggestive way:

$$\langle x \rangle = \int \Psi^*(x)\Psi \, dx, \tag{1.34}$$

$$\langle p \rangle = \int \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi \, dx. \tag{1.35}$$

We say that the **operator**[11] x "represents" position, and the operator $(\hbar/i)(\partial/\partial x)$ "represents" momentum, in quantum mechanics; to calculate expectation values, we "sandwich" the appropriate operator between Ψ^* and Ψ, and integrate.

That's cute, but what about other dynamical variables? The fact is, *all* such quantities can be written in terms of position and momentum. Kinetic energy, for example, is

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m},$$

and angular momentum is

$$\mathbf{L} = \mathbf{r} \times m\mathbf{v} = \mathbf{r} \times \mathbf{p}$$

(the latter, of course, does not occur for motion in one dimension). To calculate the expectation value of such a quantity, we simply replace every p by $(\hbar/i)(\partial/\partial x)$, insert the resulting operator between Ψ^* and Ψ, and integrate:

$$\boxed{\langle Q(x, p) \rangle = \int \Psi^* Q\left(x, \frac{\hbar}{i}\frac{\partial}{\partial x}\right) \Psi \, dx.} \tag{1.36}$$

[11] An operator is an instruction to *do something* to the function that follows. The position operator tells you to *multiply* by x; the momentum operator tells you to *differentiate* with respect to x (and multiply the result by $-i\hbar$). In this book *all* operators will be derivatives (d/dt, d^2/dt^2, $\partial^2/\partial x \partial y$, etc.) or multipliers (2, i, x^2, etc.) or combinations of these.

For example,

$$\langle T \rangle = \frac{-\hbar^2}{2m} \int \Psi^* \frac{\partial^2 \Psi}{\partial x^2}\, dx. \qquad [1.37]$$

Equation 1.36 is a recipe for computing the expectation value of any dynamical quantity for a particle in state Ψ; it subsumes Equations 1.34 and 1.35 as special cases. I have tried in this section to make Equation 1.36 seem plausible, given Born's statistical interpretation, but the truth is that this equation represents such a radically new way of doing business (as compared with classical mechanics) that it's a good idea to get some practice using it before we come back (in Chapter 3) and put it on a firmer theoretical foundation. In the meantime, if you prefer to think of it as an *axiom*, that's fine with me.

Problem 1.11 Why can't you do integration by parts directly on the middle expression in Equation 1.29—pull the time derivative over onto x, note that $\partial x/\partial t = 0$, and conclude that $d\langle x \rangle/dt = 0$?

***Problem 1.12** Calculate $d\langle p \rangle/dt$. *Answer*:

$$\frac{d\langle p \rangle}{dt} = \left\langle -\frac{\partial V}{\partial x} \right\rangle. \qquad [1.38]$$

(This is known as **Ehrenfest's theorem**; it tells us that *expectation values* obey Newton's second law.)

Problem 1.13 Suppose you add a constant V_0 to the potential energy (by "constant" I mean independent of x as well as t). In *classical* mechanics this doesn't change anything, but what about *quantum* mechanics? Show that the wave function picks up a time-dependent phase factor: $\exp(-iV_0 t/\hbar)$. What effect does this have on the expectation value of a dynamical variable?

1.6 THE UNCERTAINTY PRINCIPLE

Imagine that you're holding one end of a very long rope, and you generate a wave by shaking it up and down rhythmically (Figure 1.6). If someone asked you, "Precisely where *is* that wave?" you'd probably think he was a little bit nutty: The wave isn't precisely *any*where—it's spread out over 50 feet or so. On the other hand, if he asked you what its *wavelength* is, you could give him a reasonable answer: It looks like about 6 feet. By contrast, if you gave the rope a sudden jerk (Figure 1.7), you'd get a relatively narrow bump traveling down the line. This time the first question (Where precisely is the wave?) is a sensible one, and the second (What is its wavelength?) seems nutty—it isn't even vaguely periodic, so how can you assign a wavelength to it?

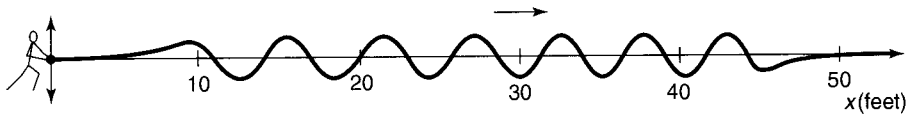

Figure 1.6: A wave with a (fairly) well-defined wavelength but an ill-defined position.

Of course, you can draw intermediate cases, in which the wave is *fairly* well localized and the wavelength is *fairly* well defined, but there is an inescapable trade-off here: The more precise a wave's position is, the less precise is its wavelength, and vice versa.[12] A theorem in Fourier analysis makes all this rigorous, but for the moment I am only concerned with the qualitative argument.

This applies, of course, to *any* wave phenomenon, and hence in particular to the quantum mechanical wave function. Now the wavelength of Ψ is related to the *momentum* of the particle by the **de Broglie formula**[13]:

$$p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda}. \qquad [1.39]$$

Thus a spread in *wavelength* corresponds to a spread in *momentum*, and our general observation now says that the more precisely determined a particle's position is, the less precisely its momentum is determined. Quantitatively,

$$\boxed{\sigma_x \sigma_p \geq \frac{\hbar}{2},} \qquad [1.40]$$

where σ_x is the standard deviation in x, and σ_p is the standard deviation in p. This is Heisenberg's famous **uncertainty principle**. (We'll prove it in Chapter 3, but I wanted to mention it here so you can test it out on the examples in Chapter 2.)

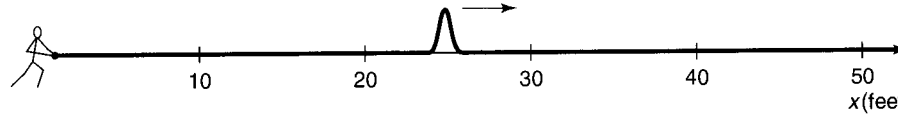

Figure 1.7: A wave with a (fairly) well-defined position but an ill-defined wavelength.

[12] That's why a piccolo player must be right on pitch, whereas a double-bass player can afford to wear garden gloves. For the piccolo, a sixty-fourth note contains many full cycles, and the frequency (we're working in the time domain now, instead of space) is well defined, whereas for the bass, at a much lower register, the sixty-fourth note contains only a few cycles, and all you hear is a general sort of "oomph," with no very clear pitch.

[13] I'll prove this in due course. Many authors take the de Broglie formula as an *axiom*, from which they then deduce the association of momentum with the operator $(\hbar/i)(\partial/\partial x)$. Although this is a conceptually cleaner approach, it involves diverting mathematical complications that I would rather save for later.

Please understand what the uncertainty principle *means*: Like position measurements, momentum measurements yield precise answers—the "spread" here refers to the fact that measurements on identical systems do not yield consistent results. You can, if you want, prepare a system such that repeated position measurements will be very close together (by making Ψ a localized "spike"), but you will pay a price: Momentum measurements on this state will be widely scattered. Or you can prepare a system with a reproducible momentum (by making Ψ a long sinusoidal wave), but in that case position measurements will be widely scattered. And, of course, if you're in a really bad mood you can prepare a system in which neither position nor momentum is well defined: Equation 1.40 is an inequality, and there's no limit on how *big* σ_x and σ_p can be—just make Ψ some long wiggly line with lots of bumps and potholes and no periodic structure.

∗**Problem 1.14** A particle of mass m is in the state

$$\Psi(x, t) = Ae^{-a[(mx^2/\hbar)+it]},$$

where A and a are positive real constants.

(a) Find A.

(b) For what potential energy function $V(x)$ does Ψ satisfy the Schrödinger equation?

(c) Calculate the expectation values of x, x^2, p, and p^2.

(d) Find σ_x and σ_p. Is their product consistent with the uncertainty principle?

CHAPTER 2

THE TIME-INDEPENDENT SCHRÖDINGER EQUATION

2.1 STATIONARY STATES

In Chapter 1 we talked a lot about the wave function and how you use it to calculate various quantities of interest. The time has come to stop procrastinating and confront what is, logically, the prior question: How do you *get* $\Psi(x, t)$ in the first place—how do you go about solving the Schrödinger equation? I shall assume for all of this chapter (and most of this book) that the potential,[1] V, is *independent of* t. In that case the Schrödinger equation can be solved by the method of **separation of variables** (the physicist's first line of attack on any partial differential equation): We look for solutions that are simple *products*,

$$\Psi(x, t) = \psi(x)\, f(t), \qquad [2.1]$$

where ψ (*lower*case) is a function of x alone, and f is a function of t alone. On its face, this is an absurd restriction, and we cannot hope to get more than a tiny subset of all solutions in this way. But hang on, because the solutions we *do* obtain turn out to be of great interest. Moreover, as is typically the case with separation of variables, we will be able at the end to patch together the separable solutions in such a way as to construct the most general solution.

[1] It is tiresome to keep saying "potential energy function," so most people just call V the "potential", even though this invites occasional confusion with *electric* potential, which is actually potential energy *per unit charge*.

For separable solutions we have

$$\frac{\partial \Psi}{\partial t} = \psi \frac{df}{dt}, \quad \frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2\psi}{dx^2} f$$

(*ordinary* derivatives, now), and the Schrödinger equation (Equation 1.1) reads

$$i\hbar \psi \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} f + V\psi f.$$

Or, dividing through by ψf:

$$i\hbar \frac{1}{f} \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V. \qquad [2.2]$$

Now the left side is a function of t alone, and the right side is a function of x alone.[2] The only way this can possibly be true is if both sides are in fact *constant*—otherwise, by varying t, I could change the left side without touching the right side, and the two would no longer be equal. (That's a subtle but crucial argument, so if it's new to you, be sure to pause and think it through.) For reasons that will appear in a moment, we shall call the separation constant E. Then

$$i\hbar \frac{1}{f} \frac{df}{dt} = E,$$

or

$$\frac{df}{dt} = -\frac{iE}{\hbar} f, \qquad [2.3]$$

and

$$-\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V = E,$$

or

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi.} \qquad [2.4]$$

Separation of variables has turned a *partial* differential equation into two *ordinary* differential equations (Equations 2.3 and 2.4). The first of these is easy to solve (just multiply through by dt and integrate); the general solution is $C \exp(-iEt/\hbar)$, but we might as well absorb the constant C into ψ (since the quantity of interest is the product ψf). Then

$$f(t) = e^{-iEt/\hbar}. \qquad [2.5]$$

The second (Equation 2.4) is called the **time-independent Schrödinger equation**; we can go no further with it until the potential $V(x)$ is specified.

[2]Note that this would *not* be true if V were a function of t as well as x.

The rest of this chapter will be devoted to solving the time-independent Schrödinger equation, for a variety of simple potentials. But before we get to that I would like to consider further the question: *What's so great about separable solutions?* After all, *most* solutions to the (time-dependent) Schrödinger equation do *not* take the form $\psi(x)f(t)$. I offer three answers—two of them physical and one mathematical:

1. They are **stationary states**. Although the wave function itself,

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar}, \qquad [2.6]$$

does (obviously) depend on t, the probability density

$$|\Psi(x, t)|^2 = \Psi^*\Psi = \psi^* e^{+iEt/\hbar}\psi e^{-iEt/\hbar} = |\psi(x)|^2 \qquad [2.7]$$

does *not*—the time dependence cancels out.[3] The same thing happens in calculating the expectation value of any dynamical variable; Equation 1.36 reduces to

$$\langle Q(x, p)\rangle = \int \psi^* Q(x, \frac{\hbar}{i}\frac{d}{dx})\psi \, dx. \qquad [2.8]$$

Every expectation value is constant in time; we might as well drop the factor $f(t)$ altogether, and simply use ψ in place of Ψ. (Indeed, it is common to refer to ψ as "the wave function", but this is sloppy language that can be dangerous, and it is important to remember that the *true* wave function always carries that exponential time-dependent factor.) In particular, $\langle x\rangle$ is constant, and hence (Equation 1.33) $\langle p\rangle = 0$. Nothing ever *happens* in a stationary state.

2. They are states of *definite total energy*. In classical mechanics, the total energy (kinetic plus potential) is called the **Hamiltonian**:

$$H(x, p) = \frac{p^2}{2m} + V(x). \qquad [2.9]$$

The corresponding Hamiltonian *operator*, obtained by the canonical substitution $p \to (\hbar/i)(\partial/\partial x)$, is therefore[4]

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x). \qquad [2.10]$$

Thus the time-independent Schrödinger equation (Equation 2.4) can be written

$$\hat{H}\psi = E\psi, \qquad [2.11]$$

---

[3] For normalizable solutions, E must be real (see Problem 2.1a).

[4] Whenever confusion might arise, I'll put a "hat" (^) on the operator to distinguish it from the dynamical variable it represents.

and the expectation value of the total energy is

$$\langle H \rangle = \int \psi^* \hat{H} \psi \, dx = E \int |\psi|^2 \, dx = E. \qquad [2.12]$$

(Note that the normalization of Ψ entails the normalization of ψ.) Moreover,

$$\hat{H}^2 \psi = \hat{H}(\hat{H}\psi) = \hat{H}(E\psi) = E(\hat{H}\psi) = E^2 \psi,$$

and hence

$$\langle H^2 \rangle = \int \psi^* \hat{H}^2 \psi \, dx = E^2 \int |\psi|^2 \, dx = E^2.$$

So the standard deviation in H is given by

$$\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = E^2 - E^2 = 0. \qquad [2.13]$$

But remember, if $\sigma = 0$, then every member of the sample must share the same value (the distribution has zero spread). Conclusion: A separable solution has the property that *every measurement of the total energy is certain to return the value* E. (That's why I chose that letter for the separation constant.)

3. The general solution is a **linear combination** of separable solutions. As we're about to discover, the time-independent Schrödinger equation (Equation 2.4) yields an infinite collection of solutions ($\psi_1(x)$, $\psi_2(x)$, $\psi_3(x)$, ...), each with its associated value of the separation constant (E_1, E_2, E_3, ...); thus there is a different wave function for each **allowed energy**:

$$\Psi_1(x,t) = \psi_1(x)e^{-iE_1 t/\hbar}, \quad \Psi_2(x,t) = \psi_2(x)e^{-iE_2 t/\hbar}, \ldots.$$

Now (as you can easily check for yourself) the (time-*de*pendent) Schrödinger equation (Equation 1.1) has the property that any linear combination[5] of solutions is itself a solution. Once we have found the separable solutions, then, we can immediately construct a much more general solution, of the form

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar}. \qquad [2.14]$$

It so happens that *every* solution to the (time-dependent) Schrödinger equation can be written in this form—it is simply a matter of finding the right constants (c_1, c_2, ...) so as to fit the initial conditions for the problem at hand. You'll see in the following sections how all this works out in practice, and in Chapter 3 we'll put it into more elegant language, but the main point is this: Once you've solved the time-*in*dependent

[5] A linear combination of the functions $f_1(z)$, $f_2(z)$, ... is an expression of the form

$$f(z) = c_1 f_1(z) + c_2 f_2(z) + \cdots,$$

where $c_1, c_2, \ldots$ are any (complex) constants.

Schrödinger equation, you're essentially done; getting from there to the general solution of the time-*de*pendent Schrödinger equation is simple and straightforward.

***Problem 2.1** Prove the following theorems:

(a) For normalizable solutions, the separation constant E must be *real*. *Hint*: Write E (in Equation 2.6) as $E_0 + i\Gamma$ (with E_0 and Γ real), and show that if Equation 1.20 is to hold for all t, Γ must be zero.

(b) ψ can always be taken to be *real* (unlike Ψ, which is necessarily complex). *Note*: This doesn't mean that every solution to the time-independent Schrödinger equation *is* real; what it says is that if you've got one that is *not*, it can always be expressed as a linear combination of solutions (with the same energy) that *are*. So in Equation 2.14 you *might as well* stick to ψ's that are real. *Hint*: If $\psi(x)$ satisfies the time-independent Schrödinger equation for a given E, so too does its complex conjugate, and hence also the real linear combinations $(\psi + \psi^*)$ and $i(\psi - \psi^*)$.

(c) If $V(x)$ is an *even* function [i.e., $V(-x) = V(x)$], then $\psi(x)$ can always be taken to be either even or odd. *Hint*: If $\psi(x)$ satisfies the time-independent Schrödinger equation for a given E, so too does $\psi(-x)$, and hence also the even and odd linear combinations $\psi(x) \pm \psi(-x)$.

***Problem 2.2** Show that E must exceed the minimum value of $V(x)$ for every normalizable solution to the time-independent Schrödinger equation. What is the classical analog to this statement? *Hint*: Rewrite Equation 2.4 in the form

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}[V(x) - E]\psi;$$

if $E < V_{\text{min}}$, then ψ and its second derivative always have the *same sign*—argue that such a function cannot be normalized.

2.2 THE INFINITE SQUARE WELL

Suppose

$$V(x) = \begin{cases} 0, & \text{if } 0 \le x \le a, \\ \infty, & \text{otherwise} \end{cases} \qquad [2.15]$$

(Figure 2.1). A particle in this potential is completely free, except at the two ends ($x = 0$ and $x = a$), where an infinite force prevents it from escaping. A classical model would be a cart on a frictionless horizontal air track, with perfectly elastic bumpers—it just keeps bouncing back and forth forever. (This potential is awfully artificial, but I urge you to treat it with respect. Despite its simplicity—or rather,

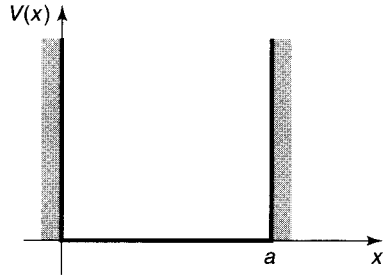

Figure 2.1: The infinite square well potential (Equation 2.15).

precisely *because* of its simplicity—it serves as a wonderfully accessible test case for all the fancy stuff that comes later. We'll refer back to it frequently.)

Outside the well, $\psi(x) = 0$ (the probability of finding the particle there is zero). Inside the well, where $V = 0$, the time-independent Schrödinger equation (Equation 2.4) reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi, \qquad [2.16]$$

or

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}. \qquad [2.17]$$

(By writing it in this way, I have tacitly assumed that $E \geq 0$; we know from Problem 2.2 that $E < 0$ doesn't work.) Equation 2.17 is the (classical) **simple harmonic oscillator** equation; the general solution is

$$\psi(x) = A\sin kx + B\cos kx, \qquad [2.18]$$

where A and B are arbitrary constants. Typically, these constants are fixed by the **boundary conditions** of the problem. What are the appropriate boundary conditions for $\psi(x)$? Ordinarily, both ψ and $d\psi/dx$ are continuous, but where the potential goes to infinity only the first of these applies. (I'll *prove* these boundary conditions, and account for the exception when $V = \infty$, later on; for now I hope you will trust me.)

Continuity of $\psi(x)$ requires that

$$\psi(0) = \psi(a) = 0, \qquad [2.19]$$

so as to join onto the solution outside the well. What does this tell us about A and B? Well,

$$\psi(0) = A\sin 0 + B\cos 0 = B,$$

so $B = 0$, and hence

$$\psi(x) = A\sin kx. \qquad [2.20]$$

Then $\psi(a) = A\sin ka$, so either $A = 0$ [in which case we're left with the trivial—nonnormalizable—solution $\psi(x) = 0$], or else $\sin ka = 0$, which means that

$$ka = 0,\ \pm\pi,\ \pm 2\pi,\ \pm 3\pi, \ldots. \qquad [2.21]$$

But $k = 0$ is no good [again, that would imply $\psi(x) = 0$], and the negative solutions give nothing new, since $\sin(-\theta) = -\sin(\theta)$ and we can absorb the minus sign into A. So the *distinct* solutions are

$$k_n = \frac{n\pi}{a}, \quad \text{with } n = 1,\ 2,\ 3, \ldots. \tag{2.22}$$

Curiously, the boundary condition at $x = a$ does not determine the constant A, but rather the constant k, and hence the possible values of E:

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}.} \tag{2.23}$$

In sharp contrast to the classical case, a quantum particle in the infinite square well cannot have just *any* old energy—only these special **allowed** values. Well, how *do* we fix the constant A? Answer: We *normalize* ψ:

$$\int_0^a |A|^2 \sin^2(kx)\, dx = |A|^2 \frac{a}{2} = 1, \quad \text{so} \quad |A|^2 = \frac{2}{a}.$$

This only determines the *magnitude* of A, but it is simplest to pick the positive real root: $A = \sqrt{2/a}$ (the phase of A carries no physical significance anyway). Inside the well, then, the solutions are

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right).} \tag{2.24}$$

As promised, the time-independent Schrödinger equation has delivered an infinite set of solutions, one for each integer n. The first few of these are plotted in Figure 2.2; they look just like the standing waves on a string of length a. ψ_1, which carries the lowest energy, is called the **ground state**; the others, whose energies increase in proportion to n^2, are called **excited states**. As a group, the functions $\psi_n(x)$ have some interesting and important properties:

1. They are alternately **even** and **odd**, with respect to the center of the well. (ψ_1 is even, ψ_2 is odd, ψ_3 is even, and so on.[6])

2. As you go up in energy, each successive state has one more **node** (zero crossing). ψ_1 has none (the end points don't count), ψ_2 has one, ψ_3 has two, and so on.

[6]To make this symmetry more apparent, some authors center the well at the origin (so that it runs from $-a/2$ to $+a/2$. The even functions are then cosines, and the odd ones are sines. See Problem 2.4.

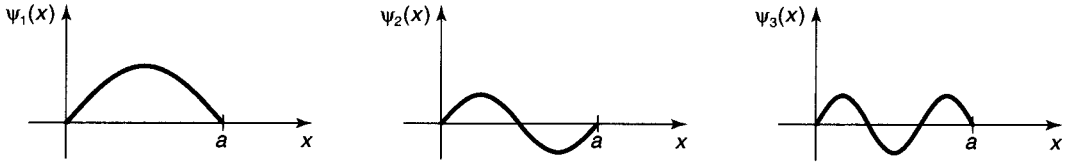

Figure 2.2: The first three stationary states of the infinite square well (Equation 2.24).

3. They are mutually **orthogonal**, in the sense that

$$\int \psi_m(x)^* \psi_n(x)\, dx = 0, \qquad [2.25]$$

whenever $m \neq n$. Proof

$$\int \psi_m(x)^* \psi_n(x)\, dx = \frac{2}{a}\int_0^a \sin\left(\frac{m\pi}{a}x\right)\sin\left(\frac{n\pi}{a}x\right) dx$$

$$= \frac{1}{a}\int_0^a \left[\cos\left(\frac{m-n}{a}\pi x\right) - \cos\left(\frac{m+n}{a}\pi x\right)\right] dx$$

$$= \left\{\frac{1}{(m-n)\pi}\sin\left(\frac{m-n}{a}\pi x\right) - \frac{1}{(m+n)\pi}\sin\left(\frac{m+n}{a}\pi x\right)\right\}\Bigg|_0^a$$

$$= \frac{1}{\pi}\left\{\frac{\sin[(m-n)\pi]}{(m-n)} - \frac{\sin[(m+n)\pi]}{(m+n)}\right\} = 0.$$

Note that this argument does *not* work if $m = n$ (can you spot the point at which it fails?); in that case normalization tells us that the integral is 1. In fact, we can combine orthogonality and normalization into a single statement[7]:

$$\int \psi_m(x)^* \psi_n(x)\, dx = \delta_{mn}, \qquad [2.26]$$

where δ_{mn} (the so-called **Kronecker delta**) is defined in the usual way,

$$\delta_{mn} = \begin{cases} 0, & \text{if } m \neq n; \\ 1, & \text{if } m = n. \end{cases} \qquad [2.27]$$

We say that the ψ's are **orthonormal**.

4. They are **complete**, in the sense that any *other* function, $f(x)$, can be expressed as a linear combination of them:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}}\sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right). \qquad [2.28]$$

[7] In this case the ψ's are real, so the * on ψ_m is unnecessary, but for future purposes it's a good idea to get in the habit of putting it there.

I'm not about to *prove* the completeness of the functions $\sqrt{2/a}\sin(n\pi x/a)$, but if you've studied advanced calculus you will recognize that Equation 2.28 is nothing but the **Fourier series** for $f(x)$, and the fact that "any" function can be expanded in this way is sometimes called **Dirichlet's theorem.**[8] The expansion coefficients (c_n) can be evaluated—for a given $f(x)$—by a method I call **Fourier's trick**, which beautifully exploits the orthonormality of $\{\psi_n\}$: Multiply both sides of Equation 2.28 by $\psi_m(x)^*$, and integrate.

$$\int \psi_m(x)^* f(x)\,dx = \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x)\,dx = \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m. \quad [2.29]$$

(Notice how the Kronecker delta kills every term in the sum except the one for which $n = m$.) Thus the mth coefficient in the expansion of $f(x)$ is given by

$$c_m = \int \psi_m(x)^* f(x)\,dx. \quad [2.30]$$

These four properties are extremely powerful, and they are not peculiar to the infinite square well. The first is true whenever the potential itself is an even function; the second is universal, regardless of the shape of the potential.[9] Orthogonality is also quite general—I'll show you the proof in Chapter 3. Completeness holds for all the potentials you are likely to encounter, but the proofs tend to be nasty and laborious; I'm afraid most physicists simply *assume* completeness and hope for the best.

The stationary states (Equation 2.6) for the infinite square well are evidently

$$\Psi_n(x,t) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)e^{-i(n^2\pi^2\hbar/2ma^2)t}. \quad [2.31]$$

I claimed (Equation 2.14) that the most general solution to the (time-dependent) Schrödinger equation is a linear combination of stationary states:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)e^{-i(n^2\pi^2\hbar/2ma^2)t}. \quad [2.32]$$

If you doubt that this *is* a solution, by all means *check* it! It remains only for me to demonstrate that I can fit any prescribed initial wave function, $\Psi(x,0)$, by appropriate choice of the coefficients c_n. According to Equation 2.32,

$$\Psi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x).$$

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[8] See, for example, Mary Boas, *Mathematical Methods in the Physical Sciences*, 2nd ed. (New York: John Wiley & Sons, 1983), p. 313; $f(x)$ can even have a finite number of finite discontinuities.

[9] See, for example, John L. Powell and Bernd Crasemann, *Quantum Mechanics* (Reading, MA: Addison-Wesley, 1961), p. 126.

The completeness of the ψ's (confirmed in this case by Dirichlet's theorem) guarantees that I can always express $\Psi(x, 0)$ in this way, and their orthonormality licenses the use of Fourier's trick to determine the actual coefficients:

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x, 0)\, dx. \qquad [2.33]$$

That does it: Given the initial wave function, $\Psi(x, 0)$, we first compute the expansion coefficients c_n, using Equation 2.33, and then plug these into Equation 2.32 to obtain $\Psi(x, t)$. Armed with the wave function, we are in a position to compute any dynamical quantities of interest, using the procedures in Chapter 1. And this same ritual applies to *any* potential—the only things that change are the functional form of the ψ's and the equation for the allowed energies.

Problem 2.3 Show that there is no acceptable solution to the (time-independent) Schrödinger equation (for the infinite square well) with $E = 0$ or $E < 0$. (This is a special case of the general theorem in Problem 2.2, but this time do it by explicitly solving the Schrödinger equation and showing that you cannot meet the boundary conditions.)

Problem 2.4 Solve the time-independent Schrödinger equation with appropriate boundary conditions for an infinite square well centered at the origin [$V(x) = 0$, for $-a/2 < x < +a/2$; $V(x) = \infty$ otherwise]. Check that your allowed energies are consistent with mine (Equation 2.23), and confirm that your ψ's can be obtained from mine (Equation 2.24) by the substitution $x \to x - a/2$.

***Problem 2.5** Calculate $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$, $\langle p^2 \rangle$, σ_x, and σ_p, for the nth stationary state of the infinite square well. Check that the uncertainty principle is satisfied. Which state comes closest to the uncertainty limit?

****Problem 2.6** A particle in the infinite square well has as its initial wave function an even mixture of the first two stationary states:

$$\Psi(x, 0) = A[\psi_1(x) + \psi_2(x)].$$

(a) Normalize $\Psi(x, 0)$. (That is, find A. This is very easy if you exploit the orthonormality of ψ_1 and ψ_2. Recall that, having normalized Ψ at $t = 0$, you can rest assured that it *stays* normalized—if you doubt this, check it explicitly after doing part b.)

(b) Find $\Psi(x, t)$ and $|\Psi(x, t)|^2$. (Express the latter in terms of sinusoidal functions of time, eliminating the exponentials with the help of **Euler's formula**: $e^{i\theta} = \cos\theta + i \sin\theta$.) Let $\omega \equiv \pi^2\hbar/2ma^2$.

(c) Compute $\langle x \rangle$. Notice that it oscillates in time. What is the frequency of the oscillation? What is the amplitude of the oscillation? (If your amplitude is greater than $a/2$, go directly to jail.)

(d) Compute $\langle p \rangle$. (As Peter Lorre would say, "Do it ze *kveek* vay, Johnny!")

(e) Find the expectation value of H. How does it compare with E_1 and E_2?

(f) A *classical* particle in this well would bounce back and forth between the walls. If its energy is equal to the expectation value you found in (e), what is the frequency of the classical motion? How does it compare with the quantum frequency you found in (c)?

Problem 2.7 Although the *overall* phase constant of the wave function is of no physical significance (it cancels out whenever you calculate a measureable quantity), the *relative* phase of the expansion coefficients in Equation 2.14 *does* matter. For example, suppose we change the relative phase of ψ_1 and ψ_2 in Problem 2.6:

$$\Psi(x, 0) = A[\psi_1(x) + e^{i\phi}\psi_2(x)],$$

where ϕ is some constant. Find $\Psi(x, t)$, $|\Psi(x, t)|^2$, and $\langle x \rangle$, and compare your results with what you got before. Study the special cases $\phi = \pi/2$ and $\phi = \pi$.

***Problem 2.8** A particle in the infinite square well has the initial wave function

$$\Psi(x, 0) = Ax(a - x).$$

(a) Normalize $\Psi(x, 0)$. Graph it. Which stationary state does it most closely resemble? On that basis, estimate the expectation value of the energy.

(b) Compute $\langle x \rangle$, $\langle p \rangle$, and $\langle H \rangle$, at $t = 0$. (*Note*: This time you cannot get $\langle p \rangle$ by differentiating $\langle x \rangle$, because you only know $\langle x \rangle$ at one instant of time.) How does $\langle H \rangle$ compare with your estimate in (a)?

***Problem 2.9** Find $\Psi(x, t)$ for the initial wave function in Problem 2.8. Evaluate c_1, c_2, and c_3 numerically, to five decimal places, and comment on these numbers. (c_n tells you, roughly speaking, how much ψ_n is "contained in" Ψ.) Suppose you measured the energy at time $t_0 > 0$, and got the value E_3. Knowing that immediate repetition of the measurement must return the same value, what can you say about the coefficients c_n *after* the measurement? (This is an example of the "collapse of the wave function", which we discussed briefly in Chapter 1.)

***Problem 2.10** The wave function (Equation 2.14) has got to be normalized; given that the ψ_n's are orthonormal, what does this tell you about the coefficients c_n? *Answer*:

$$\sum_{n=1}^{\infty} |c_n|^2 = 1. \qquad [2.34]$$

(In particular, $|c_n|^2$ is always ≤ 1.) Show that

$$\langle H \rangle = \sum_{n=1}^{\infty} E_n |c_n|^2. \qquad [2.35]$$

Incidentally, it follows that $\langle H \rangle$ is constant in time, which is one manifestation of **conservation of energy** in quantum mechanics.

2.3 THE HARMONIC OSCILLATOR

The paradigm for a classical harmonic oscillator is a mass m attached to a spring of force constant k. The motion is governed by **Hooke's law**,

$$F = -kx = m\frac{d^2x}{dt^2}$$

(as always, we ignore friction), and the solution is

$$x(t) = A\sin(\omega t) + B\cos(\omega t),$$

where

$$\omega \equiv \sqrt{\frac{k}{m}} \qquad [2.36]$$

is the (angular) frequency of oscillation. The potential energy is

$$V(x) = \frac{1}{2}kx^2; \qquad [2.37]$$

its graph is a parabola.

Of course, there's no such thing as a *perfect* simple harmonic oscillator—if you stretch it too far the spring is going to break, and typically Hooke's law fails long before that point is reached. But practically any potential is *approximately* parabolic, in the neighborhood of a local minimum (Figure 2.3). Formally, if we expand $V(x)$ in a **Taylor series** about the minimum:

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + \cdots,$$

subtract $V(x_0)$ [you can add a constant to $V(x)$ with impunity, since that doesn't change the force], recognize that $V'(x_0) = 0$ (since x_0 is a minimum), and drop the higher-order terms [which are negligible as long as $(x - x_0)$ stays small], the potential becomes

$$V(x) \cong \frac{1}{2}V''(x_0)(x - x_0)^2,$$

which describes simple harmonic oscillation (about the point x_0), with an effective spring constant $k = V''(x_0)$.[10] That's why the simple harmonic oscillator is so important: Virtually *any* oscillatory motion is approximately simple harmonic, as long as the amplitude is small.

[10]Note that $V''(x_0) \geq 0$, since by assumption x_0 is a minimum. Only in the rare case $V''(x_0) = 0$ is the oscillation not even approximately simple harmonic.

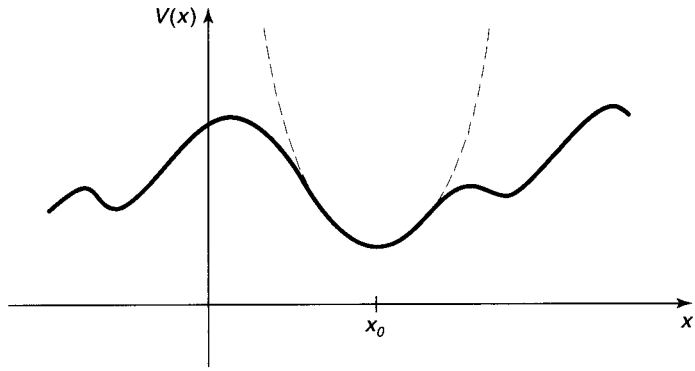


Figure 2.3: Parabolic approximation (dashed curve) to an arbitrary potential, in the neighborhood of a local minimum.

The *quantum* problem is to solve the Schrödinger equation for the potential

$$V(x) = \frac{1}{2}m\omega^2 x^2 \qquad [2.38]$$

(it is customary to eliminate the spring constant in favor of the classical frequency, using Equation 2.36). As we have seen, it suffices to solve the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi = E\psi. \qquad [2.39]$$

In the literature you will find two entirely different approaches to this problem. The first is a straighforward "brute force" solution to the differential equation, using the method of **power series expansion**; it has the virtue that the same strategy can be applied to many other potentials (in fact, we'll use it in Chapter 4 to treat the Coulomb potential). The second is a diabolically clever algebraic technique, using so-called **ladder operators**. I'll show you the algebraic method first, because it is quicker and simpler (and more fun); if you want to skip the analytic method for now, that's fine, but you should certainly plan to study it at some stage.

2.3.1 Algebraic Method

To begin with, let's rewrite Equation 2.39 in a more suggestive form:

$$\frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 + (m\omega x)^2\right]\psi = E\psi. \qquad [2.40]$$

The idea is to *factor* the term in square brackets. If these were *numbers*, it would be easy:

$$u^2 + v^2 = (u - iv)(u + iv).$$

Here, however, it's not quite so simple, because u and v are *operators*, and operators do not, in general, **commute** (uv is not the same as vu). Still, this does invite us to take a look at the expressions

$$a_{\pm} \equiv \frac{1}{\sqrt{2m}}\left(\frac{\hbar}{i}\frac{d}{dx} \pm im\omega x\right). \qquad [2.41]$$

What *is* their product, a_-a_+? *Warning*: Operators can be slippery to work with in the abstract, and you are bound to make mistakes unless you give them a "test function", $f(x)$, to act on. At the end you can throw away the test function, and you'll be left with an equation involving the operators alone. In the present case, we have

$$\begin{aligned}(a_-a_+)f(x) &= \frac{1}{2m}\left(\frac{\hbar}{i}\frac{d}{dx} - im\omega x\right)\left(\frac{\hbar}{i}\frac{d}{dx} + im\omega x\right)f(x)\\ &= \frac{1}{2m}\left(\frac{\hbar}{i}\frac{d}{dx} - im\omega x\right)\left(\frac{\hbar}{i}\frac{df}{dx} + im\omega xf\right)\\ &= \frac{1}{2m}\left[-\hbar^2\frac{d^2f}{dx^2} + \hbar m\omega\frac{d}{dx}(xf) - \hbar m\omega x\frac{df}{dx} + (m\omega x)^2 f\right]\\ &= \frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 + (m\omega x)^2 + \hbar m\omega\right]f(x).\end{aligned}$$

[I used $d(xf)/dx = x(df/dx) + f$ in the last step.] Discarding the test function, we conclude that

$$a_-a_+ = \frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 + (m\omega x)^2\right] + \frac{1}{2}\hbar\omega. \qquad [2.42]$$

Evidently Equation 2.40 does *not* factor perfectly—there's an extra term $(1/2)\hbar\omega$. However, if we pull this over to the other side, the Schrödinger equation[11] becomes

$$(a_-a_+ - \frac{1}{2}\hbar\omega)\psi = E\psi. \qquad [2.43]$$

Notice that the ordering of the factors a_+ and a_- is important here; the same argument, with a_+ on the left, yields

$$a_+a_- = \frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 + (m\omega x)^2\right] - \frac{1}{2}\hbar\omega. \qquad [2.44]$$

Thus

$$a_-a_+ - a_+a_- = \hbar\omega, \qquad [2.45]$$

[11] I'm getting tired of writing "time-independent Schrödinger equation," so when it's clear from the context which one I mean, I'll just call it the Schrödinger equation.

and the Schrödinger equation can also be written

$$(a_+a_- + \frac{1}{2}\hbar\omega)\psi = E\psi. \qquad [2.46]$$

Now, here comes the crucial step: I claim that *if ψ satisfies the Schrödinger equation, with energy E, then $a_+\psi$ satisfies the Schrödinger equation with energy $(E + \hbar\omega)$*. Proof:

$$(a_+a_- + \frac{1}{2}\hbar\omega)(a_+\psi) = (a_+a_-a_+ + \frac{1}{2}\hbar\omega a_+)\psi$$

$$= a_+(a_-a_+ + \frac{1}{2}\hbar\omega)\psi = a_+[(a_-a_+ - \frac{1}{2}\hbar\omega)\psi + \hbar\omega\psi]$$

$$= a_+(E\psi + \hbar\omega\psi) = (E + \hbar\omega)(a_+\psi). \text{ QED}$$

[Notice that whereas the ordering of a_+ and a_- *does* matter, the ordering of $a_\pm$ and any *constants* (such as $\hbar$, ω, and E) does not.] By the same token, $a_-\psi$ is a solution with energy $(E - \hbar\omega)$:

$$(a_-a_+ - \frac{1}{2}\hbar\omega)(a_-\psi) = a_-(a_+a_- - \frac{1}{2}\hbar\omega)\psi$$

$$= a_-[(a_+a_- + \frac{1}{2}\hbar\omega)\psi - \hbar\omega\psi] = a_-(E\psi - \hbar\omega\psi)$$

$$= (E - \hbar\omega)(a_-\psi).$$

Here, then, is a wonderful machine for grinding out new solutions, with higher and lower energies—if we can just find *one* solution, to get started! We call $a_\pm$ **ladder operators**, because they allow us to climb up and down in energy; a_+ is called the **raising operator**, and a_- the **lowering operator**. The "ladder" of states is illustrated in Figure 2.4.

But wait! What if I apply the lowering operator repeatedly? Eventually I'm going to reach a state with energy less than zero, which (according to the general theorem in Problem 2.2) does not exist! At some point the machine must fail. How can that happen? We know that $a_-\psi$ is a new solution to the Schrödinger equation, but *there is no guarantee that it will be normalizable*—it might be zero, or its square integral might be infinite. Problem 2.11 rules out the latter possibility. Conclusion: There must occur a "lowest rung" (let's call it ψ_0) such that

$$a_-\psi_0 = 0. \qquad [2.47]$$

That is to say,

$$\frac{1}{\sqrt{2m}}\left(\frac{\hbar}{i}\frac{d\psi_0}{dx} - im\omega x\psi_0\right) = 0,$$

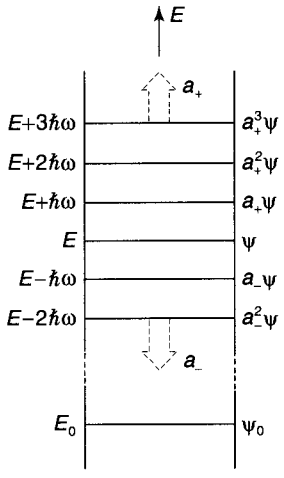


Figure 2.4: The ladder of stationary states for the simple harmonic oscillator.

or

$$\frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar}x\psi_0.$$

This differential equation for ψ_0 is easy to solve:

$$\int \frac{d\psi_0}{\psi_0} = -\frac{m\omega}{\hbar}\int x\,dx \quad \Rightarrow \quad \ln\psi_0 = -\frac{m\omega}{2\hbar}x^2 + \text{constant},$$

so

$$\psi_0(x) = A_0 e^{-\frac{m\omega}{2\hbar}x^2}. \qquad [2.48]$$

To determine the energy of this state, we plug it into the Schrödinger equation (in the form of Equation 2.46), $(a_+a_- + (1/2)\hbar\omega)\psi_0 = E_0\psi_0$, and exploit the fact that $a_-\psi_0 = 0$. Evidently

$$E_0 = \frac{1}{2}\hbar\omega. \qquad [2.49]$$

With our foot now securely planted on the bottom rung[12] (the ground state of the quantum oscillator), we simply apply the raising operator to generate the excited states[13]:

$$\boxed{\psi_n(x) = A_n(a_+)^n e^{-\frac{m\omega}{2\hbar}x^2}, \quad \text{with } E_n = (n + \frac{1}{2})\hbar\omega.} \qquad [2.50]$$

[12]Note that there can only be *one* ladder, because the lowest state is uniquely determined by Equation 2.47. Thus we have in fact obtained *all* the (normalizable) solutions.

[13]In the case of the harmonic oscillator, it is convenient to depart from our usual custom and number the states starting with $n = 0$ instead of $n = 1$. Obviously, the lower limit on the sum in equations such as Equation 2.14 should be altered accordingly.

(This method does not immediately determine the normalization factor A_n; I'll let you work that out for yourself in Problem 2.12.) For example,

$$\psi_1 = A_1 a_+ e^{-\frac{m\omega}{2\hbar}x^2} = A_1 \frac{1}{\sqrt{2m}} \left(\frac{\hbar}{i} \frac{d}{dx} + im\omega x \right) e^{-\frac{m\omega}{2\hbar}x^2}$$
$$= \frac{A_1}{\sqrt{2m}} \left[\frac{\hbar}{i} \left(-\frac{m\omega}{\hbar} x \right) e^{-\frac{m\omega}{2\hbar}x^2} + im\omega x e^{-\frac{m\omega}{2\hbar}x^2} \right],$$

which simplifies to

$$\psi_1(x) = (iA_1\omega\sqrt{2m}) x e^{-\frac{m\omega}{2\hbar}x^2}. \qquad [2.51]$$

I wouldn't want to calculate ψ_{50} in this way, but never mind: We have found all the allowed energies, and in principle we have determined the stationary states—the rest is just computation.

Problem 2.11 Show that the lowering operator cannot generate a state of infinite **norm** (i.e., $\int |a_-\psi|^2 dx < \infty$, if ψ itself is a normalized solution to the Schrödinger equation). What does this tell you in the case $\psi = \psi_0$? *Hint*: Use integration by parts to show that

$$\int_{-\infty}^{\infty} (a_-\psi)^* (a_-\psi)\, dx = \int_{-\infty}^{\infty} \psi^* (a_+ a_-\psi)\, dx.$$

Then invoke the Schrödinger equation (Equation 2.46) to obtain

$$\int_{-\infty}^{\infty} |a_-\psi|^2\, dx = E - \frac{1}{2}\hbar\omega,$$

where E is the energy of the state ψ.

****Problem 2.12**

(a) The raising and lowering operators generate new solutions to the Schrödinger equation, but these new solutions are not correctly normalized. Thus $a_+\psi_n$ is *proportional* to ψ_{n+1}, and $a_-\psi_n$ is *proportional* to ψ_{n-1}, but we'd like to know the precise proportionality constants. Use integration by parts and the Schrödinger equation (Equations 2.43 and 2.46) to show that

$$\int_{-\infty}^{\infty} |a_+\psi_n|^2\, dx = (n+1)\hbar\omega, \quad \int_{-\infty}^{\infty} |a_-\psi_n|^2\, dx = n\hbar\omega,$$

and hence (with i's to keep the wavefunctions real)

$$a_+\psi_n = i\sqrt{(n+1)\hbar\omega}\,\psi_{n+1}, \qquad [2.52]$$

$$a_-\psi_n = -i\sqrt{n\hbar\omega}\,\psi_{n-1}. \qquad [2.53]$$

(b) Use Equation 2.52 to determine the normalization constant A_n in Equation 2.50. (You'll have to normalize ψ_0 "by hand".) *Answer*:

$$A_n = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{(-i)^n}{\sqrt{n!(\hbar\omega)^n}}. \qquad [2.54]$$

***Problem 2.13** Using the methods and results of this section,

(a) Normalize ψ_1 (Equation 2.51) by direct integration. Check your answer against the general formula (Equation 2.54).

(b) Find ψ_2, but don't bother to normalize it.

(c) Sketch ψ_0, ψ_1, and ψ_2.

(d) Check the orthogonality of ψ_0, ψ_1, and ψ_2. *Note*: If you exploit the evenness and oddness of the functions, there is really only one integral left to evaluate explicitly.

***Problem 2.14** Using the results of Problems 2.12 and 2.13,

(a) Compute $\langle x\rangle$, $\langle p\rangle$, $\langle x^2\rangle$, and $\langle p^2\rangle$, for the states ψ_0 and ψ_1. *Note*: In this and most problems involving the harmonic oscillator, it simplifies the notation if you introduce the variable $\xi \equiv \sqrt{m\omega/\hbar}\, x$ and the constant $\alpha \equiv (m\omega/\pi\hbar)^{1/4}$.

(b) Check the uncertainty principle for these states.

(c) Compute $\langle T\rangle$ and $\langle V\rangle$ for these states (no new integration allowed!). Is their sum what you would expect?

2.3.2 Analytic Method

We return now to the Schrödinger equation for the harmonic oscillator (Equation 2.39):

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi.$$

Things look a little cleaner if we introduce the dimensionless variable

$$\xi \equiv \sqrt{\frac{m\omega}{\hbar}}x; \qquad [2.55]$$

in terms of ξ, the Schrödinger equation reads

$$\frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi, \qquad [2.56]$$

where K is the energy, in units of $(1/2)\hbar\omega$:

$$K \equiv \frac{2E}{\hbar\omega}. \qquad [2.57]$$

Our problem is to solve Equation 2.56, and in the process obtain the "allowed" values of K (and hence of E).

To begin with, note that at very large ξ (which is to say, at very large x), ξ^2 completely dominates over the constant K, so in this regime

$$\frac{d^2\psi}{d\xi^2} \approx \xi^2\psi, \qquad [2.58]$$

which has the approximate solution (check it!)

$$\psi(\xi) \approx Ae^{-\xi^2/2} + Be^{+\xi^2/2}. \qquad [2.59]$$

The B term is clearly not normalizable (it blows up as $|x| \to \infty$); the physically acceptable solutions, then, have the asymptotic form

$$\psi(\xi) \to (\ )e^{-\xi^2/2}, \quad \text{at large } \xi. \qquad [2.60]$$

This suggests that we "peel off" the exponential part,

$$\psi(\xi) = h(\xi)e^{-\xi^2/2}, \qquad [2.61]$$

in hopes that what remains $[h(\xi)]$ has a simpler functional form than $\psi(\xi)$ itself.[14] Differentiating Equation 2.61, we have

$$\frac{d\psi}{d\xi} = \left(\frac{dh}{d\xi} - \xi h\right)e^{-\xi^2/2}$$

and

$$\frac{d^2\psi}{d\xi^2} = \left(\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (\xi^2 - 1)h\right)e^{-\xi^2/2},$$

so the Schrödinger equation (Equation 2.56) becomes

$$\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (K - 1)h = 0. \qquad [2.62]$$

I propose to look for a solution to Equation 2.62 in the form of a power series in ξ[15]:

$$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \cdots = \sum_{j=0}^{\infty} a_j\xi^j. \qquad [2.63]$$

---

[14] Note that although we invoked some approximations to *motivate* Equation 2.61, what follows is *exact*. The device of stripping off the asymptotic behavior is the standard first step in the power series method for solving differential equations—see, for example, Boas (cited in footnote 8), Chapter 12.

[15] According to Taylor's theorem, any reasonably well-behaved function can be expressed as a power series, so Equation 2.63 involves no real loss of generality. For conditions on the applicability of the series method, see Boas (cited in footnote 8) or George Arfken, *Mathematical Methods for Physicists*, 3rd ed. (Orlando, FL: Academic Press, 1985), Section 8.5.

Differentiating the series term by term,

$$\frac{dh}{d\xi} = a_1 + 2a_2\xi + 3a_3\xi^2 + \cdots = \sum_{j=0}^{\infty} j a_j \xi^{j-1},$$

and

$$\frac{d^2h}{d\xi^2} = 2a_2 + 2 \cdot 3a_3\xi + 3 \cdot 4a_4\xi^2 + \cdots = \sum_{j=0}^{\infty} (j+1)(j+2)a_{j+2}\xi^j.$$

Putting these into Equation 2.62, we find

$$\sum_{j=0}^{\infty} \left[(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j\right]\xi^j = 0. \qquad [2.64]$$

It follows (from the uniqueness of power series expansions[16]) that the coefficient of *each power* of ξ must vanish,

$$(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j = 0,$$

and hence that

$$a_{j+2} = \frac{(2j+1-K)}{(j+1)(j+2)}a_j. \qquad [2.65]$$

This **recursion formula** is entirely equivalent to the Schrödinger equation itself. Given a_0 it enables us (in principle) to generate $a_2, a_4, a_6, \ldots$, and given a_1 it generates $a_3, a_5, a_7, \ldots$. Let us write

$$h(\xi) = h_{\text{even}}(\xi) + h_{\text{odd}}(\xi), \qquad [2.66]$$

where

$$h_{\text{even}}(\xi) \equiv a_0 + a_2\xi^2 + a_4\xi^4 + \cdots$$

is an *even* function of ξ (since it involves only even powers), built on a_0, and

$$h_{\text{odd}}(\xi) \equiv a_1\xi + a_3\xi^3 + a_5\xi^5 + \cdots$$

is an *odd* function, built on a_1. Thus Equation 2.65 determines $h(\xi)$ in terms of two arbitrary constants (a_0 and a_1)—which is just what we would expect, for a second-order differential equation.

However, not all the solutions so obtained are normalizable. For at very large j, the recursion formula becomes (approximately)

$$a_{j+2} \approx \frac{2}{j}a_j,$$

[16] See, for example, Arfken (footnote 15), Section 5.7.

with the (approximate) solution

$$a_j \approx \frac{C}{(j/2)!},$$

for some constant C, and this yields (at large ξ, where the higher powers dominate)

$$h(\xi) \approx C \sum \frac{1}{(j/2)!} \xi^j \approx C \sum \frac{1}{k!} \xi^{2k} \approx C e^{\xi^2}.$$

Now, if h goes like $\exp(\xi^2)$, then ψ (remember ψ?—that's what we're trying to calculate) goes like $\exp(\xi^2/2)$ (Equation 2.61), which is precisely the asymptotic behavior we *don't* want.[17] There is only one way to wiggle out of this: For normalizable solutions *the power series must terminate.* There must occur some "highest" j (call it n) such that the recursion formula spits out $a_{n+2} = 0$ (this will truncate *either* the series h_{even} *or* the series h_{odd}; the *other* one must be zero from the start). For physically acceptable solutions, then, we must have

$$K = 2n + 1,$$

for some positive integer n, which is to say (referring to Equation 2.57) that the *energy* must be of the form

$$E_n = (n + \frac{1}{2})\hbar\omega, \quad \text{for } n = 0, 1, 2, \ldots. \tag{2.67}$$

Thus we recover, by a completely different method, the fundamental quantization condition we found algebraically in Equation 2.50.

For the allowed values of K, the recursion formula reads

$$a_{j+2} = \frac{-2(n-j)}{(j+1)(j+2)} a_j. \tag{2.68}$$

If $n = 0$, there is only one term in the series (we must pick $a_1 = 0$ to kill h_{odd}, and $j = 0$ in Equation 2.68 yields $a_2 = 0$):

$$h_0(\xi) = a_0,$$

and hence

$$\psi_0(\xi) = a_0 e^{-\xi^2/2}$$

(which reproduces Equation 2.48). For $n = 1$ we pick $a_0 = 0$,[18] and Equation 2.68 with $j = 1$ yields $a_3 = 0$, so

$$h_1(\xi) = a_1 \xi,$$

[17] It's no surprise that the ill-behaved solutions are still contained in Equation 2.65; this recursion relation is equivalent to the Schrödinger equation, so it's got to include both the asymptotic forms we found in Equation 2.59.

[18] Note that there is a completely different set of coefficients a_j for each value of n.

and hence

$$\psi_1(\xi) = a_1 \xi e^{-\xi^2/2}$$

(confirming Equation 2.51). For $n = 2$, $j = 0$ yields $a_2 = -2a_0$, and $j = 2$ gives $a_4 = 0$, so

$$h_2(\xi) = a_0(1 - 2\xi^2)$$

and

$$\psi_2(\xi) = a_0(1 - 2\xi^2)e^{-\xi^2/2},$$

and so on. (Compare Problem 2.13, where the same result was obtained by algebraic means.)

In general, $h_n(\xi)$ will be a polynomial of degree n in ξ, involving even powers only, if n is an even integer, and odd powers only, if n is an odd integer. Apart from the overall factor (a_0 or a_1) they are the so-called **Hermite polynomials**, $H_n(\xi)$.[19] The first few of them are listed in Table 2.1. By tradition, the arbitrary multiplicative factor is chosen so that the coefficient of the highest power of ξ is 2^n. With this convention, the normalized[20] stationary states for the harmonic oscillator are

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}. \qquad [2.69]$$

They are identical (of course) to the ones we obtained algebraically in Equation 2.50. In Figure 2.5a I have plotted $\psi_n(x)$ for the first few n's.

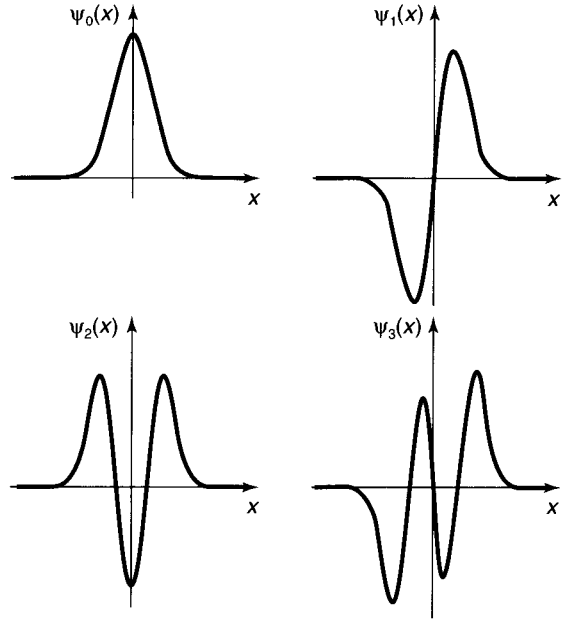
The quantum oscillator is strikingly different from its classical counterpart—not only are the energies quantized, but the position distributions have some bizarre features. For instance, the probability of finding the particle outside the classically allowed range (that is, with x greater than the classical amplitude for the energy in question) is *not* zero (see Problem 2.15), and in all odd states the probability of

Table 2.1: The first few Hermite polynomials, $H_n(x)$.

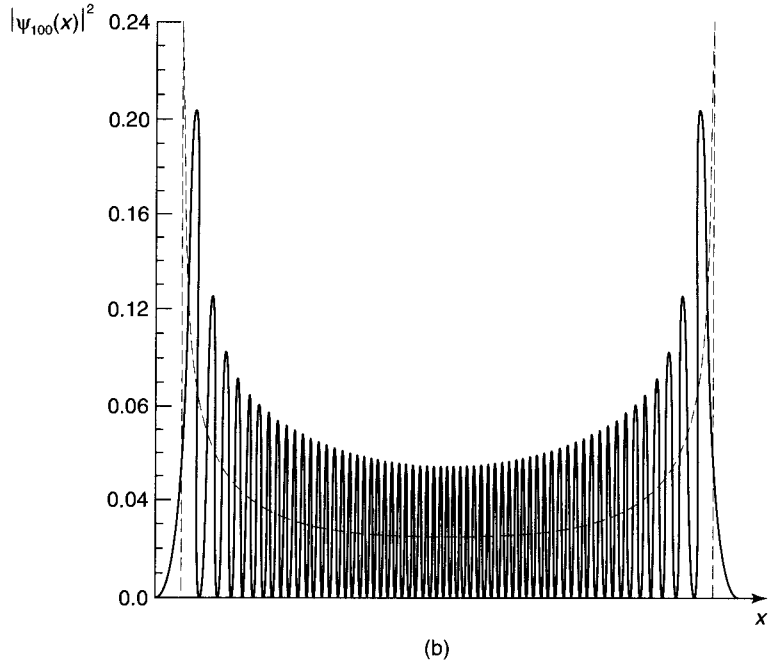
$H_0 = 1,$
$H_1 = 2x,$
$H_2 = 4x^2 - 2,$
$H_3 = 8x^3 - 12x,$
$H_4 = 16x^4 - 48x^2 + 12,$
$H_5 = 32x^5 - 160x^3 + 120x.$

[19]The Hermite polynomials have been studied extensively in the mathematical literature, and there are many tools and tricks for working with them. A few of these are explored in Problem 2.18.

[20]I shall not work out the normalization constant here; if you are interested in knowing how it is done, see, for example, Leonard Schiff, *Quantum Mechanics*, 3rd ed. (New York: McGraw-Hill, 1968), Section 13.



(a)



(b)

Figure 2.5: (a) The first four stationary states of the harmonic oscillator. (b) Graph of $|\psi_{100}|^2$, with the classical distribution (dashed curve) superimposed.

finding the particle at the center of the potential well is zero. Only at relatively large n do we begin to see some resemblance to the classical case. In Figure 2.5b I have superimposed the classical position distribution on the quantum one (for $n = 100$); if you smoothed out the bumps in the latter, the two would fit pretty well (however, in the classical case we are talking about the distribution of positions over *time* for *one* oscillator, whereas in the quantum case we are talking about the distribution over an *ensemble* of identically-prepared systems).[21]

Problem 2.15 In the ground state of the harmonic oscillator, what is the probability (correct to three significant digits) of finding the particle outside the classically allowed region? *Hint:* Look in a math table under "Normal Distribution" or "Error Function".

Problem 2.16 Use the recursion formula (Equation 2.68) to work out $H_5(\xi)$ and $H_6(\xi)$.

---

*__Problem 2.17__ A particle in the harmonic oscillator potential has the initial wave function

$$\Psi(x, 0) = A[\psi_0(x) + \psi_1(x)]$$

for some constant A.

(a) Normalize $\Psi(x, 0)$.

(b) Find $\Psi(x, t)$ and $|\Psi(x, t)|^2$.

(c) Find the expectation value of x as a function of time. Notice that it oscillates sinusoidally. What is the amplitude of the oscillation? What is its (angular) frequency?

(d) Use your result in (c) to determine $\langle p \rangle$. Check that Ehrenfest's theorem holds for this wave function.

(e) Referring to Figure 2.5, sketch the graph of $|\Psi|$ at $t = 0$, π/ω, $2\pi/\omega$, $3\pi/\omega$, and $4\pi/\omega$. (Your graphs don't have to be fancy—just a rough picture to show the oscillation.)

**__Problem 2.18__ In this problem we explore some of the more useful theorems (stated without proof) involving Hermite polynomials.

(a) The **Rodrigues formula** states that

$$H_n(\xi) = (-1)^n e^{\xi^2} \left(\frac{d}{d\xi}\right)^n e^{-\xi^2}. \qquad [2.70]$$

Use it to derive H_3 and H_4.

---

[21] The analogy is perhaps more telling if you interpret the classical distribution as an ensemble of oscillators all with the same energy, but with random starting times.

(b) The following recursion relation gives you H_{n+1} in terms of the two preceding Hermite polynomials:

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi). \quad [2.71]$$

Use it, together with your answer to (a), to obtain H_5 and H_6.

(c) If you differentiate an nth-order polynomial, you get a polynomial of order $(n-1)$. For the Hermite polynomials, in fact,

$$\frac{dH_n}{d\xi} = 2nH_{n-1}(\xi). \quad [2.72]$$

Check this, by differentiating H_5 and H_6.

(d) $H_n(\xi)$ is the nth z-derivative, at $z = 0$, of the **generating function** $\exp(-z^2 + 2z\xi)$; or, to put it another way, it is the coefficient of $z^n/n!$ in the Taylor series expansion for this function:

$$e^{-z^2+2z\xi} = \sum_{n=0}^{\infty} \frac{z^n}{n!} H_n(\xi). \quad [2.73]$$

Use this to rederive H_0, H_1, and H_2.

2.4 THE FREE PARTICLE

We turn next to what should have been the simplest case of all: the free particle [$V(x) = 0$ everywhere]. As you'll see in a moment, the free particle is in fact a surprisingly subtle and tricky example. The time-independent Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi, \quad [2.74]$$

or

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}. \quad [2.75]$$

So far, it's the same as inside the infinite square well (Equation 2.17), where the potential is also zero; this time, however, I prefer to write the general solution in exponential form (instead of sines and cosines) for reasons that will appear in due course:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}. \quad [2.76]$$

Unlike the infinite square well, there are no boundary conditions to restrict the possible values of k (and hence of E); the free particle can carry *any* (positive) energy. Tacking on the standard time dependence, $\exp(-iEt/\hbar)$,

$$\Psi(x,t) = Ae^{ik(x-\frac{\hbar k}{2m}t)} + Be^{-ik(x+\frac{\hbar k}{2m}t)}. \quad [2.77]$$

Now, any function of x and t that depends on these variables in the special combination $(x \pm vt)$ (for some constant v) represents a wave of fixed profile, traveling in the $\mp x$-direction, at speed v. A fixed point on the waveform (for example, a maximum or a minimum) corresponds to a fixed value of the argument, and hence to x and t such that

$$x \pm vt = \text{constant}, \quad \text{or} \quad x = \mp vt + \text{constant},$$

which is the formula for motion in the $\mp x$-direction with constant speed v. Since every point on the waveform is moving along with the same velocity, its shape doesn't change as it propagates. Thus the first term in Equation 2.77 represents a wave traveling to the *right*, and the second term represents a wave (of the same energy) going to the *left*. By the way, since they only differ by the sign in front of k, we might as well write

$$\Psi_k(x,t) = Ae^{i(kx - \frac{\hbar k^2}{2m}t)}, \qquad [2.78]$$

and let k run negative to cover the case of waves traveling to the left:

$$k \equiv \pm\frac{\sqrt{2mE}}{\hbar}, \quad \text{with} \begin{cases} k > 0 \Rightarrow & \text{traveling to the right,} \\ k < 0 \Rightarrow & \text{traveling to the left.} \end{cases} \qquad [2.79]$$

The speed of these waves (the coefficient of t over the coefficient of x) is

$$v_{\text{quantum}} = \frac{\hbar|k|}{2m} = \sqrt{\frac{E}{2m}}. \qquad [2.80]$$

On the other hand, the *classical* speed of a free particle with energy E is given by $E = (1/2)mv^2$ (pure kinetic, since $V = 0$), so

$$v_{\text{classical}} = \sqrt{\frac{2E}{m}} = 2v_{\text{quantum}}. \qquad [2.81]$$

Evidently the quantum mechanical wave function travels at *half* the speed of the particle it is supposed to represent! We'll return to this paradox in a moment—there is an even more serious problem we need to confront first: *This wave function is not normalizable!* For

$$\int_{-\infty}^{+\infty} \Psi_k^* \Psi_k \, dx = |A|^2 \int_{-\infty}^{+\infty} 1 \, dx = |A|^2(\infty). \qquad [2.82]$$

In the case of the free particle, then, the separable solutions do not represent physically realizable states. A free particle cannot exist in a stationary state; or, to put it another way, *there is no such thing as a free particle with a definite energy.*

But that doesn't mean the separable solutions are of no use to us. For they play a *mathematical* role that is entirely independent of their *physical* interpretation: The general solution to the time-dependent Schrödinger equation is still a linear

combination of separable solutions (only this time it's an integral over the continuous variable k, instead of a sum over the discrete index n):

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m}t)}\, dk. \qquad [2.83]$$

[The quantity $1/\sqrt{2\pi}$ is factored out for convenience; what plays the role of the coefficient c_n in Equation 2.14 is the combination $(1/\sqrt{2\pi})\phi(k)\,dk$.] Now *this* wave function *can* be normalized [for appropriate $\phi(k)$]. But it necessarily carries a *range* of k's, and hence a range of energies and speeds. We call it a **wave packet**.

In the generic quantum problem, we are given $\Psi(x,0)$, and we are to find $\Psi(x,t)$. For a free particle the solution has the form of Equation 2.83; the only remaining question is how to determine $\phi(k)$ so as to fit the initial wave function:

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{ikx}\, dk. \qquad [2.84]$$

This is a classic problem in Fourier analysis; the answer is provided by **Plancherel's theorem** (see Problem 2.20):

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(k) e^{ikx}\, dk \iff F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{-ikx}\, dx. \qquad [2.85]$$

$F(k)$ is called the **Fourier transform** of $f(x)$; $f(x)$ is the **inverse Fourier transform** of $F(k)$ (the only difference is in the sign of the exponent). There is, of course, some restriction on the allowable functions: The integrals have to *exist*.[22] For our purposes this is guaranteed by the physical requirement that $\Psi(x,0)$ itself be normalized. So the solution to the generic quantum problem, for the free particle, is Equation 2.83, with

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \Psi(x,0) e^{-ikx}\, dx. \qquad [2.86]$$

I'd love to work out an example for you—starting with a specific function $\Psi(x,0)$ for which we could actually calculate $\phi(k)$, and then doing the integral in Equation 2.83 to obtain $\Psi(x,t)$ in closed form. Unfortunately, manageable cases are hard to

[22] The necessary and sufficient condition on $f(x)$ is that $\int_{-\infty}^{\infty} |f(x)|^2 dx$ be finite. (In that case $\int_{-\infty}^{\infty} |F(k)|^2 dk$ is also finite, and in fact the two integrals are equal.) See Arfken (footnote 15), Section 15.5.

come by, and I want to save the best example for you to work out yourself. Be sure, therefore, to study Problem 2.22 with particular care.

I return now to the paradox noted earlier—the fact that the separable solution $\Psi_k(x, t)$ travels at the "wrong" speed for the particle it ostensibly represents. Strictly speaking, the problem evaporated when we discovered that Ψ_k is not a physically achievable state. Nevertheless, it is of interest to discover how information about the particle velocity *is* carried by the wave function (Equation 2.83). The essential idea is this: A wave packet is a sinusoidal function whose amplitude is modulated by ϕ (Figure 2.6); it consists of "ripples" contained within an "envelope." What corresponds to the particle velocity is not the speed of the individual ripples (the so-called **phase velocity**), but rather the speed of the envelope (the **group velocity**)—which, depending on the nature of the waves, can be greater than, less than, or equal to the velocity of the ripples that go to make it up. For waves on a string, the group velocity is the same as the phase velocity. For water waves it is one half the phase velocity, as you may have noticed when you toss a rock into a pond: If you concentrate on a particular ripple, you will see it build up from the rear, move forward through the group, and fade away at the front, while the group as a whole propagates out at half the speed. What I need to show is that for the wave function of a free particle in quantum mechanics the group velocity is *twice* the phase velocity—just right to represent the classical particle speed.

The problem, then, is to determine the group velocity of a wave packet with the general form

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{i(kx - \omega t)}\, dk.$$

[In our case $\omega = (\hbar k^2/2m)$, but what I have to say now applies to *any* kind of wave packet, regardless of its **dispersion relation**—the formula for ω as a function of k.] Let us assume that $\phi(k)$ is narrowly peaked about some particular value k_0. [There is nothing *illegal* about a broad spread in k, but such wave packets change shape rapidly (since different components travel at different speeds), so the whole notion of a "group," with a well-defined velocity, loses its meaning.] Since the integrand

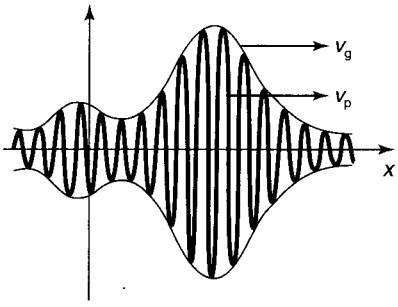


Figure 2.6: A wave packet. The "envelope" travels at the group velocity; the "ripples" travel at the phase velocity.

is negligible except in the vicinity of k_0, we may as well Taylor-expand the function $\omega(k)$ about that point and keep only the leading terms:

$$\omega(k) \cong \omega_0 + \omega_0'(k - k_0),$$

where ω_0' is the derivative of ω with respect to k, at the point k_0.

Changing variables from k to $s \equiv k - k_0$, to center the integral at k_0, we have

$$\Psi(x, t) \cong \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k_0 + s) e^{i[(k_0+s)x - (\omega_0 + \omega_0' s)t]}\, ds.$$

At $t = 0$,

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k_0 + s) e^{i(k_0+s)x}\, ds,$$

and at later times

$$\Psi(x, t) \cong \frac{1}{\sqrt{2\pi}} e^{i(-\omega_0 t + k_0 \omega_0' t)} \int_{-\infty}^{+\infty} \phi(k_0 + s) e^{i(k_0+s)(x - \omega_0' t)}\, ds.$$

Except for the shift from x to $(x - \omega_0' t)$, the integral is the same as the one in $\Psi(x, 0)$. Thus

$$\Psi(x, t) \cong e^{-i(\omega_0 - k_0\omega_0')t} \Psi(x - \omega_0' t, 0). \qquad [2.87]$$

Apart from the phase factor in front (which won't affect $|\Psi|^2$ in any event), the wave packet evidently moves along at a speed

$$v_{\text{group}} = \frac{d\omega}{dk} \qquad [2.88]$$

(evaluated at $k = k_0$), which is to be contrasted with the ordinary phase velocity

$$v_{\text{phase}} = \frac{\omega}{k}. \qquad [2.89]$$

In our case, $\omega = (\hbar k^2/2m)$, so $\omega/k = (\hbar k/2m)$, whereas $d\omega/dk = (\hbar k/m)$, which is twice as great. This confirms that it is the group velocity of the wave packet, not the phase velocity of the stationary states, that matches the classical particle velocity:

$$v_{\text{classical}} = v_{\text{group}} = 2v_{\text{phase}}. \qquad [2.90]$$

Problem 2.19 Show that the expressions $[Ae^{ikx} + Be^{-ikx}]$, $[C \cos kx + D \sin kx]$, $[F \cos(kx + \alpha)]$, and $[G \sin(kx + \beta)]$ are equivalent ways of writing the same function of x, and determine the constants C, D, F, G, α, and β in terms of A and B. (In quantum mechanics, with $V = 0$, the exponentials give rise to *traveling* waves, and are most convenient in discussing the free particle, whereas sines and cosines

correspond to *standing* waves, which arise naturally in the case of the infinite square well.) Assume the function is real.

****Problem 2.20** This problem is designed to guide you through a "proof" of Plancherel's theorem, by starting with the theory of ordinary Fourier series on a *finite* interval, and allowing that interval to expand to infinity.

(a) Dirichlet's theorem says that "any" function $f(x)$ on the interval $[-a, +a]$ can be expanded as a Fourier series:

$$f(x) = \sum_{n=0}^{\infty} [a_n \sin(n\pi x/a) + b_n \cos(n\pi x/a)].$$

Show that this can be written equivalently as

$$f(x) = \sum_{n=-\infty}^{\infty} c_n e^{in\pi x/a}.$$

What is c_n, in terms of a_n and b_n?

(b) Show (by appropriate modification of Fourier's trick) that

$$c_n = \frac{1}{2a} \int_{-a}^{+a} f(x) e^{-in\pi x/a}\, dx.$$

(c) Eliminate n and c_n in favor of the new variables $k = (n\pi/a)$ and $F(k) = \sqrt{2/\pi}\, a c_n$. Show that (a) and (b) now become

$$f(x) = \frac{1}{\sqrt{2\pi}} \sum_{n=-\infty}^{\infty} F(k) e^{ikx} \Delta k; \quad F(k) = \frac{1}{\sqrt{2\pi}} \int_{-a}^{+a} f(x) e^{-ikx}\, dx,$$

where Δk is the increment in k from one n to the next.

(d) Take the limit $a \to \infty$ to obtain Plancherel's theorem. *Note*: In view of their quite different origins, it is surprising (and delightful) that the two formulas [one for $F(k)$ in terms of $f(x)$, the other for $f(x)$ in terms of $F(k)$] have such a similar structure in the limit $a \to \infty$.

Problem 2.21 Suppose a free particle, which is initially localized in the range $-a < x < a$, is released at time $t = 0$:

$$\Psi(x, 0) = \begin{cases} A, & \text{if } -a < x < a, \\ 0, & \text{otherwise,} \end{cases}$$

where A and a are positive real constants.

(a) Determine A, by normalizing Ψ.

(b) Determine $\phi(k)$ (Equation 2.86).

(c) Comment on the behavior of $\phi(k)$ for very small and very large values of a. How does this relate to the uncertainty principle?

***Problem 2.22** A free particle has the initial wave function

$$\Psi(x, 0) = Ae^{-ax^2},$$

where A and a are constants (a is real and positive).

(a) Normalize $\Psi(x, 0)$.

(b) Find $\Psi(x, t)$. *Hint*: Integrals of the form

$$\int_{-\infty}^{+\infty} e^{-(ax^2+bx)}\, dx$$

can be handled by "completing the square." Let $y \equiv \sqrt{a}[x + (b/2a)]$, and note that $(ax^2 + bx) = y^2 - (b^2/4a)$. *Answer*:

$$\Psi(x, t) = \left(\frac{2a}{\pi}\right)^{1/4} \frac{e^{-ax^2/[1+(2i\hbar at/m)]}}{\sqrt{1 + (2i\hbar at/m)}}.$$

(c) Find $|\Psi(x, t)|^2$. Express your answer in terms of the quantity $w \equiv \sqrt{a/[1 + (2\hbar at/m)^2]}$. Sketch $|\Psi|^2$ (as a function of x) at $t = 0$, and again for some very large t. Qualitatively, what happens to $|\Psi|^2$ as time goes on?

(d) Find $\langle x\rangle$, $\langle p\rangle$, $\langle x^2\rangle$, $\langle p^2\rangle$, σ_x, and σ_p. *Partial answer*: $\langle p^2\rangle = a\hbar^2$, but it may take some algebra to reduce it to this simple form.

(e) Does the uncertainty principle hold? At what time t does the system come closest to the uncertainty limit?

2.5 THE DELTA-FUNCTION POTENTIAL

We have encountered two very different kinds of solutions to the time-independent Schrödinger equation: For the infinite square well and the harmonic oscillator they are normalizable, and labeled by a discrete index n; for the free paticle they are non-normalizable, and labeled by a continuous variable k. The former represent physically realizable states in their own right, the latter do not; but in both cases the general solution to the time-dependent Schrödinger equation is a linear combination of stationary states—for the first type this combination takes the form of a sum

(over n), whereas for the second it is an integral (over k). What is the physical significance of this distinction?

In *classical* mechanics a one-dimensional time-independent potential can give rise to two rather different kinds of motion. If $V(x)$ rises higher than the particle's total energy (E) on either side (Figure 2.7a), then the particle is "stuck" in the potential well—it rocks back and forth between the **turning points**, but it cannot escape (unless,

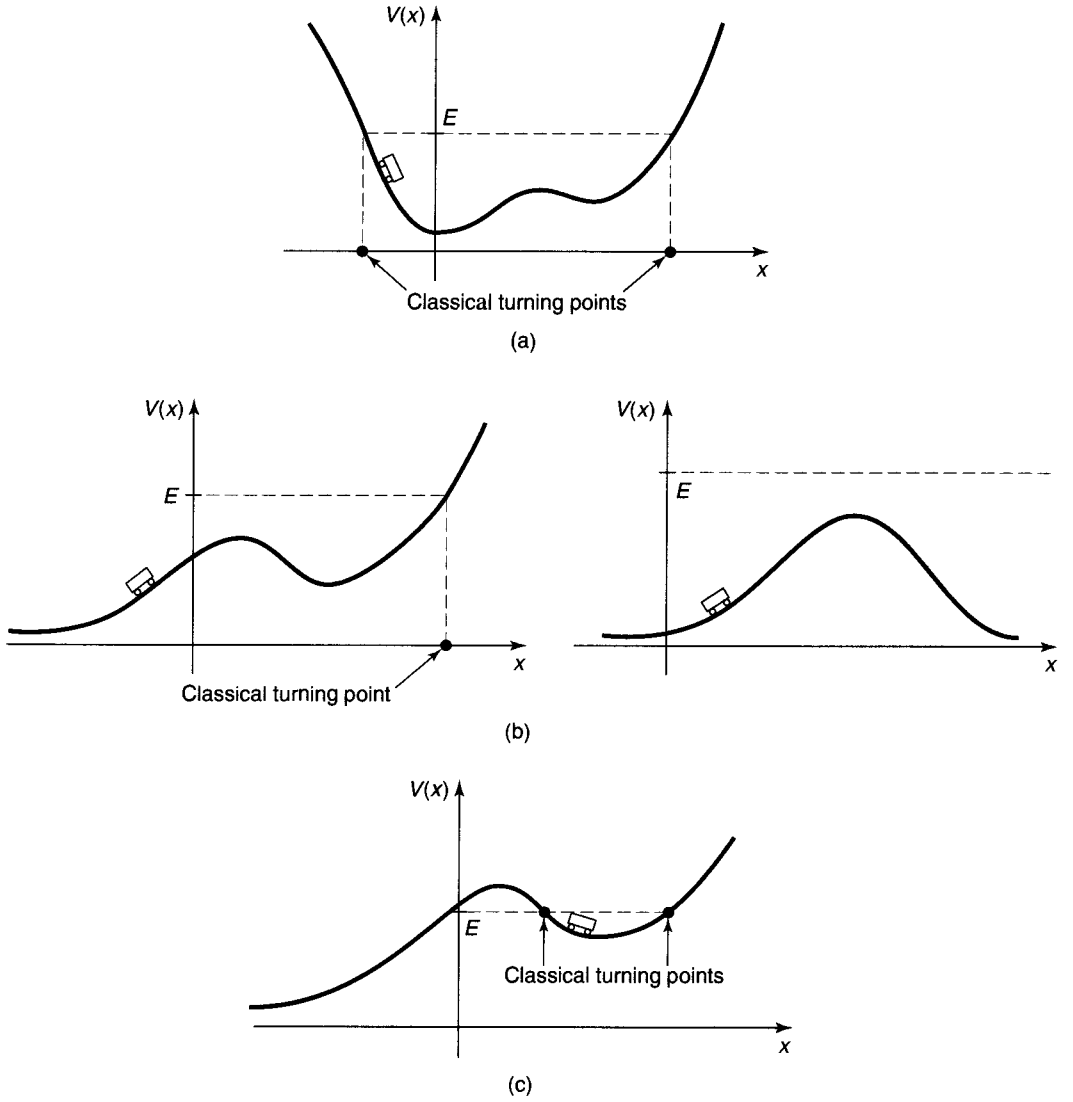


Figure 2.7: (a) A bound state. (b) Scattering states. (c) A classical bound state, but a quantum scattering state.

of course, you provide it with a source of extra energy, such as a motor, but we're not talking about that). We call this a **bound state**. If, on the other hand, E exceeds $V(x)$ on one side (or both), then the particle comes in from "infinity", slows down or speeds up under the influence of the potential, and returns to infinity (Figure 2.7b). (It can't get trapped in the potential unless there is some mechanism, such as friction, to dissipate energy, but again, we're not talking about that.) We call this a **scattering state**. Some potentials admit only bound states (for instance, the harmonic oscillator); some allow only scattering states (a potential hill with no dips in it, for example); some permit both kinds, depending on the energy of the particle.

As you have probably guessed, the two kinds of solutions to the Schrödinger equation correspond precisely to bound and scattering states. The distinction is even cleaner in the quantum domain, because the phenomenon of **tunneling** (which we'll come to shortly) allows the particle to "leak" through any finite potential barrier, so the only thing that matters is the potential at infinity (Figure 2.7c):

$$\begin{cases} E < V(-\infty) \text{ and } V(+\infty) \Rightarrow & \text{bound state,} \\ E > V(-\infty) \text{ or } V(+\infty) \Rightarrow & \text{scattering state.} \end{cases} \quad [2.91]$$

In "real life" most potentials go to zero at infinity, in which case the criterion simplifies even further:

$$\begin{cases} E < 0 \Rightarrow & \text{bound state,} \\ E > 0 \Rightarrow & \text{scattering state.} \end{cases} \quad [2.92]$$

Because the infinite square well and harmonic oscillator potentials go to infinity as $x \to \pm\infty$, they admit bound states only; because the free particle potential is zero everywhere, it only allows scattering states.[23] In this section (and the following one) we shall explore potentials that give rise to both kinds of states.

The **Dirac delta function**, $\delta(x)$, is defined informally as follows:

$$\delta(x) = \begin{cases} 0, & \text{if } x \neq 0 \\ \infty, & \text{if } x = 0 \end{cases}, \text{ with } \int_{-\infty}^{+\infty} \delta(x)\,dx = 1. \quad [2.93]$$

It is an infinitely high, infinitesimally narrow spike at the origin, whose *area* is 1 (Figure 2.8). Technically, it's not a function at all, since it is not finite at $x = 0$ (mathematicians call it a **generalized function**, or **distribution**).[24] Nevertheless, it is an extremely useful construct in theoretical physics. (For example, in electrodynamics the charge density of a point charge is a delta function.) Notice that $\delta(x-a)$ would

[23] If you are very observant, and awfully fastidious, you may have noticed that the general theorem requiring $E > V_{\min}$ (Problem 2.2) does not really apply to scattering states, since they are not normalizable anyway. If this bothers you, try solving the Schrödinger equation with $E < 0$, for the free particle, and note that *even linear combinations* of these solutions cannot be normalized. The positive energy solutions by themselves constitute a complete set.

[24] The delta function can be thought of as the *limit* of a *sequence* of functions, such as rectangles (or triangles) of ever-increasing height and ever-decreasing width.

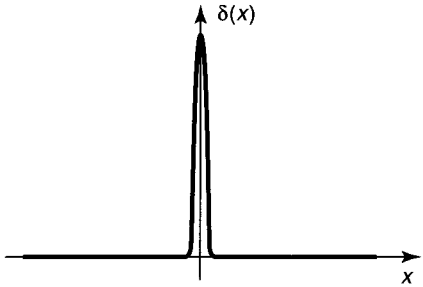


Figure 2.8: The Dirac delta function (Equation 2.93).

be a spike of area 1 at the point a. If you multiply $\delta(x-a)$ by an *ordinary* function $f(x)$, it's the same as multiplying by $f(a)$:

$$f(x)\delta(x-a) = f(a)\delta(x-a), \qquad [2.94]$$

because the product is zero *anyway* except at the point a. In particular,

$$\int_{-\infty}^{+\infty} f(x)\delta(x-a)\,dx = f(a)\int_{-\infty}^{+\infty} \delta(x-a)\,dx = f(a). \qquad [2.95]$$

That's the most important property of the delta function: Under the integral sign it serves to "pick out" the value of $f(x)$ at the point a. (Of course, the integral need not go from $-\infty$ to $+\infty$; all that matters is that the domain of integration include the point a, so $a-\epsilon$ to $a+\epsilon$ would do, for any $\epsilon > 0$.)

Let's consider a potential of the form

$$V(x) = -\alpha\delta(x), \qquad [2.96]$$

where α is some constant. This is an artificial potential (so was the infinite square well), but it's beautifully simple and in some respects closer to reality than any of the potentials we have considered so far. The Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - \alpha\delta(x)\psi = E\psi. \qquad [2.97]$$

This potential yields both bound states ($E < 0$) and scattering states ($E > 0$); we'll look first at the bound states.

In the region $x < 0$, $V(x) = 0$, so

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = \kappa^2\psi, \qquad [2.98]$$

where

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}. \qquad [2.99]$$

(E is negative, by assumption, so κ is real and positive.) The general solution to Equation 2.98 is

$$\psi(x) = Ae^{-\kappa x} + Be^{\kappa x}, \qquad [2.100]$$

but the first term blows up as $x \to -\infty$, so we must choose $A = 0$:

$$\psi(x) = Be^{\kappa x}, \quad (x < 0). \qquad [2.101]$$

In the region $x > 0$, $V(x)$ is again zero, and the general solution is of the form $F\exp(-\kappa x) + G\exp(\kappa x)$; this time it's the second term that blows up (as $x \to +\infty$), so

$$\psi(x) = Fe^{-\kappa x}, \quad (x > 0). \qquad [2.102]$$

It remains only to stitch these two functions together, using the appropriate boundary conditions at $x = 0$. I quoted earlier the standard boundary conditions for ψ:

> 1. ψ is always continuous, and
> 2. $d\psi/dx$ is continuous except at points where the potential is infinite. [2.103]

In this case the first boundary condition tells us that $F = B$, so

$$\psi(x) = \begin{cases} Be^{\kappa x}, & (x \leq 0), \\ Be^{-\kappa x}, & (x \geq 0). \end{cases} \qquad [2.104]$$

[$\psi(x)$ is plotted in Figure 2.9.] The second boundary condition tells us nothing; this is (like the infinite square well) the exceptional case where V is infinite at the join, and it's clear from the graph that this function has a kink at $x = 0$. Moreover, up to this point the delta function has not come into the story at all. Evidently the delta function must determine the discontinuity in the derivative of ψ, at $x = 0$. I'll show you now how this works, and as a byproduct we'll see why $d\psi/dx$ is ordinarily continuous.

The idea is to *integrate* the Schrödinger equation, from $-\epsilon$ to $+\epsilon$, and then take the limit as $\epsilon \to 0$:

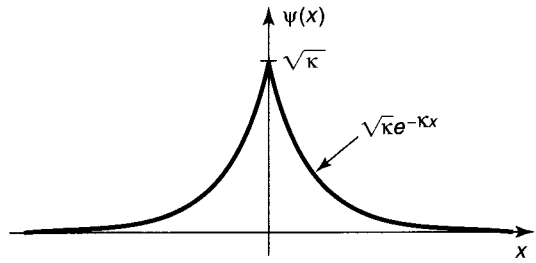


Figure 2.9: Bound state wave function for the delta function potential (Equation 2.104).

$$-\frac{\hbar^2}{2m}\int_{-\epsilon}^{+\epsilon}\frac{d^2\psi}{dx^2}\,dx+\int_{-\epsilon}^{+\epsilon}V(x)\psi(x)\,dx=E\int_{-\epsilon}^{+\epsilon}\psi(x)\,dx. \quad [2.105]$$

The first integral is nothing but $d\psi/dx$, evaluated at the two end points; the last integral is *zero*, in the limit $\epsilon \to 0$, since it's the area of a sliver with vanishing width and finite height. Thus

$$\Delta\left(\frac{d\psi}{dx}\right)=\frac{2m}{\hbar^2}\lim_{\epsilon\to 0}\int_{-\epsilon}^{+\epsilon}V(x)\psi(x)\,dx. \quad [2.106]$$

Ordinarily, the limit on the right is again zero, and hence $d\psi/dx$ is continuous. But when $V(x)$ is *infinite* at the boundary, that argument fails. In particular, if $V(x)=-\alpha\delta(x)$, Equation 2.95 yields

$$\Delta\left(\frac{d\psi}{dx}\right)=-\frac{2m\alpha}{\hbar^2}\psi(0). \quad [2.107]$$

For the case at hand (Equation 2.104),

$$\begin{cases} d\psi/dx=-B\kappa e^{-\kappa x}, \text{ for } (x>0), & \text{so } d\psi/dx\big|_+=-B\kappa, \\ d\psi/dx=+B\kappa e^{+\kappa x}, \text{ for } (x<0), & \text{so } d\psi/dx\big|_-=+B\kappa, \end{cases}$$

and hence $\Delta(d\psi/dx)=-2B\kappa$. And $\psi(0)=B$. So Equation 2.107 says

$$\kappa=\frac{m\alpha}{\hbar^2}, \quad [2.108]$$

and the allowed energy (Equation 2.99) is

$$E=-\frac{\hbar^2\kappa^2}{2m}=-\frac{m\alpha^2}{2\hbar^2}. \quad [2.109]$$

Finally, we normalize ψ:

$$\int_{-\infty}^{+\infty}|\psi(x)|^2\,dx=2|B|^2\int_0^{\infty}e^{-2\kappa x}\,dx=\frac{|B|^2}{\kappa}=1,$$

so (choosing, for convenience, the positive real root):

$$B=\sqrt{\kappa}=\frac{\sqrt{m\alpha}}{\hbar}. \quad [2.110]$$

Evidently the delta-function well, regardless of its "strength" α, has exactly one bound state:

$$\boxed{\psi(x)=\frac{\sqrt{m\alpha}}{\hbar}e^{-m\alpha|x|/\hbar^2}; \quad E=-\frac{m\alpha^2}{2\hbar^2}.} \quad [2.111]$$

What about scattering states, with $E > 0$? For $x < 0$ the Schrödinger equation reads

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi,$$

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar} \qquad [2.112]$$

is real and positive. The general solution is

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \qquad [2.113]$$

and this time we cannot rule out either term, since neither of them blows up. Similarly, for $x > 0$,

$$\psi(x) = Fe^{ikx} + Ge^{-ikx}. \qquad [2.114]$$

The continuity of $\psi(x)$ at $x = 0$ requires that

$$F + G = A + B. \qquad [2.115]$$

The derivatives are

$$\begin{cases} d\psi/dx = ik\left(Fe^{ikx} - Ge^{-ikx}\right), & \text{for } (x > 0), \quad \text{so } d\psi/dx\big|_+ = ik(F - G), \\ d\psi/dx = ik\left(Ae^{ikx} - Be^{-ikx}\right), & \text{for } (x < 0), \quad \text{so } d\psi/dx\big|_- = ik(A - B), \end{cases}$$

and hence $\Delta(d\psi/dx) = ik(F - G - A + B)$. Meanwhile, $\psi(0) = (A + B)$, so the second boundary condition (Equation 2.107) says

$$ik(F - G - A + B) = -\frac{2m\alpha}{\hbar^2}(A + B), \qquad [2.116]$$

or, more compactly,

$$F - G = A(1 + 2i\beta) - B(1 - 2i\beta), \quad \text{where } \beta \equiv \frac{m\alpha}{\hbar^2 k}. \qquad [2.117]$$

Having imposed the boundary conditions, we are left with two equations (Equations 2.115 and 2.117) in four unknowns (A, B, F, and G)—*five*, if you count k. Normalization won't help—this isn't a normalizable state. Perhaps we'd better pause, then, and examine the physical significance of these various constants. Recall that $\exp(ikx)$ gives rise [when coupled with the time-dependent factor $\exp(-iEt/\hbar)$] to a wave function propagating to the *right*, and $\exp(-ikx)$ leads to a wave propagating to the *left*. It follows that A (in Equation 2.113) is the amplitude of a wave coming in from the left, B is the amplitude of a wave returning to the left, F (in Equation 2.114) is the amplitude of a wave traveling off to the right, and G is the amplitude of a wave coming in from the right (Figure 2.10). In a typical scattering experiment particles are fired in from one direction—let's say, from the left. In that case the amplitude of the wave coming in from the *right* will be zero:

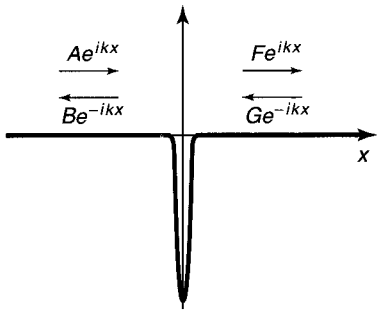


Figure 2.10: Scattering from a delta-function well.

$$G = 0 \quad \text{(for scattering from the left).} \tag{2.118}$$

A is then the amplitude of the **incident wave**, B is the amplitude of the **reflected wave**, and F is the amplitude of the **transmitted wave**. Solving Equations 2.115 and 2.117 for B and F, we find

$$B = \frac{i\beta}{1 - i\beta}A, \quad F = \frac{1}{1 - i\beta}A. \tag{2.119}$$

(If you want to study scattering from the *right*, set $A = 0$; then G is the incident amplitude, F is the reflected amplitude, and B is the transmitted amplitude.)

Now, the probability of finding the particle at a specified location is given by $|\Psi|^2$, so the *relative*[25] probability that an incident particle will be reflected back is

$$R \equiv \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2}. \tag{2.120}$$

R is called the **reflection coefficient**. (If you have a *beam* of particles, it tells you the *fraction* of the incoming number that will bounce back.) Meanwhile, the probability of transmission is given by the **transmission coefficient**

$$T \equiv \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2}. \tag{2.121}$$

Of course, the sum of these probabilities should be 1—and it *is*:

$$R + T = 1. \tag{2.122}$$

Notice that R and T are functions of β, and hence (Equations 2.112 and 2.117) of E:

$$\boxed{R = \frac{1}{1 + (2\hbar^2 E/m\alpha^2)}, \quad T = \frac{1}{1 + (m\alpha^2/2\hbar^2 E)}.} \tag{2.123}$$

[25]This is not a normalizable wave function, so the *absolute* probability of finding the particle at a particular location is not well defined; nevertheless, the *ratio* of probabilities for two different locations is meaningful. More on this in the next paragraph.

The higher the energy, the greater the probability of transmission (which seems reasonable).

This is all very tidy, but there is a sticky matter of principle that we cannot altogether ignore: These scattering wave functions are not normalizable, so they don't actually represent possible particle states. But we know what the resolution to this problem is: We must form normalizable linear combinations of the stationary states, just as we did for the free particle—true physical particles are represented by the resulting wave packets. Though straightforward in principle, this is a messy business in practice, and at this point it is best to turn the problem over to a computer.[26] Meanwhile, since it is impossible to create a normalizable free particle wave function without involving a range of energies, R and T should be interpreted as the *approximate* reflection and transmission probabilities for particles in a narrow energy range about E. Incidentally, it might strike you as peculiar that we were able to analyse a quintessentially time-dependent problem (particle comes in, scatters off a potential, and flies off to infinity) using *stationary* states. After all, ψ (in Equations 2.113 and 2.114) is simply a complex, time-independent, sinusoidal function, extending (with constant amplitude) to infinity in both directions. And yet, by imposing appropriate boundary conditions on this function, we were able to determine the probability that a particle (represented by a *localized* wave packet) would bounce off, or pass through, the potential. The mathematical miracle behind this is, I suppose, the fact that by taking linear combinations of states spread over all space, and with essentially trivial time dependence, we can *construct* wave functions that are concentrated about a (moving) point, with quite elaborate behavior in time (see Problem 2.40).

As long as we've got the relevant equations on the table, let's look briefly at the case of a delta-function *barrier* (Figure 2.11). Formally, all we have to do is change the sign of α. This kills the bound state, of course (see Problem 2.2). On the other hand, the reflection and transmission coefficients, which depend only on α^2, are unchanged. Strange to say, the particle is just as likely to pass through the barrier as to cross over the well! *Classically*, of course, the particle could not make it over an infinitely high barrier, regardless of its energy. In fact, the classical scattering

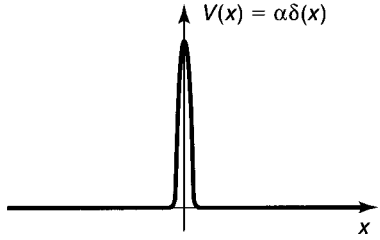


Figure 2.11: The delta-function barrier.

[26]There exist some powerful programs for analysing the scattering of a wave packet from a one-dimensional potential; see, for instance, A. Goldberg, H. M. Schey, and J. L. Schwartz, *Am. J. Phys.* **35**, 177 (1967).

problem is pretty dull: If $E > V_{\max}$, then $T = 1$ and $R = 0$—the particle certainly makes it over; conversely, if $E < V_{\max}$, then $T = 0$ and $R = 1$—it rides "up the hill" until it runs out of energy, and then returns the same way it came. The *quantum* scattering problem is much richer; the particle has some nonzero probability of passing through the potential even if $E < V_{\max}$. We call this phenomenon **tunneling**; it is the mechanism that makes possible much of modern electronics—not to mention spectacular recent advances in microscopy. Conversely, even if $E > V_{\max}$, there is a possibility that the particle will bounce back—though I wouldn't advise driving off a cliff in the expectation that quantum mechanics will save you (see Problem 2.41).

Problem 2.23 Evaluate the following integrals:

(a) $\int_{-3}^{+1} (x^3 - 3x^2 + 2x - 1)\delta(x + 2)\, dx$

(b) $\int_0^{\infty} [\cos(3x) + 2]\delta(x - \pi)\, dx$

(c) $\int_{-1}^{+1} \exp(|x| + 3)\delta(x - 2)\, dx$.

Problem 2.24 Two expressions [$D_1(x)$ and $D_2(x)$] involving delta functions are said to be equal if

$$\int_{-\infty}^{+\infty} f(x) D_1(x)\, dx = \int_{-\infty}^{+\infty} f(x) D_2(x)\, dx,$$

for any (ordinary) function $f(x)$.

(a) Show that

$$\delta(cx) = \frac{1}{|c|}\delta(x), \qquad [2.124]$$

where c is a real constant.

(b) Let $\theta(x)$ be the **step function**:

$$\theta(x) \equiv \begin{cases} 1, & \text{if } x > 0, \\ 0, & \text{if } x < 0. \end{cases} \qquad [2.125]$$

[In the rare case where it actually matters, we define $\theta(0)$ to be 1/2.] Show that $d\theta/dx = \delta(x)$.

***Problem 2.25** What is the Fourier transform of $\delta(x)$? Using Plancherel's theorem, show that

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx}\, dk. \qquad [2.126]$$

Comment: This formula gives any respectable mathematician apoplexy. Although the integral is clearly infinite when $x = 0$, it doesn't converge (to zero or anything else) when $x \neq 0$, since the integrand oscillates forever. There are ways to patch it up

(for instance, you can integrate from $-L$ to $+L$, and interpret the integral in Equation 2.126 to mean the *average* value of the finite integral, as $L \to \infty$). The source of the problem is that the delta function doesn't meet the requirement (square integrability) for Plancherel's theorem (see footnote 22). In spite of this, Equation 2.126 can be extremely useful, if handled with care.

***Problem 2.26** Consider the *double* delta-function potential

$$V(x) = -\alpha[\delta(x+a) + \delta(x-a)],$$

where α and a are positive constants.

(a) Sketch this potential.

(b) How many bound states does it possess? Find the allowed energies, for $\alpha = \hbar^2/ma$ and for $\alpha = \hbar^2/4ma$, and sketch the wave functions.

****Problem 2.27** Find the transmission coefficient for the potential in Problem 2.26.

2.6 THE FINITE SQUARE WELL

As a last example, consider the finite square well

$$V(x) = \begin{cases} -V_0, & \text{for } -a < x < a, \\ 0, & \text{for } |x| > a, \end{cases} \qquad [2.127]$$

where V_0 is a (positive) constant (Figure 2.12). Like the delta-function well, the finite square well admits both bound states (with $E < 0$) and scattering states (with $E > 0$). We'll look first at the bound states.

In the region $x < -a$ the potential is zero, so the Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi, \quad \text{or} \quad \frac{d^2\psi}{dx^2} = \kappa^2\psi,$$

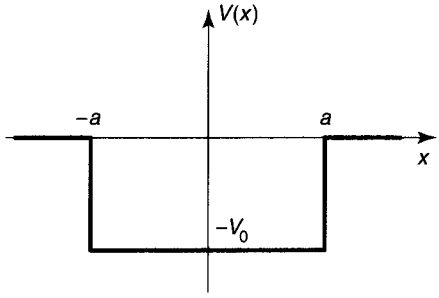


Figure 2.12: The finite square well (Equation 2.127).

where

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar} \qquad [2.128]$$

is real and positive. The general solution is $\psi(x) = A\exp(-\kappa x) + B\exp(\kappa x)$, but the first term blows up (as $x \to -\infty$), so the physically admissable solution (as before—see Equation 2.101) is

$$\psi(x) = Be^{\kappa x}, \quad \text{for } (x < -a). \qquad [2.129]$$

In the region $-a < x < a$, $V(x) = -V_0$, and the Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - V_0\psi = E\psi, \quad \text{or} \quad \frac{d^2\psi}{dx^2} = -l^2\psi,$$

where

$$l \equiv \frac{\sqrt{2m(E+V_0)}}{\hbar}. \qquad [2.130]$$

Although E is negative, for a bound state, it must be greater than $-V_0$, by the old theorem $E > V_{\text{min}}$ (Problem 2.2); so l is also real and positive. The general solution is

$$\psi(x) = C\sin(lx) + D\cos(lx), \quad \text{for } (-a < x < a), \qquad [2.131]$$

where C and D are arbitrary constants. Finally, in the region $x > a$ the potential is again zero; the general solution is $\psi(x) = F\exp(-\kappa x) + G\exp(\kappa x)$, but the second term blows up (as $x \to \infty$), so we are left with

$$\psi(x) = Fe^{-\kappa x}, \quad \text{for } (x > a). \qquad [2.132]$$

The next step is to impose boundary conditions: ψ and $d\psi/dx$ continuous at $-a$ and $+a$. But we can save a little time by noting that this potential is an even function, so we can assume with no loss of generality that the solutions are either even or odd (Problem 2.1c). The advantage of this is that we need only impose the boundary conditions on one side (say, at $+a$); the other side is then automatic, since $\psi(-x) = \pm\psi(x)$. I'll work out the even solutions; you get to do the odd ones in Problem 2.28. The cosine is even (and the sine is odd), so I'm looking for solutions of the form

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, & \text{for } (x > a), \\ D\cos(lx), & \text{for } (0 < x < a), \\ \psi(-x), & \text{for } (x < 0). \end{cases} \qquad [2.133]$$

The continuity of $\psi(x)$, at $x = a$, says

$$Fe^{-\kappa a} = D\cos(la), \qquad [2.134]$$

and the continuity of $d\psi/dx$ says

$$-\kappa Fe^{-\kappa a} = -lD\sin(la). \qquad [2.135]$$

Dividing Equation 2.135 by Equation 2.134, we find that

$$\kappa = l \tan(la). \tag{2.136}$$

Equation 2.136 is a formula for the allowed energies, since κ and l are both functions of E. To solve for E, it pays to adopt some nicer notation. Let

$$z \equiv la, \quad \text{and} \quad z_0 \equiv \frac{a}{\hbar}\sqrt{2mV_0}. \tag{2.137}$$

According to Equations 2.128 and 2.130, $(\kappa^2 + l^2) = 2mV_0/\hbar^2$, so $\kappa a = \sqrt{z_0^2 - z^2}$, and Equation 2.136 reads

$$\tan z = \sqrt{(z_0/z)^2 - 1}. \tag{2.138}$$

This is a transcendental equation for z (and hence for E) as a function of z_0 (which is a measure of the "size" of the well). It can be solved numerically, using a calculator or a computer, or graphically, by plotting $\tan z$ and $\sqrt{(z_0/z)^2 - 1}$ on the same grid, and looking for points of intersection (see Figure 2.13). Two limiting cases are of special interest:

1. Wide, deep well. If z_0 is very large, the intersections occur just slightly below $z_n = n\pi/2$, with n odd; it follows that

$$E_n + V_0 \cong \frac{n^2\pi^2\hbar^2}{2m(2a)^2}. \tag{2.139}$$

Here $(E + V_0)$ is the energy above the bottom of the well, and on the right we have precisely the infinite square well energies, for a well of width $2a$ (see Equation 2.23)—or rather, *half* of them, since n is odd. (The other ones, of course, come from the *odd* wave functions, as you'll find in Problem 2.28.) So the finite square well goes over to the infinite square well, as $V_0 \to \infty$; however, for any *finite* V_0 there are only finitely many bound states.

2. Shallow, narrow well. As z_0 decreases, there are fewer and fewer bound states, until finally (for $z_0 < \pi/2$, where the lowest *odd* state disappears) only one remains. It is interesting to note, however, that there is always *one* bound state, no matter how "weak" the well becomes.

You're welcome to normalize ψ (Equation 2.133), if you're interested (see Problem 2.29), but I'm going to move on now to the scattering states ($E > 0$). To the left, where $V(x) = 0$, we have

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad \text{for } (x < -a), \tag{2.140}$$

where (as usual)

$$k \equiv \frac{\sqrt{2mE}}{\hbar}. \tag{2.141}$$

Inside the well, where $V(x) = -V_0$,

$$\psi(x) = C\sin(lx) + D\cos(lx), \quad \text{for } (-a < x < a), \tag{2.142}$$

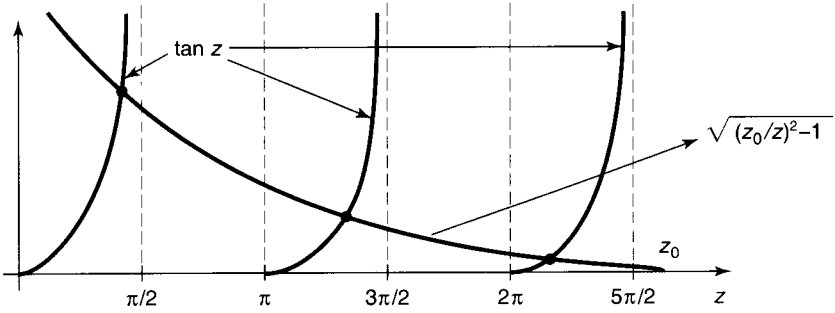


Figure 2.13: Graphical solution to Equation 2.138, for $z_0 = 8$ (*even* states).

where, as before,

$$l \equiv \frac{\sqrt{2m(E+V_0)}}{\hbar}. \qquad [2.143]$$

To the right, assuming there is no incoming wave in this region, we have

$$\psi(x) = Fe^{ikx}. \qquad [2.144]$$

A is the incident amplitude, B is the reflected amplitude, and F is the transmitted amplitude.[27]

There are four boundary conditions: Continuity of $\psi(x)$ at $-a$ says

$$Ae^{-ika} + Be^{ika} = -C\sin(la) + D\cos(la), \qquad [2.145]$$

continuity of $d\psi/dx$ at $-a$ gives

$$ik[Ae^{-ika} - Be^{ika}] = l[C\cos(la) + D\sin(la)], \qquad [2.146]$$

continuity of $\psi(x)$ at $+a$ yields

$$C\sin(la) + D\cos(la) = Fe^{ika}, \qquad [2.147]$$

and continuity of $d\psi/dx$ at $+a$ requires

$$l[C\cos(la) - D\sin(la)] = ikFe^{ika}. \qquad [2.148]$$

We can use two of these to eliminate C and D, and solve the remaining two for B and F (see Problem 2.31):

$$B = i\frac{\sin(2la)}{2kl}(l^2 - k^2)F, \qquad [2.149]$$

[27] We could use even and odd functions, as we did for bound states, but these would represent standing waves, and the scattering problem is more naturally formulated in terms of traveling waves.

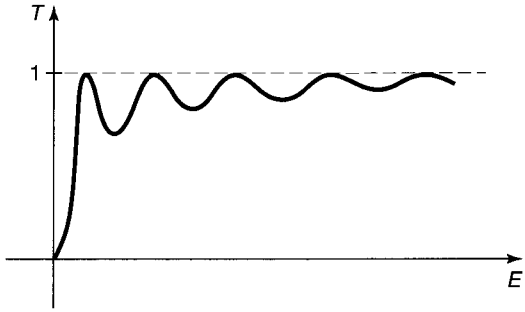


Figure 2.14: Transmission coefficient as a function of energy (Equation 2.151).

$$F = \frac{e^{-2ika}A}{\cos(2la) - i\frac{\sin(2la)}{2kl}(k^2 + l^2)}. \qquad [2.150]$$

The transmission coefficient ($T = |F|^2/|A|^2$), expressed in terms of the original variables, is given by

$$T^{-1} = 1 + \frac{V_0^2}{4E(E + V_0)} \sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E + V_0)}\right). \qquad [2.151]$$

Notice that $T = 1$ (the well becomes "transparent") whenever the argument of the sine is zero, which is to say, for

$$\frac{2a}{\hbar}\sqrt{2m(E_n + V_0)} = n\pi, \qquad [2.152]$$

where n is any integer. The energies for perfect transmission, then, are given by

$$E_n + V_0 = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}, \qquad [2.153]$$

which happen to be precisely the allowed energies for the infinite square well. T is plotted in Figure 2.14 as a function of energy.

∗**Problem 2.28** Analyze the *odd* bound-state wave functions for the finite square well. Derive the transcendental equation for the allowed energies, and solve it graphically. Examine the two limiting cases. Is there always at least one odd bound state?

Problem 2.29 Normalize $\psi(x)$ in Equation 2.133 to determine the constants D and F.

Problem 2.30 The Dirac delta function can be thought of as the limiting case of a rectangle of area 1, as the height goes to infinity and the width goes to zero. Show that the delta-function well (Equation 2.96) is a "weak" potential (even though it is

infinitely deep), in the sense that $z_0 \to 0$. Determine the bound-state energy for the delta-function potential, by treating it as the limit of a finite square well. Check that your answer is consistent with Equation 2.111. Also show that Equation 2.151 reduces to Equation 2.123 in the appropriate limit.

***Problem 2.31** Derive Equations 2.149 and 2.150. *Hint*: Use Equations 2.147 and 2.148 to solve for C and D in terms of F:

$$C = \left[\sin(la) + i\frac{k}{l}\cos(la)\right]e^{ika}F; \quad D = \left[\cos(la) - i\frac{k}{l}\sin(la)\right]e^{ika}F.$$

Plug these back into Equations 2.145 and 2.146. Obtain the transmission coefficient, and confirm Eqation 2.151. Work out the reflection coefficient, and check that $T + R = 1$.

****Problem 2.32** Determine the transmission coefficient for a rectangular *barrier* (same as Equation 2.127, only with $+V_0$ in the region $-a < x < a$). Treat separately the three cases $E < V_0$, $E = V_0$, and $E > V_0$ (note that the wave function inside the barrier is different in the three cases). *Partial answer*: For $E < V_0$,[28]

$$T^{-1} = 1 + \frac{V_0^2}{4E(V_0 - E)}\sinh^2\left(\frac{2a}{\hbar}\sqrt{2m(V_0 - E)}\right).$$

****Problem 2.33** Consider the step function potential:

$$V(x) = \begin{cases} 0, & \text{if } x \leq 0, \\ V_0, & \text{if } x > 0. \end{cases}$$

(a) Calculate the reflection coefficient, for the case $E < V_0$, and comment on the answer.

(b) Calculate the reflection coefficient for the case $E > V_0$.

(c) For a potential such as this that does not go back to zero to the right of the barrier, the transmission coefficient is *not* simply $|F|^2/|A|^2$, with A the incident amplitude and F the transmitted amplitude, because the transmitted wave travels at a different *speed*. Show that

$$T = \sqrt{\frac{E - V_0}{E}}\frac{|F|^2}{|A|^2}, \qquad [2.154]$$

for $E > V_0$. *Hint*: You can figure it out using Equation 2.81, or—more elegantly, but less informatively—from the probability current (Problem 1.9a). What is T for $E < V_0$?

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[28] This is a good example of tunneling—*classically* the particle would bounce back.

(d) For $E > V_0$, calculate the transmission coefficient for the step potential, and check that $T + R = 1$.

2.7 THE SCATTERING MATRIX

The theory of scattering generalizes in a pretty obvious way to arbitrary localized potentials (Figure 2.15). To the left (Region I), $V(x) = 0$, so

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}. \tag{2.155}$$

To the right (Region III), $V(x)$ is again zero, so

$$\psi(x) = Fe^{ikx} + Ge^{-ikx}. \tag{2.156}$$

In between (Region II), of course, I can't tell you what ψ is until you specify the potential, but because the Schrödinger equation is a linear, second-order differential equation, the general solution has got to be of the form

$$\psi(x) = Cf(x) + Dg(x), \tag{2.157}$$

where $f(x)$ and $g(x)$ are any two linearly independent particular solutions.[29] There will be four boundary conditions (two joining Regions I and II, and two joining Regions II and III). Two of these can be used to eliminate C and D, and the other two can be "solved" for B and F in terms of A and G:

$$B = S_{11}A + S_{12}G, \quad F = S_{21}A + S_{22}G. \tag{2.158}$$

The four coefficients S_{ij}, which depend on k (and hence on E), constitute a 2×2 matrix

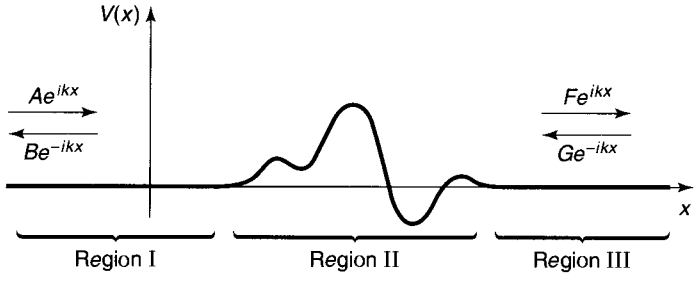

Figure 2.15: Scattering from an arbitrary localized potential [$V(x) = 0$ except in Region II].

[29] See any book on differential equations—for example, J. L. Van Iwaarden, *Ordinary Differential Equations with Numerical Techniques* (San Diego, CA: Harcourt Brace Jovanovich, 1985), Chapter 3.

$$\mathbf{S} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}, \qquad [2.159]$$

called the **scattering matrix** (or **S-matrix**, for short). The S-matrix tells you the outgoing amplitudes (B and F) in terms of the incoming amplitudes (A and G):

$$\begin{pmatrix} B \\ F \end{pmatrix} = \mathbf{S} \begin{pmatrix} A \\ G \end{pmatrix}. \qquad [2.160]$$

In the typical case of scattering from the left, $G = 0$, so the reflection and transmission coefficients are

$$R_l = \frac{|B|^2}{|A|^2}\Big|_{G=0} = |S_{11}|^2, \quad T_l = \frac{|F|^2}{|A|^2}\Big|_{G=0} = |S_{21}|^2. \qquad [2.161]$$

For scattering from the right, $A = 0$, and

$$R_r = \frac{|F|^2}{|G|^2}\Big|_{A=0} = |S_{22}|^2, \quad T_r = \frac{|B|^2}{|G|^2}\Big|_{A=0} = |S_{12}|^2. \qquad [2.162]$$

The S-matrix tells you everything there is to know about scattering from a localized potential. Surprisingly, it *also* contains (albeit in a concealed form) information about the bound states (if there *are* any). For if $E < 0$, then $\psi(x)$ has the form

$$\psi(x) = \begin{cases} Be^{\kappa x} & \text{(Region I)}, \\ Cf(x) + Dg(x) & \text{(Region II)}, \\ Fe^{-\kappa x} & \text{(Region III)}, \end{cases} \qquad [2.163]$$

with

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}. \qquad [2.164]$$

The boundary conditions are the same as before, so the S-matrix has the same structure—only now E is *negative*, so $k \to i\kappa$. But this time A and G are necessarily zero, whereas B and F are not, and hence (Equation 2.158) at least two elements in the S-matrix must be infinite. To put it the other way around, if you've got the S-matrix (for $E > 0$), and you want to locate the bound states, put in $k \to i\kappa$, and look for energies at which the S-matrix blows up.

For example, in the case of the finite square well,

$$S_{21} = \frac{e^{-2ika}}{\cos(2la) - i\frac{\sin(2la)}{2kl}(k^2 + l^2)}$$

(Equation 2.150). Substituting $k \to i\kappa$, we see that S_{21} blows up whenever

$$\cot(2la) = \frac{l^2 - \kappa^2}{2\kappa l}.$$

Using the trigonometric identity

$$\tan\left(\frac{\theta}{2}\right) = \pm\sqrt{1+\cot^2\theta} - \cot\theta,$$

we obtain

$$\tan(la) = \frac{l}{\kappa} \text{ (plus sign), and } \cot(la) = -\frac{\kappa}{l} \text{ (minus sign).}$$

These are precisely the conditions for bound states of the finite square well (Equation 2.136 and Problem 2.28).

***Problem 2.34** Construct the S-matrix for scattering from a delta-function well (Equation 2.96). Use it to obtain the bound state energy, and check your answer against Equation 2.111.

Problem 2.35 Find the S-matrix for the finite square well (Equation 2.127). *Hint*: This requires no new work if you carefully exploit the symmetry of the problem.

FURTHER PROBLEMS FOR CHAPTER 2

Problem 2.36 A particle in the infinite square well (Equation 2.15) has the initial wave function

$$\Psi(x,0) = A\sin^3(\pi x/a).$$

Find $\langle x\rangle$ as a function of time.

***Problem 2.37** Find $\langle x\rangle$, $\langle p\rangle$, $\langle x^2\rangle$, $\langle p^2\rangle$, $\langle T\rangle$, and $\langle V(x)\rangle$ for the nth stationary state of the harmonic oscillator. Check that the uncertainty principle is satisfied. *Hint:* Express x and $(\hbar/i)(d/dx)$ in terms of $(a_+ \pm a_-)$, and use Equations 2.52 and 2.53; you may assume that the states are orthogonal.

Problem 2.38 Find the allowed energies of the half-harmonic oscillator

$$V(x) = \begin{cases} (1/2)m\omega^2x^2, & \text{for } (x > 0), \\ \infty, & \text{for } (x < 0). \end{cases}$$

(This represents, for example, a spring that can be stretched, but not compressed.) *Hint*: This requires some careful thought, but very little actual computation.

****Problem 2.39** Solve the time-independent Schrödinger equation for an infinite square well with a delta-function barrier at the center:

$$V(x) = \begin{cases} \alpha\delta(x), & \text{for } (-a < x < +a), \\ \infty, & \text{for } (|x| \geq a). \end{cases}$$

Treat the even and odd wave functions separately. Don't bother to normalize them. Find the allowed energies (graphically, if necessary). How do they compare with the corresponding energies in the absence of the delta function? Comment on the limiting cases $\alpha \to 0$ and $\alpha \to \infty$.

****Problem 2.40** In Problem 2.22 you analyzed the *stationary* Gaussian free particle wave packet. Now solve the same problem for the *traveling* Gaussian wave packet, starting with the initial wave function

$$\Psi(x, 0) = Ae^{-ax^2}e^{ilx},$$

where l is a real constant.

Problem 2.41 A particle of mass m and kinetic energy $E > 0$ approaches an abrupt potential drop V_0 (Figure 2.16).

(a) What is the probability that it will "reflect" back, if $E = V_0/3$?

(b) I drew the figure so as to make you think of a car approaching a cliff, but obviously the probability of "bouncing back" from the edge of a cliff is *far* smaller than what you got in (a)—unless you're Bugs Bunny. Explain why this potential does *not* correctly represent a cliff.

Problem 2.42 If two (or more) distinct[30] solutions to the (time-independent) Schrödinger equation have the same energy E, these states are said to be **degenerate**. For example, the free particle states are doubly degenerate—one solution representing motion to the right, and the other motion to the left. But we have encountered no

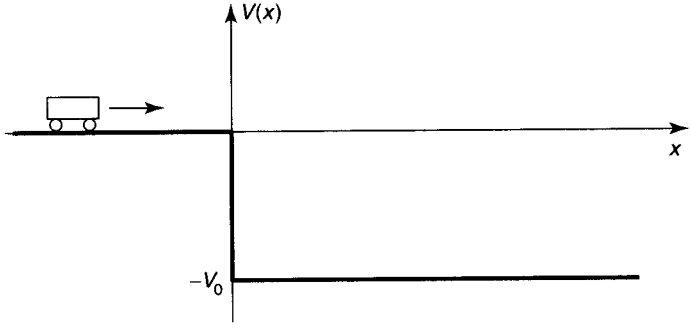

Figure 2.16: Scattering from a "cliff" (Problem 2.41).

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[30] If the two solutions differ only by a multiplicative constant (so that, once normalized, they differ only by a phase factor $e^{i\phi}$), they represent the same physical state, and in this case they are not distinct solutions. Technically, by "distinct" I mean "linearly independent."

normalizable degenerate solutions, and this is not an accident. Prove the following theorem: In one dimension[31] there are no degenerate bound states. *Hint*: Suppose there are two solutions, ψ_1 and ψ_2, with the same energy E. Multiply the Schrödinger equation for ψ_1 by ψ_2, and the Schrödinger equation for ψ_2 by ψ_1, and subtract, to show that $(\psi_2 d\psi_1/dx - \psi_1 d\psi_2/dx)$ is a constant. Use the fact that for normalizable solutions $\psi \to 0$ at $\pm\infty$ to demonstrate that this constant is in fact zero. Conclude that ψ_2 is a multiple of ψ_1, and hence that the two solutions are not distinct.

Problem 2.43 Imagine a bead of mass m that slides frictionlessly around a circular wire ring of circumference a. [This is just like a free particle, except that $\psi(x) = \psi(x + a)$.] Find the stationary states (with appropriate normalization) and the corresponding allowed energies. Note that there are *two* independent solutions for each energy E_n—corresponding to clockwise and counterclockwise circulation; call them $\psi_n^+(x)$ and $\psi_n^-(x)$. How do you account for this degeneracy, in view of the theorem in Problem 2.42—that is, why does the theorem fail in this case?

****Problem 2.44** (*Attention*: This is a strictly qualitative problem—no calculations allowed!) Consider the "double square well" potential (Figure 2.17). Suppose the depth V_0 and the width a are fixed, and great enough so that several bound states occur.

(a) Sketch the ground-state wave function ψ_1 and the first excited state ψ_2, (i) for the case $b = 0$, (ii) for $b \approx a$, and (iii) for $b \gg a$.

(b) Qualitatively, how do the corresponding energies (E_1 and E_2) vary, as b goes from 0 to ∞? Sketch $E_1(b)$ and $E_2(b)$ on the same graph.

(c) The double well is a very primitive one-dimensional model for the potential experienced by an electron in a diatomic molecule (the two wells represent the attractive force of the nuclei). If the nuclei are free to move, they will adopt the configuration of minimum energy. In view of your conclusions in (b), does the electron tend to draw the nuclei together, or push them apart? (Of course, there is also the internuclear repulsion to consider, but that's a separate problem.)

*****Problem 2.45**

(a) Show that

$$\Psi(x,t) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left[-\frac{m\omega}{2\hbar}\left(x^2 + \frac{a^2}{2}(1 + e^{-2i\omega t}) + \frac{i\hbar t}{m} - 2axe^{-i\omega t}\right)\right]$$

---

[31] In higher dimensions such degeneracy is very common, as we shall see in Chapter 4. Assume that the potential does not consist of isolated pieces separated by regions where $V = \infty$—two isolated infinite square wells, for instance, would give rise to degenerate bound states, for which the particle is either in the one or in the other.

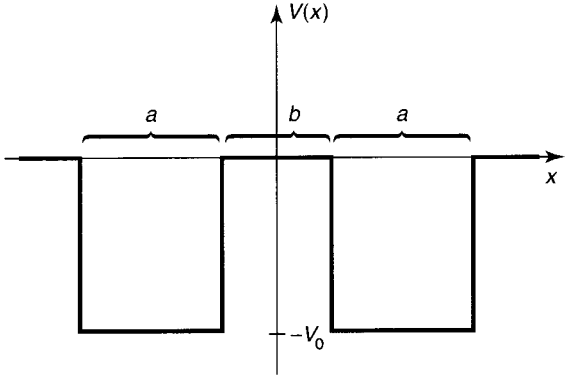

Figure 2.17: The double square well (Problem 2.44).

satisfies the time-*dependent* Schrödinger equation for the harmonic oscillator potential (Equation 2.38). Here a is any real constant (with the dimensions of length).[32]

(b) Find $|\Psi(x,t)|^2$, and describe the motion of the wave packet.

(c) Compute $\langle x \rangle$ and $\langle p \rangle$, and check that Ehrenfest's theorem (Equation 1.38) is satisfied.

Problem 2.46 Consider the potential

$$V(x) = \begin{cases} \infty, & \text{if } x < 0, \\ \alpha\delta(x-a), & \text{if } x \geq 0, \end{cases}$$

where a and α are positive real constants with the appropriate units (see Figure 2.18). A particle starts out in the "well" ($0 < x < a$), but because of tunneling its wave function gradually "leaks" out through the delta-function barrier.

(a) Solve the (time-independent) Schrödinger equation for this potential; impose appropriate boundary conditions, and determine the "energy", E. (An implicit equation will do.)

(b) I put the word "energy" in quotes because you'll notice that it is a *complex number*! How do you account for this, in view of the theorem you proved in Problem 2.1a?

(c) Writing $E = E_0 + i\Gamma$ (with E_0 and Γ real), calculate (in terms of Γ) the characteristic time it takes the particle to leak out of the well (that is, the time it takes before the probability is $1/e$ that it's still in the region $0 < x < a$).

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[32]This rare example of an exact closed-form solution to the time-dependent Schrödinger equation was discovered by Schrödinger himself, in 1926.

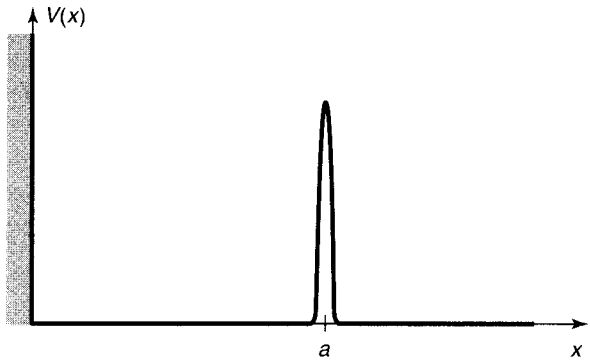

Figure 2.18: The potential for Problem 2.46.

****Problem 2.47** Consider the *moving* delta-function well:

$$V(x,t) = -\alpha\delta(x - vt),$$

where v is the (constant) velocity of the well.

(a) Show that the time-dependent Schrödinger equation admits the exact solution

$$\Psi(x,t) = \frac{\sqrt{m\alpha}}{\hbar} e^{-m\alpha|x-vt|/\hbar^2} e^{-i[(E+(1/2)mv^2)t - mvx]/\hbar},$$

where $E = -m\alpha^2/2\hbar^2$ is the bound-state energy of the *stationary* delta function. *Hint*: Plug it in and *check* it! Use Problem 2.24b.

(b) Find the expectation value of the Hamiltonian in this state, and comment on the result.

*****Problem 2.48** Consider the potential

$$V(x) = -\frac{\hbar^2 a^2}{m}\text{sech}^2(ax),$$

where a is a positive constant and "sech" stands for the hyperbolic secant.

(a) Show that this potential has the bound state

$$\psi_0(x) = A\ \text{sech}(ax),$$

and find its energy. Normalize ψ_0, and sketch its graph.

(b) Show that the function

$$\psi_k(x) = A\left(\frac{ik - a\tanh(ax)}{ik + a}\right)e^{ikx}$$

(where $k \equiv \sqrt{2mE}/\hbar$, as usual) solves the Schrödinger equation for any (positive) energy E. Since $\tanh z \to -1$ as $z \to -\infty$,

$$\psi_k(x) \approx Ae^{ikx}, \quad \text{for large negative } x.$$

This represents, then, a wave coming in from the left with *no accompanying reflected wave* [i.e., no term $\exp(-ikx)$]. What is the asymptotic form of $\psi_k(x)$ at large positive x? What are R and T for this potential? *Note*: sech^2 is a famous example of a "reflectionless" potential—every incident particle, regardless of its energy, passes right through. See R. E. Crandall and B. R. Litt, *Annals of Physics* **146**, 458 (1983).

(c) Construct the S-matrix for this potential, and use it to locate the bound states. How many of them are there? What are their energies? Check that your answer is consistent with part (a).

***Problem 2.49** The S-matrix tells you the *outgoing* amplitudes (B and F) in terms of the *incoming* amplitudes (A and G):

$$\begin{pmatrix} B \\ F \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} A \\ G \end{pmatrix}.$$

For some purposes it is more convenient to work with the **transfer matrix**, **M**, which gives you the amplitudes to the *right* of the potential (F and G) in terms of those to the *left* (A and B):

$$\begin{pmatrix} F \\ G \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix}.$$

(a) Find the four elements of the M-matrix in terms of the elements of the S-matrix, and vice versa. Express R_l, T_l, R_r, and T_r (Equations 2.161 and 2.162) in terms of elements of the M-matrix.

(b) Suppose you have a potential consisting of two isolated pieces (Figure 2.19). Show that the M-matrix for the combination is the *product* of the two M-matrices for each section separately:

$$\mathbf{M} = \mathbf{M}_2\mathbf{M}_1.$$

(This obviously generalizes to any number of pieces, and accounts for the usefulness of the M-matrix.)

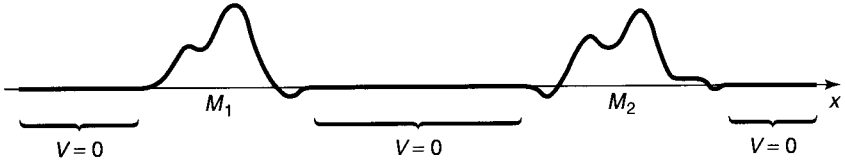

Figure 2.19: A potential consisting of two isolated pieces (Problem 2.49).

(c) Construct the M-matrix for scattering from a single delta-function potential at point a:

$$V(x) = -\alpha\delta(x - a).$$

(d) By the method of part (b), find the M-matrix for scattering from the double delta function

$$V(x) = -\alpha[\delta(x + a) + \delta(x - a)].$$

What is the transmission coefficient for this potential?

CHAPTER 3

FORMALISM

3.1 LINEAR ALGEBRA

The purpose of this chapter is to develop the *formalism* of quantum mechanics—terminology, notation, and mathematical background that illuminate the structure of the theory, facilitate practical calculations, and motivate a fundamental extension of the statistical interpretation. I begin with a brief survey of linear algebra.[1] Linear algebra abstracts and generalizes the arithmetic of ordinary vectors, as we encounter them in first-year physics. The generalization is in two directions: (1) We allow the scalars to be *complex*, and (2) we do not restrict ourselves to three dimensions (indeed, in Section 3.2 we shall be working with vectors that live in spaces of *infinite* dimension).

3.1.1 Vectors

A **vector space** consists of a set of **vectors** ($|\alpha\rangle$, $|\beta\rangle$, $|\gamma\rangle$, ...), together with a set of **scalars** (a, b, c, ...),[2] which are subject to two operations—vector addition and scalar multiplication:

[1] If you have already studied linear algebra, you should be able to skim this section quickly, but I wouldn't skip it altogether, because some of the notation may be unfamiliar. If, on the other hand, this material is new to you, be warned that I am only summarizing (often without proof) those aspects of the theory we will be needing later. For details, you should refer to a text on linear algebra, such as the classic by P. R. Halmos: *Finite Dimensional Vector Spaces*, 2nd ed. (Princeton, NJ: van Nostrand, 1958).

[2] For our purposes, the scalars will be ordinary complex numbers. Mathematicians can tell you about vector spaces over more exotic fields, but such objects play no role in quantum mechanics.

Vector addition. The "sum" of any two vectors is another vector:

$$|\alpha\rangle + |\beta\rangle = |\gamma\rangle. \tag{3.1}$$

Vector addition is **commutative**

$$|\alpha\rangle + |\beta\rangle = |\beta\rangle + |\alpha\rangle, \tag{3.2}$$

and **associative**

$$|\alpha\rangle + (|\beta\rangle + |\gamma\rangle) = (|\alpha\rangle + |\beta\rangle) + |\gamma\rangle. \tag{3.3}$$

There exists a **zero** (or **null**) **vector**,[3] $|0\rangle$, with the property that

$$|\alpha\rangle + |0\rangle = |\alpha\rangle, \tag{3.4}$$

for every vector $|\alpha\rangle$. And for every vector $|\alpha\rangle$ there is an associated **inverse vector** ($|-\alpha\rangle$), such that

$$|\alpha\rangle + |-\alpha\rangle = |0\rangle. \tag{3.5}$$

Scalar multiplication. The "product" of any scalar with any vector is another vector:

$$a|\alpha\rangle = |\gamma\rangle. \tag{3.6}$$

Scalar multiplication is **distributive** with respect to vector addition

$$a(|\alpha\rangle + |\beta\rangle) = a|\alpha\rangle + a|\beta\rangle \tag{3.7}$$

and with respect to scalar addition

$$(a + b)|\alpha\rangle = a|\alpha\rangle + b|\alpha\rangle. \tag{3.8}$$

It is also **associative** with respect to the ordinary multiplication of scalars:

$$a(b|\alpha\rangle) = (ab)|\alpha\rangle. \tag{3.9}$$

Multiplication by the scalars 0 and 1 has the effect you would expect:

$$0|\alpha\rangle = |0\rangle; \quad 1|\alpha\rangle = |\alpha\rangle. \tag{3.10}$$

Evidently $|-\alpha\rangle = (-1)|\alpha\rangle$.

There's a lot less here than meets the eye—all I have done is to write down in abstract language the familiar rules for manipulating vectors. The virtue of such abstraction is that we will be able to apply our knowledge and intuition about the behavior of ordinary vectors to other systems that happen to share the same formal properties.

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[3] It is customary, where no confusion can arise, to write the null vector without the adorning bracket: $|0\rangle \to 0$.

A **linear combination** of the vectors $|\alpha\rangle$, $|\beta\rangle$, $|\gamma\rangle$, ... is an expression of the form

$$a|\alpha\rangle + b|\beta\rangle + c|\gamma\rangle + \cdots. \qquad [3.11]$$

A vector $|\lambda\rangle$ is said to be **linearly independent** of the set $|\alpha\rangle$, $|\beta\rangle$, $|\gamma\rangle$, ... if it cannot be written as a linear combination of them. (For example, in three dimensions the unit vector $\hat{k}$ is linearly independent of $\hat{\imath}$ and $\hat{\jmath}$, but any vector in the xy-plane is linearly *dependent* on $\hat{\imath}$ and $\hat{\jmath}$.) By extension, a *set* of vectors is linearly independent if each one is linearly independent of all the rest. A collection of vectors is said to **span** the space if *every* vector can be written as a linear combination of the members of this set.[4] A set of *linearly independent* vectors that spans the space is called a **basis**. The number of vectors in any basis is called the **dimension** of the space. For the moment we shall assume that the dimension (n) is *finite*.

With respect to a prescribed basis

$$|e_1\rangle, \ |e_2\rangle, \ \ldots, \ |e_n\rangle, \qquad [3.12]$$

any given vector

$$|\alpha\rangle = a_1|e_1\rangle + a_2|e_2\rangle + \cdots + a_n|e_n\rangle \qquad [3.13]$$

is uniquely represented by the (ordered) n-tuple of its **components**:

$$|\alpha\rangle \leftrightarrow (a_1, a_2, \ldots, a_n). \qquad [3.14]$$

It is often easier to work with the components than with the abstract vectors themselves. To add vectors, you add their corresponding components:

$$|\alpha\rangle + |\beta\rangle \leftrightarrow (a_1 + b_1, a_2 + b_2, \ldots, a_n + b_n); \qquad [3.15]$$

to multiply by a scalar you multiply each component:

$$c|\alpha\rangle \leftrightarrow (ca_1, ca_2, \ldots, ca_n); \qquad [3.16]$$

the null vector is represented by a string of zeroes:

$$|0\rangle \leftrightarrow (0, 0, \ldots, 0); \qquad [3.17]$$

and the components of the inverse vector have their signs reversed:

$$|-\alpha\rangle \leftrightarrow (-a_1, -a_2, \ldots, -a_n). \qquad [3.18]$$

The only *dis*advantage of working with components is that you have to commit yourself to a particular basis, and the same manipulations will look very different to someone working in a different basis.

Problem 3.1 Consider the ordinary vectors in three dimensions ($a_x\hat{\imath} + a_y\hat{\jmath} + a_z\hat{k}$) with complex components.

---

[4] A set of vectors that spans the space is also called **complete**, though I personally reserve that word for the infinite-dimensional case, where subtle questions of convergence arise.

(a) Does the subset of all vectors with $a_z = 0$ constitute a vector space? If so, what is its dimension; if not, why not?

(b) What about the subset of all vectors whose z component is 1?

(c) How about the subset of vectors whose components are all equal?

***Problem 3.2** Consider the collection of all polynomials (with complex coefficients) of degree $< N$ in x.

(a) Does this set constitute a vector space (with the polynomials as "vectors")? If so, suggest a convenient basis, and give the dimension of the space. If not, which of the defining properties does it lack?

(b) What if we require that the polynomials be *even* functions?

(c) What if we require that the leading coefficient (i.e., the number multiplying x^{N-1}) be 1?

(d) What if we require that the polynomials have the value 0 at $x = 1$?

(e) What if we require that the polynomials have the value 1 at $x = 0$?

Problem 3.3 Prove that the components of a vector with respect to a given basis are *unique*.

3.1.2 Inner Products

In three dimensions we encounter two kinds of vector products: the dot product and the cross product. The latter does not generalize in any natural way to n-dimensional vector spaces, but the former *does*—in this context it is usually called the **inner product**. The inner product of two vectors ($|\alpha\rangle$ and $|\beta\rangle$) is a complex number (which we write as $\langle\alpha|\beta\rangle$), with the following properties:

$$\langle\beta|\alpha\rangle = \langle\alpha|\beta\rangle^*, \qquad [3.19]$$

$$\langle\alpha|\alpha\rangle \geq 0, \quad \text{and } \langle\alpha|\alpha\rangle = 0 \Leftrightarrow |\alpha\rangle = |0\rangle, \qquad [3.20]$$

$$\langle\alpha|\left(b|\beta\rangle + c|\gamma\rangle\right) = b\langle\alpha|\beta\rangle + c\langle\alpha|\gamma\rangle. \qquad [3.21]$$

Apart from the generalization to complex numbers, these axioms simply codify the familiar behavior of dot products. A vector space with an inner product is called an **inner product space**.

Because the inner product of any vector with itself is a nonnegative number (Equation 3.20), its square root is *real*—we call this the **norm** of the vector:

$$\|\alpha\| \equiv \sqrt{\langle\alpha|\alpha\rangle}; \qquad [3.22]$$

it generalizes the notion of "length". A "unit" vector, whose norm is 1, is said to be **normalized** (the word should really be "normal", but I guess that sounds too anthropomorphic). Two vectors whose inner product is zero are called **orthogonal** (generalizing the notion of "perpendicular"). A collection of mutually orthogonal normalized vectors,

$$\langle \alpha_i | \alpha_j \rangle = \delta_{ij}, \tag{3.23}$$

is called an **orthonormal set**. It is always possible (see Problem 3.4), and almost always convenient, to choose an *orthonormal basis*; in that case the inner product of two vectors can be written very neatly in terms of their components:

$$\langle \alpha | \beta \rangle = a_1^* b_1 + a_2^* b_2 + \cdots + a_n^* b_n, \tag{3.24}$$

the norm (squared) becomes

$$\langle \alpha | \alpha \rangle = |a_1|^2 + |a_2|^2 + \cdots + |a_n|^2, \tag{3.25}$$

and the components themselves are

$$a_i = \langle e_i | \alpha \rangle. \tag{3.26}$$

(These results generalize the familiar formulas $\mathbf{a} \cdot \mathbf{b} = a_x b_x + a_y b_y + a_z b_z$, $\mathbf{a} \cdot \mathbf{a} = a_x^2 + a_y^2 + a_z^2$, and $a_x = \hat{\imath} \cdot \mathbf{a}$, $a_y = \hat{\jmath} \cdot \mathbf{a}$, $a_z = \hat{k} \cdot \mathbf{a}$, for the three-dimensional orthonormal basis $\hat{\imath}$, $\hat{\jmath}$, $\hat{k}$.) From now on we shall *always* work in orthonormal bases unless it is explicitly indicated otherwise.

Another geometrical quantity one might wish to generalize is the *angle* between two vectors. In ordinary vector analysis $\cos\theta = (\mathbf{a} \cdot \mathbf{b})/|\mathbf{a}||\mathbf{b}|$. But because the inner product is in general a complex number, the analogous formula (in an arbitrary inner product space) does not define a (real) angle θ. Nevertheless, it is still true that the *absolute value* of this quantity is a number no greater than 1,

$$|\langle \alpha | \beta \rangle|^2 \leq \langle \alpha | \alpha \rangle \langle \beta | \beta \rangle. \tag{3.27}$$

(This important result is known as the **Schwarz inequality**; the proof is given in Problem 3.5.) So you can, if you like, define the angle between $|\alpha\rangle$ and $|\beta\rangle$ by the formula

$$\cos\theta = \sqrt{\frac{\langle \alpha | \beta \rangle \langle \beta | \alpha \rangle}{\langle \alpha | \alpha \rangle \langle \beta | \beta \rangle}}. \tag{3.28}$$

***Problem 3.4** Suppose you start out with a basis $(|e_1\rangle, |e_2\rangle, \ldots, |e_n\rangle)$ that is *not* orthonormal. The **Gram-Schmidt procedure** is a systematic ritual for generating from it an orthonormal basis $(|e_1'\rangle, |e_2'\rangle, \ldots, |e_n'\rangle)$. It goes like this:

(i) Normalize the first basis vector (divide by its norm):

$$|e_1'\rangle = \frac{|e_1\rangle}{\||e_1\|}.$$

(ii) Find the projection of the second vector along the first, and subtract it off:

$$|e_2\rangle - \langle e_1'|e_2\rangle|e_1'\rangle.$$

This vector is orthogonal to $|e_1'\rangle$; normalize it to get $|e_2'\rangle$.

(iii) Subtract from $|e_3\rangle$ its projections along $|e_1'\rangle$ and $|e_2'\rangle$:

$$|e_3\rangle - \langle e_1'|e_3\rangle|e_1'\rangle - \langle e_2'|e_3\rangle|e_2'\rangle.$$

This is orthogonal to $|e_1'\rangle$ and $|e_2'\rangle$; normalize it to get $|e_3'\rangle$. And so on.

Use the Gram-Schmidt procedure to orthonormalize the three-space basis $|e_1\rangle = (1+i)\hat{\imath} + (1)\hat{\jmath} + (i)\hat{k}$, $|e_2\rangle = (i)\hat{\imath} + (3)\hat{\jmath} + (1)\hat{k}$, $|e_3\rangle = (0)\hat{\imath} + (28)\hat{\jmath} + (0)\hat{k}$.

Problem 3.5 Prove the Schwarz inequality (Equation 3.27). *Hint*: Let $|\gamma\rangle = |\beta\rangle - (\langle\alpha|\beta\rangle/\langle\alpha|\alpha\rangle)|\alpha\rangle$, and use $\langle\gamma|\gamma\rangle \geq 0$.

Problem 3.6 Find the angle (in the sense of Equation 3.28) between the vectors $|\alpha\rangle = (1+i)\hat{\imath} + (1)\hat{\jmath} + (i)\hat{k}$ and $|\beta\rangle = (4-i)\hat{\imath} + (0)\hat{\jmath} + (2-2i)\hat{k}$.

Problem 3.7 Prove the **triangle inequality**: $\|(|\alpha\rangle + |\beta\rangle)\| \leq \|\alpha\| + \|\beta\|$.

3.1.3 Linear Transformations

Suppose you take every vector (in three-space) and multiply it by 17, or you rotate every vector by 39° about the z-axis, or you reflect every vector in the xy-plane—these are all examples of **linear transformations**. A linear transformation[5] ($\hat{T}$) takes each vector in a vector space and "transforms" it into some other vector ($|\alpha\rangle \to |\alpha'\rangle = \hat{T}|\alpha\rangle$), with the proviso that the operation is *linear*:

$$\hat{T}(a|\alpha\rangle + b|\beta\rangle) = a(\hat{T}|\alpha\rangle) + b(\hat{T}|\beta\rangle), \qquad [3.29]$$

for any vectors $|\alpha\rangle$, $|\beta\rangle$ and any scalars a, b.

If you know what a particular linear transformation does to a set of *basis* vectors, you can easily figure out what it does to *any* vector. For suppose that

$$\begin{aligned}
\hat{T}|e_1\rangle &= T_{11}|e_1\rangle + T_{21}|e_2\rangle + \cdots + T_{n1}|e_n\rangle,\\
\hat{T}|e_2\rangle &= T_{12}|e_1\rangle + T_{22}|e_2\rangle + \cdots + T_{n2}|e_n\rangle,\\
&\cdots\\
\hat{T}|e_n\rangle &= T_{1n}|e_1\rangle + T_{2n}|e_2\rangle + \cdots + T_{nn}|e_n\rangle,
\end{aligned}$$

or, more compactly,

$$\hat{T}|e_j\rangle = \sum_{i=1}^{n} T_{ij}|e_i\rangle, \quad (j = 1, 2, \ldots, n). \qquad [3.30]$$

---

[5] In this chapter I'll use a hat (ˆ) to denote linear transformations; this is not inconsistent with my earlier convention (putting hats on operators), for (as we shall see) our operators *are* linear transformations.

If $|\alpha\rangle$ is an arbitrary vector:

$$|\alpha\rangle = a_1|e_1\rangle + a_2|e_2\rangle + \cdots + a_n|e_n\rangle = \sum_{j=1}^{n} a_j|e_j\rangle, \qquad [3.31]$$

then

$$\hat{T}|\alpha\rangle = \sum_{j=1}^{n} a_j(\hat{T}|e_j\rangle) = \sum_{j=1}^{n}\sum_{i=1}^{n} a_j T_{ij}|e_i\rangle = \sum_{i=1}^{n}\Big(\sum_{j=1}^{n} T_{ij}a_j\Big)|e_i\rangle. \qquad [3.32]$$

Evidently $\hat{T}$ takes a vector with components $a_1, a_2, \ldots, a_n$ into a vector with components[6]

$$a_i' = \sum_{j=1}^{n} T_{ij}a_j. \qquad [3.33]$$

Thus the n^2 **elements** T_{ij} uniquely characterize the linear transformation $\hat{T}$ (with respect to a given basis), just as the n components a_i uniquely characterize the vector $|\alpha\rangle$ (with respect to the same basis):

$$\hat{T} \leftrightarrow (T_{11}, T_{12}, \ldots, T_{nn}). \qquad [3.34]$$

If the basis is orthonormal, it follows from Equation 3.30 that

$$T_{ij} = \langle e_i|\hat{T}|e_j\rangle. \qquad [3.35]$$

It is convenient to display these complex numbers in the form of a **matrix**[7]:

$$\mathbf{T} = \begin{pmatrix} T_{11} & T_{12} & \cdots & T_{1n} \\ T_{21} & T_{22} & \cdots & T_{2n} \\ \vdots & \vdots & & \vdots \\ T_{n1} & T_{n2} & \cdots & T_{nn} \end{pmatrix}. \qquad [3.36]$$

The study of linear transformations, then, reduces to the theory of matrices. The *sum* of two linear transformations $(\hat{S} + \hat{T})$ is defined in the natural way:

$$(\hat{S} + \hat{T})|\alpha\rangle = \hat{S}|\alpha\rangle + \hat{T}|\alpha\rangle; \qquad [3.37]$$

this matches the usual rule for adding matrices (you add their corresponding elements):

$$\mathbf{U} = \mathbf{S} + \mathbf{T} \Leftrightarrow U_{ij} = S_{ij} + T_{ij}. \qquad [3.38]$$

---

[6]Notice the reversal of indices between Equations 3.30 and 3.33. This is not a typographical error. Another way of putting it (switching $i \leftrightarrow j$ in Equation 3.30) is that if the *components* transform with T_{ij}, the *basis* vectors transform with T_{ji}.

[7]I'll use boldface to denote matrices.

The *product* of two linear transformations ($\hat{S}\hat{T}$) is the net effect of performing them in succession—first $\hat{T}$, then $\hat{S}$:

$$|\alpha\rangle \rightarrow |\alpha'\rangle = \hat{T}|\alpha\rangle \rightarrow |\alpha''\rangle = \hat{S}|\alpha'\rangle = \hat{S}(\hat{T}|\alpha\rangle) = \hat{S}\hat{T}|\alpha\rangle. \qquad [3.39]$$

What matrix **U** represents the combined transformation $\hat{U} = \hat{S}\hat{T}$? It's not hard to work it out:

$$a_i'' = \sum_{j=1}^{n} S_{ij}a_j' = \sum_{j=1}^{n} S_{ij}\left(\sum_{k=1}^{n} T_{jk}a_k\right) = \sum_{k=1}^{n}\left(\sum_{J=1}^{n} S_{ij}T_{jk}\right)a_k = \sum_{k=1}^{n} U_{ik}a_k.$$

Evidently

$$\mathbf{U} = \mathbf{ST} \Leftrightarrow U_{ik} = \sum_{j=1}^{n} S_{ij}T_{jk}; \qquad [3.40]$$

this is the standard rule for matrix multiplication—to find the ik^{th} element of the product, you look at the i^{th} row of **S** and the k^{th} column of **T**, multiply corresponding entries, and add. The same procedure allows you to multiply *rectangular* matrices, as long as the number of columns in the first matches the number of rows in the second. In particular, if we write the n-tuple of components of $|\alpha\rangle$ as an $n \times 1$ **column matrix**

$$\mathbf{a} \equiv \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}, \qquad [3.41]$$

the transformation rule (Equation 3.33) can be written

$$\mathbf{a}' = \mathbf{Ta}. \qquad [3.42]$$

And now, some useful matrix terminology: The **transpose** of a matrix (which we shall write with a tilde: $\tilde{\mathbf{T}}$) is the same set of elements, but with rows and columns interchanged:

$$\tilde{\mathbf{T}} = \begin{pmatrix} T_{11} & T_{21} & \cdots & T_{n1} \\ T_{12} & T_{22} & \cdots & T_{n2} \\ \vdots & \vdots & & \vdots \\ T_{1n} & T_{2n} & \cdots & T_{nn} \end{pmatrix}. \qquad [3.43]$$

Notice that the transpose of a *column* matrix is a **row matrix**:

$$\tilde{\mathbf{a}} = (a_1 \quad a_2 \quad \cdots \quad a_n). \qquad [3.44]$$

A square matrix is **symmetric** if it is equal to its transpose (reflection in the **main diagonal**—upper left to lower right—leaves it unchanged); it is **antisymmetric** if this operation reverses the sign:

$$\text{SYMMETRIC: } \tilde{\mathbf{T}} = \mathbf{T}; \quad \text{ANTISYMMETRIC: } \tilde{\mathbf{T}} = -\mathbf{T}. \qquad [3.45]$$

To construct the (complex) **conjugate** of a matrix (which we denote, as usual, with an asterisk: $\mathbf{T}^*$), you take the complex conjugate of every element:

$$\mathbf{T}^* = \begin{pmatrix} T_{11}^* & T_{12}^* & \cdots & T_{1n}^* \\ T_{21}^* & T_{22}^* & \cdots & T_{2n}^* \\ \vdots & \vdots & & \vdots \\ T_{n1}^* & T_{n2}^* & \cdots & T_{nn}^* \end{pmatrix}; \quad \mathbf{a}^* = \begin{pmatrix} a_1^* \\ a_2^* \\ \vdots \\ a_n^* \end{pmatrix}. \tag{3.46}$$

A matrix is **real** if all its elements are real and **imaginary** if they are all imaginary:

$$\text{REAL: } \mathbf{T}^* = \mathbf{T}; \quad \text{IMAGINARY: } \mathbf{T}^* = -\mathbf{T}. \tag{3.47}$$

The **Hermitian conjugate** (or **adjoint**) of a matrix (indicated by a dagger: $\mathbf{T}^\dagger$) is the transposed conjugate:

$$\mathbf{T}^\dagger \equiv \tilde{\mathbf{T}}^* = \begin{pmatrix} T_{11}^* & T_{21}^* & \cdots & T_{n1}^* \\ T_{12}^* & T_{22}^* & \cdots & T_{n2}^* \\ \vdots & \vdots & & \vdots \\ T_{1n}^* & T_{2n}^* & \cdots & T_{nn}^* \end{pmatrix}; \quad \mathbf{a}^\dagger \equiv \tilde{\mathbf{a}}^* = (a_1^* \quad a_2^* \quad \cdots \quad a_n^*). \tag{3.48}$$

A square matrix is **Hermitian** (or **self-adjoint**) if it is equal to its Hermitian conjugate; if Hermitian conjugation introduces a minus sign, the matrix is **skew Hermitian** (or **anti-Hermitian**):

$$\text{HERMITIAN: } \mathbf{T}^\dagger = \mathbf{T}; \quad \text{SKEW HERMITIAN: } \mathbf{T}^\dagger = -\mathbf{T}. \tag{3.49}$$

With this notation the inner product of two vectors (with respect to an orthonormal basis—Equation 3.24), can be written very neatly in matrix form:

$$\langle \alpha | \beta \rangle = \mathbf{a}^\dagger \mathbf{b}. \tag{3.50}$$

(Notice that each of the three operations discussed in this paragraph, if applied twice, returns you to the original matrix.)

Matrix multiplication is not, in general, commutative ($\mathbf{ST} \neq \mathbf{TS}$); the difference between the two orderings is called the **commutator**:

$$[\mathbf{S}, \mathbf{T}] \equiv \mathbf{ST} - \mathbf{TS}. \tag{3.51}$$

The transpose of a product is the product of the transposes *in reverse order*:

$$\widetilde{(\mathbf{ST})} = \tilde{\mathbf{T}}\tilde{\mathbf{S}} \tag{3.52}$$

(see Problem 3.12), and the same goes for Hermitian conjugates:

$$(\mathbf{ST})^\dagger = \mathbf{T}^\dagger \mathbf{S}^\dagger. \tag{3.53}$$

The **unit matrix** (representing a linear transformation that carries every vector into itself) consists of ones on the main diagonal and zeroes everywhere else:

$$\mathbf{1} \equiv \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & & \vdots \\ 0 & 0 & \cdots & 1 \end{pmatrix}. \tag{3.54}$$

In other words,

$$\mathbf{1}_{ij} = \delta_{ij}. \tag{3.55}$$

The **inverse** of a matrix (written $\mathbf{T}^{-1}$) is defined in the obvious way:

$$\mathbf{T}^{-1}\mathbf{T} = \mathbf{T}\mathbf{T}^{-1} = \mathbf{1}. \tag{3.56}$$

A matrix has an inverse if and only if its **determinant**[8] is nonzero; in fact,

$$\mathbf{T}^{-1} = \frac{1}{\det \mathbf{T}}\tilde{\mathbf{C}}, \tag{3.57}$$

where $\mathbf{C}$ is the matrix of **cofactors** [the cofactor of element T_{ij} is $(-1)^{i+j}$ times the determinant of the submatrix obtained from $\mathbf{T}$ by erasing the i^{th} row and the j^{th} column]. A matrix without an inverse is said to be **singular**. The inverse of a product (assuming it exists) is the product of the inverses *in reverse order*:

$$(\mathbf{S}\mathbf{T})^{-1} = \mathbf{T}^{-1}\mathbf{S}^{-1}. \tag{3.58}$$

A matrix is **unitary** if its inverse is equal to its Hermitian conjugate:

$$\text{UNITARY}: \mathbf{U}^{\dagger} = \mathbf{U}^{-1}. \tag{3.59}$$

Assuming the basis is orthonormal, the columns of a unitary matrix constitute an orthonormal set, and so too do its rows (see Problem 3.16).

The components of a given vector depend on your (arbitrary) choice of basis, as do the elements in the matrix representing a given linear transformation. We might inquire how these numbers change when we switch to a different basis. The old basis vectors $|e_i\rangle$ are—like *all* vectors—linear combinations of the new ones:

$$\begin{aligned} |e_1\rangle &= S_{11}|f_1\rangle + S_{21}|f_2\rangle + \cdots + S_{n1}|f_n\rangle, \\ |e_2\rangle &= S_{12}|f_1\rangle + S_{22}|f_2\rangle + \cdots + S_{n2}|f_n\rangle, \\ &\cdots \\ |e_n\rangle &= S_{1n}|f_1\rangle + S_{2n}|f_2\rangle + \cdots + S_{nn}|f_n\rangle \end{aligned}$$

[8] I assume you know how to evaluate determinants. If not, see M. Boas, *Mathematical Methods in the Physical Sciences*, 2nd ed. (New York: John Wiley, 1983), Section 3.3.

(for some set of complex numbers S_{ij}), or, more compactly,

$$|e_j\rangle = \sum_{i=1}^{n} S_{ij}|f_i\rangle, \quad (j = 1, 2, \ldots, n). \tag{3.60}$$

This is *itself* a linear transformation (compare Equation 3.30),[9] and we know immediately how the components transform:

$$a_i^f = \sum_{j=1}^{n} S_{ij} a_j^e \tag{3.61}$$

(where the superscript indicates the basis). In matrix form

$$\mathbf{a}^f = \mathbf{S}\mathbf{a}^e. \tag{3.62}$$

What about the matrix representing a given linear transformation $\hat{T}$—how is *it* modified by a change of basis? In the old basis we had (Equation 3.42)

$$\mathbf{a}^{e\prime} = \mathbf{T}^e \mathbf{a}^e,$$

and Equation 3.62—multiplying both sides by $\mathbf{S}^{-1}$—entails[10] $\mathbf{a}^e = \mathbf{S}^{-1}\mathbf{a}^f$, so

$$\mathbf{a}^{f\prime} = \mathbf{S}\mathbf{a}^{e\prime} = \mathbf{S}(\mathbf{T}^e\mathbf{a}^e) = \mathbf{S}\mathbf{T}^e\mathbf{S}^{-1}\mathbf{a}^f.$$

Evidently

$$\mathbf{T}^f = \mathbf{S}\mathbf{T}^e\mathbf{S}^{-1}. \tag{3.63}$$

In general, two matrices ($\mathbf{T}_1$ and $\mathbf{T}_2$) are said to be **similar** if $\mathbf{T}_2 = \mathbf{S}\mathbf{T}_1\mathbf{S}^{-1}$ for some (nonsingular) matrix $\mathbf{S}$. What we have just found is that similar matrices represent the same linear transformation with respect to two different bases. Incidentally, if the first basis is orthonormal, the second will also be orthonormal if and only if the matrix $\mathbf{S}$ is *unitary* (see Problem 3.14). Since we always work in orthonormal bases, we are interested mainly in unitary similarity transformations.

While the *elements* of the matrix representing a given linear transformation may look very different in the new basis, two numbers associated with the matrix are unchanged: the determinant and the **trace**. For the determinant of a product is the product of the determinants, and hence

$$\det(\mathbf{T}^f) = \det(\mathbf{S}\,\mathbf{T}^e\mathbf{S}^{-1}) = \det(\mathbf{S})\det(\mathbf{T}^e)\det(\mathbf{S}^{-1}) = \det\mathbf{T}^e. \tag{3.64}$$

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[9]Notice, however, the radically different perspective: In this case we're talking about one and the same *vector*, referred to two different *bases*, whereas before we were thinking of a completely *different* vector, referred to the *same* basis.

[10]Note that $\mathbf{S}^{-1}$ certainly exists—if $\mathbf{S}$ were singular, the $|f_i\rangle$'s would not span the space, so they wouldn't constitute a basis.

And the trace, which is the sum of the diagonal elements,

$$\mathrm{Tr}(\mathbf{T}) \equiv \sum_{i=1}^{m} T_{ii}, \qquad [3.65]$$

has the property (see Problem 3.15) that

$$\mathrm{Tr}(\mathbf{T}_1\mathbf{T}_2) = \mathrm{Tr}(\mathbf{T}_2\mathbf{T}_1), \qquad [3.66]$$

(for any two matrices $\mathbf{T}_1$ and $\mathbf{T}_2$), so that

$$\mathrm{Tr}(\mathbf{T}^f) = \mathrm{Tr}(\mathbf{S}\mathbf{T}^e\mathbf{S}^{-1}) = \mathrm{Tr}(\mathbf{T}^e\mathbf{S}^{-1}\mathbf{S}) = \mathrm{Tr}(\mathbf{T}^e). \qquad [3.67]$$

Problem 3.8 Using the standard basis $(\hat{\imath}, \hat{\jmath}, \hat{k})$ for vectors in three dimensions:

(a) Construct the matrix representing a rotation through angle θ (counterclockwise, looking down the axis toward the origin) about the z-axis.

(b) Construct the matrix representing a rotation by 120° (counterclockwise, looking down the axis) about an axis through the point (1,1,1).

(c) Construct the matrix representing reflection in the xy-plane.

(d) Are **translations** ($x \to x + x_0$, $y \to y + y_0$, $z \to z + z_0$, for some constants x_0, y_0, z_0) linear transformations? If so, find the matrix which represents them; if not, explain why not.

***Problem 3.9** Given the following two matrices:

$$\mathbf{A} = \begin{pmatrix} -1 & 1 & i \\ 2 & 0 & 3 \\ 2i & -2i & 2 \end{pmatrix}, \quad \mathbf{B} = \begin{pmatrix} 2 & 0 & -i \\ 0 & 1 & 0 \\ i & 3 & 2 \end{pmatrix},$$

compute (a) $\mathbf{A} + \mathbf{B}$, (b) $\mathbf{AB}$, (c) $[\mathbf{A}, \mathbf{B}]$, (d) $\tilde{\mathbf{A}}$, (e) $\mathbf{A}^*$, (f) $\mathbf{A}^\dagger$, (g) $\mathrm{Tr}(\mathbf{B})$, (h) $\det(\mathbf{B})$, and (i) $\mathbf{B}^{-1}$. Check that $\mathbf{B}\mathbf{B}^{-1} = \mathbf{1}$. Does $\mathbf{A}$ have an inverse?

***Problem 3.10** Using the square matrices in Problem 3.9 and the column matrices

$$\mathbf{a} = \begin{pmatrix} i \\ 2i \\ 2 \end{pmatrix}, \quad \mathbf{b} = \begin{pmatrix} 2 \\ (1-i) \\ 0 \end{pmatrix},$$

find (a) $\mathbf{Aa}$, (b) $\mathbf{a}^\dagger\mathbf{b}$, (c) $\tilde{\mathbf{a}}\mathbf{B}\mathbf{b}$, (d) $\mathbf{a}\mathbf{b}^\dagger$.

Problem 3.11 By explicit construction of the matrices in question, show that any matrix $\mathbf{T}$ can be written

(a) as the sum of a symmetric matrix $\mathbf{S}$ and an antisymmetric matrix $\mathbf{A}$;