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 particle's **wave function**, $\Psi(x, t)$, and we get it by solving the **Schrödinger equation**:

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

[1.1]

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[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 ($v \ll c$).
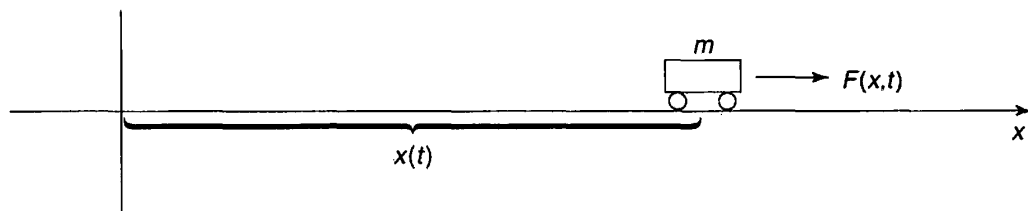
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FIGURE 1.1:   A "particle" constrained to move in one dimension under the influence of a specified force.

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

$$\hbar = \frac{h}{2\pi} = 1.054572 \times 10^{-34} \text{J s}. \tag{1.2}$$

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.[2]

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 represent 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,[3]

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

Probability is the *area* under the graph of $|\Psi|^2$. For the wave function in Figure 1.2, you would be quite likely to find the particle in the vicinity of point A, where $|\Psi|^2$ is large, and relatively *un*likely to find it near point B.

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[2]For a delightful first-hand account of the origins of the Schrödinger equation see the article by Felix Bloch in *Physics Today*, December 1976.

[3]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.
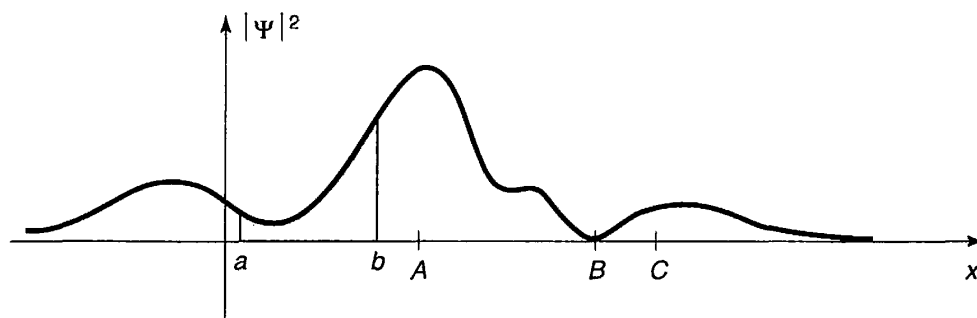
FIGURE 1.2:   A typical wave function. The shaded area represents the probability of finding the particle between a and b. The particle would be relatively likely to be found near A, and unlikely to be found near B.

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 particle (to wit: its wave function), still 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, and it is natural to wonder whether it is a fact of nature, or a defect in the theory.

Suppose I *do* measure the position of the particle, and I find it to be at point C.[4] *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."[5] 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

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[4]Of course, no measuring instrument is perfectly precise: what I *mean* is that the particle was found *in the vicinity* of C, to within the tolerance of the equipment.

[5]Bernard d'Espagnat, "The Quantum Theory and Reality" (Scientific American, November 1979, p. 165).

particle) to assume a definite position."[6] This view (the so-called **Copenhagen interpretation**), is associated with Bohr and his followers. Among physicists it has always been the 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 pejorative 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."[7] For decades this was the "fall-back" position of most physicists: They'd try to sell you the orthodox answer, but if you were persistent they'd retreat to the agnostic response, 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 whether the particle had a precise (though unknown) position prior to the measurement, or not. 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 argument; for now, suffice it to say that the experiments have decisively confirmed the orthodox interpretation:[8] 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.

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

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

[7]Quoted by Mermin (footnote 6), p. 40.

[8]This statement is a little too strong: There remain a few theoretical and experimental loopholes, some of which I shall discuss in the Afterword. There exist viable nonlocal hidden variable theories (notably David Bohm's), and 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.
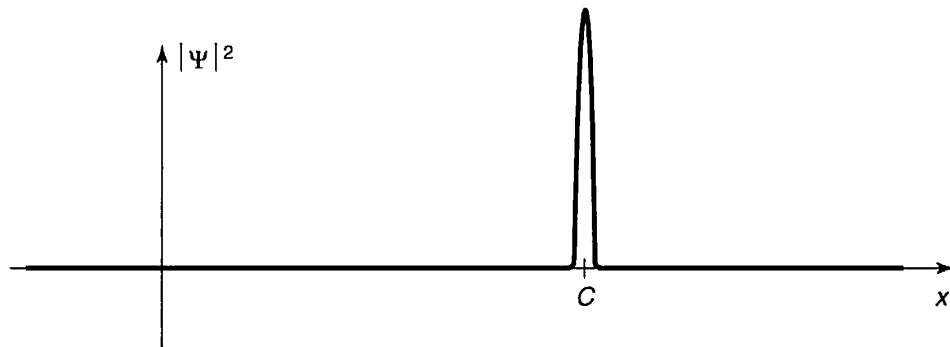
FIGURE 1.3: Collapse of the wave function: graph of $|\Psi|^2$ immediately *after* a measurement has found the particle at point C.

interpretation account for the fact that the second measurement is bound to yield 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 (it soon spreads out again, in accordance with the Schrödinger equation, so the second measurement must be made quickly). There 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.[9]

1.3 PROBABILITY

1.3.1 Discrete Variables

Because of the statistical interpretation, probability plays a central role in quantum mechanics, so I digress now for a brief discussion of probability theory. 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 fourteen people, whose ages are as follows:

one person aged 14,

one person aged 15,

three people aged 16,

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[9]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.

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

$N(14) = 1,$

$N(15) = 1,$

$N(16) = 3,$

$N(22) = 2,$

$N(24) = 2,$

$N(25) = 5,$

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 the example, 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 that 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,

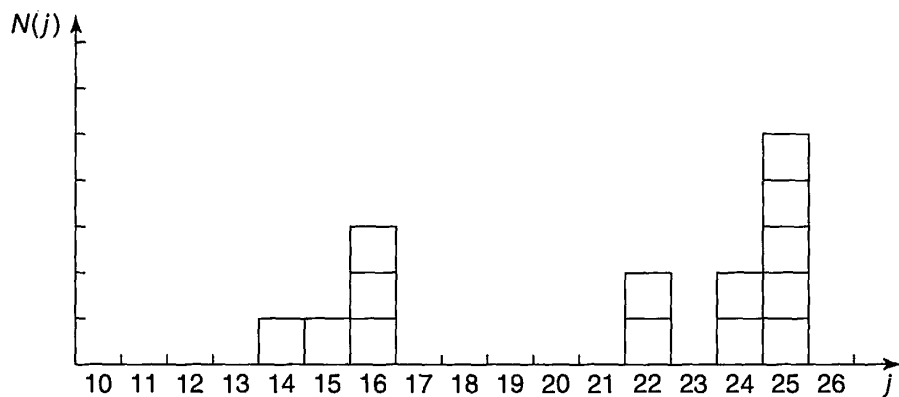$$P(j) = \frac{N(j)}{N}. \qquad [1.5]$$

FIGURE 1.4: Histogram showing the number of people, $N(j)$, with age j, for the distribution in Section 1.3.1.

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:

$$\sum_{j=0}^{\infty} P(j) = 1. \qquad [1.6]$$

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

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

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

$$\boxed{\langle f(j) \rangle = \sum_{j=0}^{\infty} f(j) P(j).} \qquad [1.9]$$
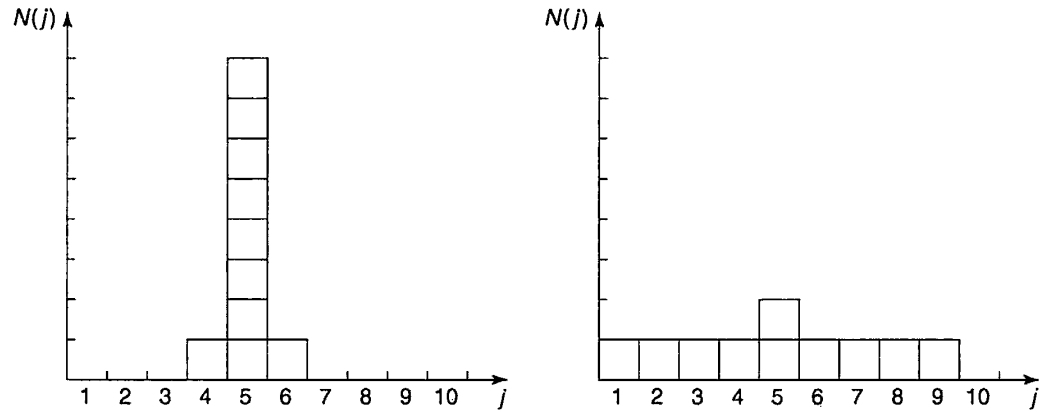
FIGURE 1.5: Two histograms with the same median, same average, and same most probable value, but different standard deviations.

(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* equal, in general, 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, the second, perhaps, a rural one-room schoolhouse.) We need a numerical measure of the amount of "spread" in a 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,

$$\Delta j = j - \langle j \rangle. \qquad [1.10]$$

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:

$$\sigma^2 \equiv \langle (\Delta j)^2 \rangle. \qquad [1.11]$$

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 on variances:

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

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

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

$$= \langle j^2 \rangle - 2\langle j \rangle \langle j \rangle + \langle j \rangle^2 = \langle j^2 \rangle - \langle j \rangle^2.$$

Taking the square root, the standard deviation itself can be written as

$$\sigma = \sqrt{\langle j^2 \rangle - \langle j \rangle^2}. \qquad [1.12]$$

In practice, this is a much faster way to get σ: Simply calculate $\langle j^2 \rangle$ and $\langle j \rangle^2$, subtract, and take the square root. 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).

1.3.2 Continuous Variables

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 3.333 ... seconds is *zero*. The only sensible thing to speak about is the probability that her age lies in some *interval*—say, between 16 and 17. 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 that day—in which case we have simply 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

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

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:

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

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

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

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

Example 1.1   Suppose I drop a rock off a cliff of height h. As it falls, I snap a million photographs, at random intervals. On each picture I measure the distance the rock has fallen. *Question:* What is the *average* of all these distances? That is to say, what is the *time average* of the distance traveled?[10]

Solution: The rock starts out at rest, and picks up speed as it falls; it spends more time near the top, so the average distance must be less than $h/2$. Ignoring air resistance, the distance x at time t is

$$x(t) = \frac{1}{2}gt^2.$$

The velocity is $dx/dt = gt$, and the total flight time is $T = \sqrt{2h/g}$. The probability that the camera flashes in the interval dt is dt/T, so the probability that a given

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[10]A statistician will complain that I am confusing the average of a *finite sample* (a million, in this case) with the "true" average (over the whole continuum). This can be an awkward problem for the experimentalist, especially when the sample size is small, but here I am only concerned, of course, with the true average, to which the sample average is presumably a good approximation.
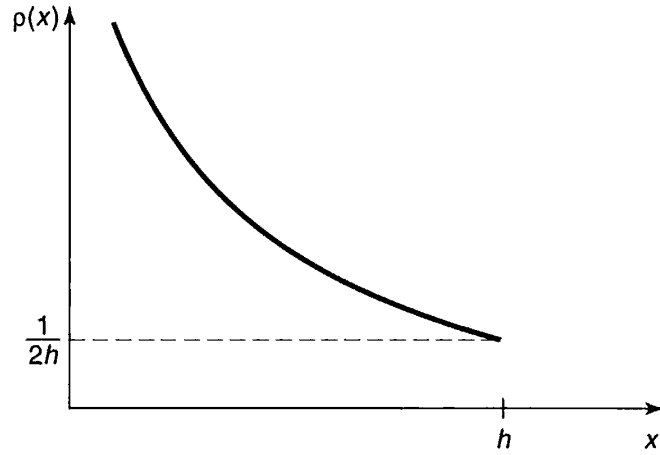
FIGURE 1.6: The probability density in Example 1.1: $\rho(x) = 1/(2\sqrt{hx})$.

photograph shows a distance in the corresponding range dx is

$$\frac{dt}{T} = \frac{dx}{gt}\sqrt{\frac{g}{2h}} = \frac{1}{2\sqrt{hx}}\,dx.$$

Evidently the probability *density* (Equation 1.14) is

$$\rho(x) = \frac{1}{2\sqrt{hx}}, \quad (0 \le x \le h)$$

(outside this range, of course, the probability density is zero).
We can check this result, using Equation 1.16:

$$\int_0^h \frac{1}{2\sqrt{hx}}\,dx = \frac{1}{2\sqrt{h}}\left(2x^{1/2}\right)\Big|_0^h = 1.$$

The *average* distance (Equation 1.17) is

$$\langle x \rangle = \int_0^h x\frac{1}{2\sqrt{hx}}\,dx = \frac{1}{2\sqrt{h}}\left(\frac{2}{3}x^{3/2}\right)\Big|_0^h = \frac{h}{3},$$

which is somewhat less than $h/2$, as anticipated.

Figure 1.6 shows the graph of $\rho(x)$. Notice that a probability *density* can be infinite, though probability itself (the *integral* of ρ) must of course be finite (indeed, less than or equal to 1).

∗Problem 1.1 For the distribution of ages in Section 1.3.1:

(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

(a) Find the standard deviation of the distribution in Example 1.1.

(b) What is the probability that a photograph, selected at random, would show a distance x more than one standard deviation away from the average?

∗Problem 1.3 Consider the **gaussian** distribution

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

where A, a, and λ are positive real 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 go imposing an extraneous condition on Ψ without checking that the two are consistent. Well, 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.[11]

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 remarkable 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.

This is important, so we'd better pause for a careful proof. To begin with,

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

(Note that the *integral* is a function only of t, so I use a *total* derivative (d/dt) in the first expression, 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

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

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[11]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.

The integral in 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.[12] It follows that

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

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

Problem 1.4 At time $t = 0$ a particle is represented by the wave function

$$\Psi(x, 0) = \begin{cases} A\dfrac{x}{a}, & \text{if } 0 \le x \le a, \\[2mm] A\dfrac{(b-x)}{(b-a)}, & \text{if } a \le x \le b, \\[2mm] 0, & \text{otherwise,} \end{cases}$$

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 1.5** Consider the wave function

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

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.

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[12] A good mathematician can supply you with pathological counterexamples, but they do not arise in physics; for us the wave function *always* goes to zero at infinity.

(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?

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 have to 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[13]

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

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[13]To keep things from getting too cluttered. I'll suppress the limits of integration.

This expression can be simplified using integration-by-parts:[14]

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

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

$$\langle v \rangle = \frac{d\langle x \rangle}{dt}.$$ [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:

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

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[14]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.

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

$$\langle x \rangle = \int \Psi^*(x)\Psi \, dx,$$ [1.34]

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

We say that the **operator**[15] 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 quantities? The fact is, *all* classical dynamical variables can be expressed 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 *any* such quantity, $Q(x, p)$, we simply replace every p by $(\hbar/i)(\partial/\partial x)$, insert the resulting operator between Ψ^* and Ψ, and integrate:

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

For example, the expectation value of the kinetic energy is

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

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[15]An "operator" is an instruction to *do something* to the function that follows it. 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.

Problem 1.6 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 $d\langle x\rangle/dt = 0$?

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*Problem 1.7 Calculate $d\langle p\rangle/dt$. *Answer*:

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

Equations 1.32 (or the first part of 1.33) and 1.38 are instances of **Ehrenfest's theorem**, which tells us that *expectation values obey classical laws.*

Problem 1.8 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: $\exp(-iV_0t/\hbar)$. 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 1.7). 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 1.8), 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? 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.[16] A theorem in Fourier analysis makes all this rigorous, but for the moment I am only concerned with the qualitative argument.

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[16]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.

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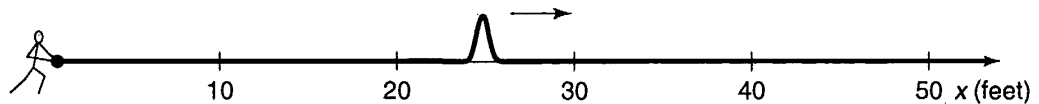

FIGURE 1.8: A wave with a (fairly) well-defined *position*, but an ill-defined *wavelength*.

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**:[17]

$$p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda}.$$ [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 is its momentum. Quantitatively,

$$\boxed{\sigma_x \sigma_p \geq \frac{\hbar}{2},}$$ [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 right away, so you can test it out on the examples in Chapter 2.)

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 identically prepared systems do not yield identical results. You can, if you want, construct a state 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 state with a reproducible momentum (by making

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[17]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.

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 create a state for 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 1.9 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?

FURTHER PROBLEMS FOR CHAPTER 1   \

Problem 1.10 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 1.11 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, $\rho(\theta)$? *Hint:* $\rho(\theta)\,d\theta$ 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 1.12 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 $\rho(x)$? 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:* $\rho(x)\,dx$ is the probability that the projection lies between x and $(x + dx)$. You know (from Problem 1.11) 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 1.11.

$\ast\ast$**Problem 1.13 Buffon's needle.** 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 1.12.

Problem 1.14 Let $P_{ab}(t)$ be the probability of finding a 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 $J(x,t)$? *Comment:* 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 Problem 1.9. (This is not a very pithy example, I'm afraid; we'll encounter more substantial ones in due course.)

∗∗**Problem 1.15** 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.

Problem 1.16 Show that

$$\frac{d}{dt}\int_{-\infty}^{\infty} \Psi_1^* \, \Psi_2 \, dx = 0$$

for any two (normalizable) solutions to the Schrödinger equation, Ψ_1 and Ψ_2.

Problem 1.17 A particle is represented (at time $t = 0$) by the wave function

$$\Psi(x,0) = \begin{cases} A(a^2 - x^2), & \text{if } -a \le x \le +a, \\ 0, & \text{otherwise.} \end{cases}$$

(a) Determine the normalization constant A.

(b) What is the expectation value of x (at time $t = 0$)?

(c) What is the expectation value of p (at time $t = 0$)? (Note that you *cannot* get it from $p = md\langle x\rangle/dt$. Why not?)

(d) Find the expectation value of x^2.

(e) Find the expectation value of p^2.

(f) Find the uncertainty in x (σ_x).

(g) Find the uncertainty in p (σ_p).

(h) Check that your results are consistent with the uncertainty principle.

Problem 1.18 In general, quantum mechanics is relevant when the de Broglie wavelength of the particle in question (h/p) is greater than the characteristic size of the system (d). In thermal equilibrium at (Kelvin) temperature T, the average kinetic energy of a particle is

$$\frac{p^2}{2m} = \frac{3}{2}k_B T$$

(where k_B is Boltzmann's constant), so the typical de Broglie wavelength is

$$\lambda = \frac{h}{\sqrt{3mk_B T}}.$$ [1.41]

The purpose of this problem is to anticipate which systems will have to be treated quantum mechanically, and which can safely be described classically.

(a) **Solids.** The lattice spacing in a typical solid is around $d = 0.3$ nm. Find the temperature below which the free[18] *electrons* in a solid are quantum mechanical. Below what temperature are the *nuclei* in a solid quantum mechanical? (Use sodium as a typical case.) *Moral:* The free electrons in a solid are *always* quantum mechanical; the nuclei are almost *never* quantum mechanical. The same goes for liquids (for which the interatomic spacing is roughly the same), with the exception of helium below 4 K.

(b) **Gases.** For what temperatures are the atoms in an ideal gas at pressure P quantum mechanical? *Hint:* Use the ideal gas law ($PV = Nk_B T$) to deduce the interatomic spacing. *Answer:* $T < (1/k_B)(h^2/3m)^{3/5} P^{2/5}$. Obviously (for the gas to show quantum behavior) we want m to be as *small* as possible, and P as *large* as possible. Put in the numbers for helium at atmospheric pressure. Is hydrogen in outer space (where the interatomic spacing is about 1 cm and the temperature is 3 K) quantum mechanical?

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[18]In a solid the inner electrons are attached to a particular nucleus, and for them the relevant size would be the radius of the atom. But the outermost electrons are not attached, and for them the relevant distance is the lattice spacing. This problem pertains to the *outer* electrons.

CHAPTER 2

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? We need to solve the Schrödinger equation,

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi,$$ [2.1]

for a specified potential[1] $V(x, t)$. In this chapter (and most of this book) I shall assume that 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*,

$$\Psi(x, t) = \psi(x)\,\varphi(t),$$ [2.2]

where ψ (*lower*-case) is a function of x alone, and φ is a function of t alone. On its face, this is an absurd restriction, and we cannot hope to get more than a tiny

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[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*.

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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.

For separable solutions we have

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

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

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

Or, dividing through by $\psi\varphi$:

$$i\hbar\frac{1}{\varphi}\frac{d\varphi}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V. \qquad [2.3]$$

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

$$i\hbar\frac{1}{\varphi}\frac{d\varphi}{dt} = E,$$

or

$$\frac{d\varphi}{dt} = -\frac{iE}{\hbar}\varphi, \qquad [2.4]$$

and

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

or

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi.} \qquad [2.5]$$

Separation of variables has turned a *partial* differential equation into two *ordinary* differential equations (Equations 2.4 and 2.5). The first of these (Equation 2.4)

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

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 $\psi\varphi$). Then

$$\varphi(t) = e^{-iEt/\hbar}. \qquad [2.6]$$

The second (Equation 2.5) is called the **time-independent Schrödinger equation**; we can go no further with it until the potential $V(x)$ is specified.

The rest of this chapter will be devoted to solving the time-independent Schrödinger equation, for a variety of simple potentials. But before I get to that you have every right to ask: *What's so great about separable solutions?* After all, *most* solutions to the (time *de*pendent) Schrödinger equation do *not* take the form $\psi(x)\varphi(t)$. I offer three answers—two of them physical, and one mathematical:

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

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

does (obviously) depend on t, the *probability density*,

$$|\Psi(x, t)|^2 = \Psi^*\Psi = \psi^* e^{+iEt/\hbar}\psi e^{-iEt/\hbar} = |\psi(x)|^2, \qquad [2.8]$$

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

$$\langle Q(x, p)\rangle = \int \psi^* Q\left(x, \frac{\hbar}{i}\frac{d}{dx}\right)\psi\,dx. \qquad [2.9]$$

Every expectation value is constant in time; we might as well drop the factor $\varphi(t)$ 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**:

$$H(x, p) = \frac{p^2}{2m} + V(x). \qquad [2.10]$$

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

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

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x).$$ [2.11]

Thus the time-independent Schrödinger equation (Equation 2.5) can be written

$$\hat{H}\psi = E\psi,$$ [2.12]

and the expectation value of the total energy is

$$\langle H \rangle = \int \psi^* \hat{H} \psi \, dx = E \int |\psi|^2 \, dx = E \int |\Psi|^2 \, dx = E.$$ [2.13]

(Notice 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 variance of H is

$$\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = E^2 - E^2 = 0.$$ [2.14]

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 2.5) 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**:

$$\Psi_1(x,t) = \psi_1(x)e^{-iE_1t/\hbar}, \quad \Psi_2(x,t) = \psi_2(x)e^{-iE_2t/\hbar}, \quad ....$$

Now (as you can easily check for yourself) the (time-*de*pendent) Schrödinger equation (Equation 2.1) has the property that any linear combination[5] of solutions

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

[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 $c_1, c_2, ...$ are any (complex) constants.

is itself a solution. Once we have found the separable solutions, then, we can immediately construct a much more general solution, of the form

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-i E_n t/\hbar}.$$ [2.15]

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

A lot has happened in the last four pages, so let me recapitulate, from a somewhat different perspective. Here's the generic problem: You're given a (time-independent) potential $V(x)$, and the starting wave function $\Psi(x, 0)$; your job is to find the wave function, $\Psi(x, t)$, for any subsequent time t. To do this you must solve the (time-dependent) Schrödinger equation (Equation 2.1). The strategy[6] is first to solve the time-*in*dependent Schrödinger equation (Equation 2.5); this yields, in general, an infinite set of solutions ($\psi_1(x)$, $\psi_2(x)$, $\psi_3(x)$, ...), each with its own associated energy (E_1, E_2, E_3, ...). To fit $\Psi(x, 0)$ you write down the general linear combination of these solutions:

$$\Psi(x, 0) = \sum_{n=1}^{\infty} c_n \psi_n(x);$$ [2.16]

the miracle is that you can *always* match the specified initial state by appropriate choice of the constants c_1, c_2, c_3, ... To construct $\Psi(x, t)$ you simply tack onto each term its characteristic time dependence, $\exp(-i E_n t/\hbar)$:

$$\boxed{\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-i E_n t/\hbar} = \sum_{n=1}^{\infty} c_n \Psi_n(x, t).}$$ [2.17]

The separable solutions themselves,

$$\Psi_n(x, t) = \psi_n(x) e^{-i E_n t/\hbar},$$ [2.18]

---

[6]Occasionally you can solve the time-dependent Schrödinger equation without recourse to separation of variables—see, for instance, Problems 2.49 and 2.50. But such cases are extremely rare.

are *stationary* states, in the sense that all probabilities and expectation values are independent of time, but this property is emphatically *not* shared by the general solution (Equation 2.17); the energies are different, for different stationary states, and the exponentials do not cancel, when you calculate $|\Psi|^2$.

Example 2.1 Suppose a particle starts out in a linear combination of just *two* stationary states:

$$\Psi(x, 0) = c_1 \psi_1(x) + c_2 \psi_2(x).$$

(To keep things simple I'll assume that the constants c_n and the states $\psi_n(x)$ are *real.*) What is the wave function $\Psi(x, t)$ at subsequent times? Find the probability density, and describe its motion.

Solution: The first part is easy:

$$\Psi(x, t) = c_1 \psi_1(x) e^{-i E_1 t/\hbar} + c_2 \psi_2(x) e^{-i E_2 t/\hbar},$$

where E_1 and E_2 are the energies associated with ψ_1 and ψ_2. It follows that

$$|\Psi(x, t)|^2 = (c_1 \psi_1 e^{i E_1 t/\hbar} + c_2 \psi_2 e^{i E_2 /\hbar})(c_1 \psi_1 e^{-i E_1 t/\hbar} + c_2 \psi_2 e^{-i E_2/\hbar})$$

$$= c_1^2 \psi_1^2 + c_2^2 \psi_2^2 + 2 c_1 c_2 \psi_1 \psi_2 \cos[(E_2 - E_1) t/\hbar].$$

(I used **Euler's formula**, $\exp i\theta = \cos\theta + i \sin\theta$, to simplify the result.) Evidently the probability density *oscillates* sinusoidally, at an angular frequency $(E_2 - E_1)/\hbar$; this is certainly *not* a stationary state. But notice that it took a *linear combination* of states (with different energies) to produce motion.[7]

---

*Problem 2.1 Prove the following three theorems:

(a) For normalizable solutions, the separation constant E must be *real*. *Hint:* Write E (in Equation 2.7) 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) The time-independent wave function $\psi(x)$ can always be taken to be *real* (unlike $\Psi(x, t)$, which is necessarily complex). 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 you *might as well* stick to ψ's that are real. *Hint:* If $\psi(x)$ satisfies Equation 2.5, for a given E, so too does its complex conjugate, and hence also the real linear combinations $(\psi + \psi^*)$ and $i(\psi - \psi^*)$.

---

[7]This is nicely illustrated by an applet at the Web site http://thorin.adnc.com/~topquark/quantum/deepwellmain.html.

(c) If $V(x)$ is an **even function** (that is, $V(-x) = V(x)$) then $\psi(x)$ can always be taken to be either even or odd. *Hint:* If $\psi(x)$ satisfies Equation 2.5, 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 2.5 in the form

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

if $E < V_{\min}$, 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

$$V(x) = \begin{cases} 0, & \text{if } 0 \le x \le a, \\ \infty, & \text{otherwise} \end{cases} \qquad [2.19]$$

(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 artificial, of course, but I urge you to treat it with respect. Despite its simplicity—or rather, precisely *because* of its simplicity—it serves as a wonderfully accessible test case for all the fancy machinery that comes later. We'll refer back to it frequently.)
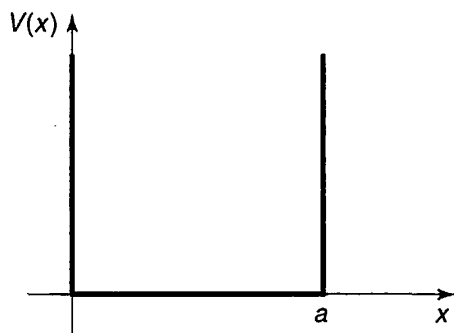
FIGURE 2.1:   The infinite square well potential (Equation 2.19).

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 2.5) reads

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

[2.20]

or

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

[2.21]

(By writing it in this way, I have tacitly assumed that $E \geq 0$; we know from Problem 2.2 that $E < 0$ won't work.) Equation 2.21 is the classical **simple harmonic oscillator** equation; the general solution is

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

[2.22]

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 $V = \infty$, in Section 2.5; for now I hope you will trust me.)

Continuity of $\psi(x)$ requires that

$$\psi(0) = \psi(a) = 0,$$

[2.23]

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

$$\psi(x) = A\sin kx.$$

[2.24]

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

$$ka = 0, \pm\pi, \pm2\pi, \pm3\pi, \ldots$$

[2.25]

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

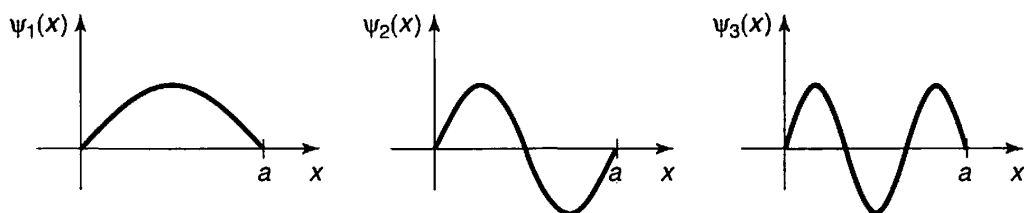$$k_n = \frac{n\pi}{a}, \quad \text{with } n = 1, 2, 3, \ldots$$

[2.26]

FIGURE 2.2: The first three stationary states of the infinite square well (Equation 2.28).

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:

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}.$$ [2.27]

In radical contrast to the classical case, a quantum particle in the infinite square well cannot have just *any* old energy—it has to be one of these special **allowed** values.[8] To find A, 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

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right).$$ [2.28]

As promised, the time-independent Schrödinger equation has delivered an infinite set of solutions (one for each positive 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 collection, 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.[9]

---

[8]Notice that the quantization of energy emerged as a rather technical consequence of the boundary conditions on solutions to the time-independent Schrödinger equation.

[9]To make this symmetry more apparent, some authors center the well at the origin (running it from $-a$ to $+a$). The even functions are then cosines, and the odd ones are sines. See Problem 2.36.

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.

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

$$\int \psi_m(x)^* \psi_n(x)\, dx = 0, \qquad\qquad [2.29]$$

whenever $m \neq n$. *Proof*:

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

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

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

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

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:[10]

$$\boxed{\int \psi_m(x)^* \psi_n(x)\, dx = \delta_{mn},} \qquad\qquad [2.30]$$

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

$$\delta_{mn} = \begin{cases} 0, & \text{if } m \neq n; \\ 1, & \text{if } m = n. \end{cases} \qquad\qquad [2.31]$$

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:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right). \qquad\qquad [2.32]$$

---

[10]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 $\sin(n\pi x/a)$, but if you've studied advanced calculus you will recognize that Equation 2.32 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.**[11]

The 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 2.32 by $\psi_m(x)^*$, and integrate.

$$\int \psi_m(x)^* f(x)\, dx = \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x)\, dx = \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m. \qquad [2.33]$$

(Notice how the Kronecker delta kills every term in the sum except the one for which $n = m$.) Thus the nth coefficient in the expansion of $f(x)$ is[12]

$$\boxed{c_n = \int \psi_n(x)^* f(x)\, dx.} \qquad [2.34]$$

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 a symmetric function; the second is universal, regardless of the shape of the potential.[13] 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 2.18) of the infinite square well are evidently

$$\Psi_n(x, t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}. \qquad [2.35]$$

I claimed (Equation 2.17) that the most general solution to the (time-dependent) Schrödinger equation is a linear combination of stationary states:

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}. \qquad [2.36]$$

---

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

[12]It doesn't matter whether you use m or n as the "dummy index" here (as long as you are consistent on the two sides of the equation, of course): *whatever* letter you use, it just stands for "any positive integer."

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

(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:

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

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:

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x, 0)\, dx. \qquad [2.37]$$

That *does* it: Given the initial wave function, $\Psi(x, 0)$, we first compute the expansion coefficients c_n, using Equation 2.37, and then plug these into Equation 2.36 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.

Example 2.2   A particle in the infinite square well has the initial wave function

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

for some constant A (see Figure 2.3). *Outside* the well, of course, $\Psi = 0$. Find $\Psi(x, t)$.
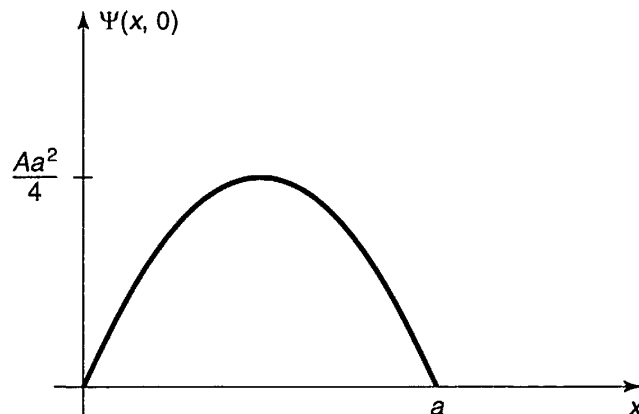

FIGURE 2.3:   The starting wave function in Example 2.2.

Solution: First we need to determine A, by normalizing $\Psi(x, 0)$:

$$1 = \int_0^a |\Psi(x, 0)|^2 \, dx = |A|^2 \int_0^a x^2(a - x)^2 \, dx = |A|^2 \frac{a^5}{30},$$

so

$$A = \sqrt{\frac{30}{a^5}}.$$

The nth coefficient is (Equation 2.37)

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \sqrt{\frac{30}{a^5}} x(a - x) \, dx$$

$$= \frac{2\sqrt{15}}{a^3} \left[a \int_0^a x \sin\left(\frac{n\pi}{a}x\right) dx - \int_0^a x^2 \sin\left(\frac{n\pi}{a}x\right) dx \right]$$

$$= \frac{2\sqrt{15}}{a^3} \left\{ a \left[\left(\frac{a}{n\pi}\right)^2 \sin\left(\frac{n\pi}{a}x\right) - \frac{ax}{n\pi} \cos\left(\frac{n\pi}{a}x\right) \right] \Big|_0^a \right.$$

$$\left. - \left[2\left(\frac{a}{n\pi}\right)^2 x \sin\left(\frac{n\pi}{a}x\right) - \frac{(n\pi x/a)^2 - 2}{(n\pi/a)^3} \cos\left(\frac{n\pi}{a}x\right) \right] \Big|_0^a \right\}$$

$$= \frac{2\sqrt{15}}{a^3} \left[-\frac{a^3}{n\pi} \cos(n\pi) + a^3 \frac{(n\pi)^2 - 2}{(n\pi)^3} \cos(n\pi) + a^3 \frac{2}{(n\pi)^3} \cos(0) \right]$$

$$= \frac{4\sqrt{15}}{(n\pi)^3} [\cos(0) - \cos(n\pi)]$$

$$= \begin{cases} 0, & \text{if } n \text{ is even.} \\ 8\sqrt{15}/(n\pi)^3, & \text{if } n \text{ is odd.} \end{cases}$$

Thus (Equation 2.36):

$$\Psi(x, t) = \sqrt{\frac{30}{a}} \left(\frac{2}{\pi}\right)^3 \sum_{n=1,3,5...} \frac{1}{n^3} \sin\left(\frac{n\pi}{a}x\right) e^{-in^2\pi^2\hbar t/2ma^2}.$$

Loosely speaking, c_n tells you the "amount of ψ_n that is contained in Ψ." Some people like to say that $|c_n|^2$ is the "probability of finding the particle in the nth stationary state," but this is bad language; the particle is in the state Ψ, *not* Ψ_n, and, anyhow, in the laboratory you don't "find a particle to be in a particular state"—you *measure* some *observable*, and what you get is a *number*. As we'll see in Chapter 3, what $|c_n|^2$ tells you is *the probability that a measurement of the*

energy would yield the value E_n (a competent measurement will always return *one* of the "allowed" values—hence the name—and $|c_n|^2$ is the probability of getting the *particular* value E_n).

Of course, the *sum* of these probabilities should be 1,

$$\sum_{n=1}^{\infty} |c_n|^2 = 1.$$ [2.38]

Indeed, this follows from the normalization of Ψ (the c_n's are independent of time, so I'm going to do the proof for $t = 0$; if this bothers you, you can easily generalize the argument to arbitrary t).

$$1 = \int |\Psi(x, 0)|^2 \, dx = \int \left(\sum_{m=1}^{\infty} c_m \psi_m(x) \right)^* \left(\sum_{n=1}^{\infty} c_n \psi_n(x) \right) dx$$

$$= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n \int \psi_m(x)^* \psi_n(x) \, dx$$

$$= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_m^* c_n \delta_{mn} = \sum_{n=1}^{\infty} |c_n|^2.$$

(Again, the Kronecker delta picks out the term $m = n$ in the summation over m.)
Moreover, the expectation value of the energy must be

$$\langle H \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n.$$ [2.39]

and this too can be checked directly: The time-independent Schrödinger equation (Equation 2.12) says

$$H \psi_n = E_n \psi_n.$$ [2.40]

so

$$\langle H \rangle = \int \Psi^* H \Psi \, dx = \int \left(\sum c_m \psi_m \right)^* H \left(\sum c_n \psi_n \right) dx$$

$$= \sum \sum c_m^* c_n E_n \int \psi_m^* \psi_n \, dx = \sum |c_n|^2 E_n.$$

Notice that the probability of getting a particular energy is independent of time, and so, *a fortiori*, is the expectation value of H. This is a manifestation of **conservation of energy** in quantum mechanics.

Example 2.3 In Example 2.2 the starting wave function (Figure 2.3) closely resembles the ground state ψ_1 (Figure 2.2). This suggests that $|c_1|^2$ should dominate, and in fact

$$|c_1|^2 = \left(\frac{8\sqrt{15}}{\pi^3}\right)^2 = 0.998555\ldots.$$

The rest of the coefficients make up the difference:[14]

$$\sum_{n=1}^{\infty} |c_n|^2 = \left(\frac{8\sqrt{15}}{\pi^3}\right)^2 \sum_{n=1,3,5,\ldots}^{\infty} \frac{1}{n^6} = 1.$$

The expectation value of the energy, in this example, is

$$\langle H \rangle = \sum_{n=1,3,5,\ldots}^{\infty} \left(\frac{8\sqrt{15}}{n^3\pi^3}\right)^2 \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{480\hbar^2}{\pi^4 ma^2} \sum_{n=1,3,5,\ldots}^{\infty} \frac{1}{n^4} = \frac{5\hbar^2}{ma^2}.$$

As one might expect, it is very close to $E_1 = \pi^2\hbar^2/2ma^2$—slightly *larger*, because of the admixture of excited states.

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

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

---

[14]You can look up the series

$$\frac{1}{1^6} + \frac{1}{3^6} + \frac{1}{5^6} + \cdots = \frac{\pi^6}{960}$$

and

$$\frac{1}{1^4} + \frac{1}{3^4} + \frac{1}{5^4} + \cdots = \frac{\pi^4}{96}$$

in math tables, under "Sums of Reciprocal Powers" or "Riemann Zeta Function."

(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 as a sinusoidal function of time, as in Example 2.1. To simplify the result, let $\omega \equiv \pi^2 \hbar / 2ma^2$.

(c) Compute $\langle x \rangle$. Notice that it oscillates in time. What is the angular 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) If you measured the energy of this particle, what values might you get, and what is the probability of getting each of them? Find the expectation value of H. How does it compare with E_1 and E_2?

Problem 2.6 Although the *overall* phase constant of the wave function is of no physical significance (it cancels out whenever you calculate a measurable quantity), the *relative* phase of the coefficients in Equation 2.17 *does* matter. For example, suppose we change the relative phase of ψ_1 and ψ_2 in Problem 2.5:

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

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 $\phi = \pi$. (For a graphical exploration of this problem see the applet in footnote 7.)

∗Problem 2.7 A particle in the infinite square well has the initial wave function[15]

$$\Psi(x, 0) = \begin{cases} Ax, & 0 \le x \le a/2, \\ A(a - x). & a/2 \le x \le a. \end{cases}$$

(a) Sketch $\Psi(x, 0)$, and determine the constant A.

(b) Find $\Psi(x, t)$.

---

[15]There is no restriction in principle on the *shape* of the starting wave function, as long as it is normalizable. In particular, $\Psi(x, 0)$ need not have a continuous derivative—in fact, it doesn't even have to be a *continuous* function. However, if you try to calculate $\langle H \rangle$ using $\int \Psi(x, 0)^* H \Psi(x, 0) \, dx$ in such a case, you may encounter technical difficulties, because the second derivative of $\Psi(x, 0)$ is ill-defined. It works in Problem 2.9 because the discontinuities occur at the end points, where the wave function is zero anyway. In Problem 2.48 you'll see how to manage cases like Problem 2.7.

(c) What is the probability that a measurement of the energy would yield the value E_1?

(d) Find the expectation value of the energy.

Problem 2.8 A particle of mass m in the infinite square well (of width a) starts out in the left half of the well, and is (at $t = 0$) equally likely to be found at any point in that region.

(a) What is its initial wave function, $\Psi(x, 0)$? (Assume it is real. Don't forget to normalize it.)

(b) What is the probability that a measurement of the energy would yield the value $\pi^2 \hbar^2 / 2ma^2$?

Problem 2.9 For the wave function in Example 2.2, find the expectation value of H, at time $t = 0$, the "old fashioned" way:

$$\langle H \rangle = \int \Psi(x, 0)^* \hat{H} \Psi(x, 0)\, dx.$$

Compare the result obtained in Example 2.3. *Note:* Because $\langle H \rangle$ is independent of time, there is no loss of generality in using $t = 0$.

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**,

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

(ignoring friction), and the solution is

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

where

$$\omega \equiv \sqrt{\frac{k}{m}} \qquad\qquad [2.41]$$

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

$$V(x) = \frac{1}{2}kx^2; \qquad\qquad [2.42]$$
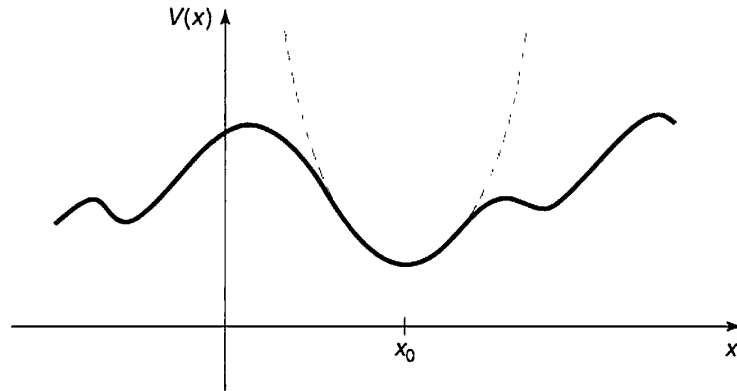
its graph is a parabola.

FIGURE 2.4: Parabolic approximation (dashed curve) to an arbitrary potential, in the neighborhood of a local minimum.

Of course, there's no such thing as a *perfect* 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 2.4). 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), we get

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

which describes simple harmonic oscillation (about the point x_0), with an effective spring constant $k = V''(x_0)$.[16] 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.

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

$$V(x) = \frac{1}{2}m\omega^2 x^2 \qquad [2.43]$$

(it is customary to eliminate the spring constant in favor of the classical frequency, using Equation 2.41). As we have seen, it suffices to solve the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi. \qquad [2.44]$$

---

[16]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.

In the literature you will find two entirely different approaches to this problem. The first is a straightforward "brute force" solution to the differential equation, using the **power series method**; 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 a lot more fun);[17] if you want to skip the power series 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 2.44 in a more suggestive form:

$$\frac{1}{2m}[p^2 + (m\omega x)^2]\psi = E\psi.\qquad[2.45]$$

where $p \equiv (\hbar/i)d/dx$ is, of course, the momentum operator. The basic idea is to *factor* the Hamiltonian,

$$H = \frac{1}{2m}[p^2 + (m\omega x)^2].\qquad[2.46]$$

If these were *numbers*, it would be easy:

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

Here, however, it's not quite so simple, because p and x are *operators*, and operators do not, in general, **commute** (xp is not the same as px). Still, this does motivate us to examine the quantities

$$a_\pm \equiv \frac{1}{\sqrt{2\hbar m\omega}}(\mp ip + m\omega x)\qquad[2.47]$$

(the factor in front is just there to make the final results look nicer).
Well, what *is* the product a_-a_+?

$$a_-a_+ = \frac{1}{2\hbar m\omega}(ip + m\omega x)(-ip + m\omega x)$$

$$= \frac{1}{2\hbar m\omega}[p^2 + (m\omega x)^2 - im\omega(xp - px)].$$

---

[17]We'll encounter some of the same strategies in the theory of angular momentum (Chapter 4), and the technique generalizes to a broad class of potentials in **super-symmetric quantum mechanics** (see, for example. Richard W. Robinett. *Quantum Mechanics*. (Oxford U.P.. New York. 1997). Section 14.4).

As anticipated, there's an extra term, involving $(xp - px)$. We call this the **commutator** of x and p; it is a measure of how badly they *fail* to commute. In general, the commutator of operators A and B (written with square brackets) is

$$[A, B] \equiv AB - BA. \tag{2.48}$$

In this notation,

$$a_-a_+ = \frac{1}{2\hbar m\omega}[p^2 + (m\omega x)^2] - \frac{i}{2\hbar}[x, p]. \tag{2.49}$$

We need to figure out the commutator of x and p. *Warning:* Operators are notoriously 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:

$$[x, p]f(x) = \left[x\frac{\hbar}{i}\frac{d}{dx}(f) - \frac{\hbar}{i}\frac{d}{dx}(xf)\right] = \frac{\hbar}{i}\left(x\frac{df}{dx} - x\frac{df}{dx} - f\right) = i\hbar f(x). \tag{2.50}$$

Dropping the test function, which has served its purpose,

$$\boxed{[x, p] = i\hbar.} \tag{2.51}$$

This lovely and ubiquitous result is known as the **canonical commutation relation.**[18]

With this, Equation 2.49 becomes

$$a_-a_+ = \frac{1}{\hbar\omega}H + \frac{1}{2}. \tag{2.52}$$

or

$$H = \hbar\omega\left(a_-a_+ - \frac{1}{2}\right). \tag{2.53}$$

Evidently the Hamiltonian does *not* factor perfectly—there's that extra $-1/2$ on the right. Notice that the ordering of a_+ and a_- is important here; the same argument, with a_+ on the left, yields

$$a_+a_- = \frac{1}{\hbar\omega}H - \frac{1}{2}. \tag{2.54}$$

In particular,

$$[a_-, a_+] = 1. \tag{2.55}$$

---

[18]In a deep sense all of the mysteries of quantum mechanics can be traced to the fact that position and momentum do not commute. Indeed, some authors take the canonical commutation relation as an *axiom* of the theory. and use it to *derive* $p = (\hbar/i)d/dx$.

So the Hamiltonian can equally well be written

$$H = \hbar\omega \left(a_+ a_- + \frac{1}{2} \right).$$ [2.56]

In terms of $a_\pm$, then, the Schrödinger equation[19] for the harmonic oscillator takes the form

$$\hbar\omega \left(a_\pm a_\mp \pm \frac{1}{2} \right) \psi = E\psi$$ [2.57]

(in equations like this you read the upper signs all the way across, or else the lower signs).

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

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

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

$$= a_+(H + \hbar\omega)\psi = a_+(E + \hbar\omega)\psi = (E + \hbar\omega)(a_+\psi).$$

(I used Equation 2.55 to replace $a_- a_+$ by $a_+ a_- + 1$, in the second line. 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*; an operator commutes with any constant.)

By the same token, $a_-\psi$ is a solution with energy $(E - \hbar\omega)$:

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

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

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

Here, then, is a wonderful machine for generating new solutions, with higher and lower energies—if we could 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 the **raising operator**, and a_- the **lowering operator**. The "ladder" of states is illustrated in Figure 2.5.

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[19]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."
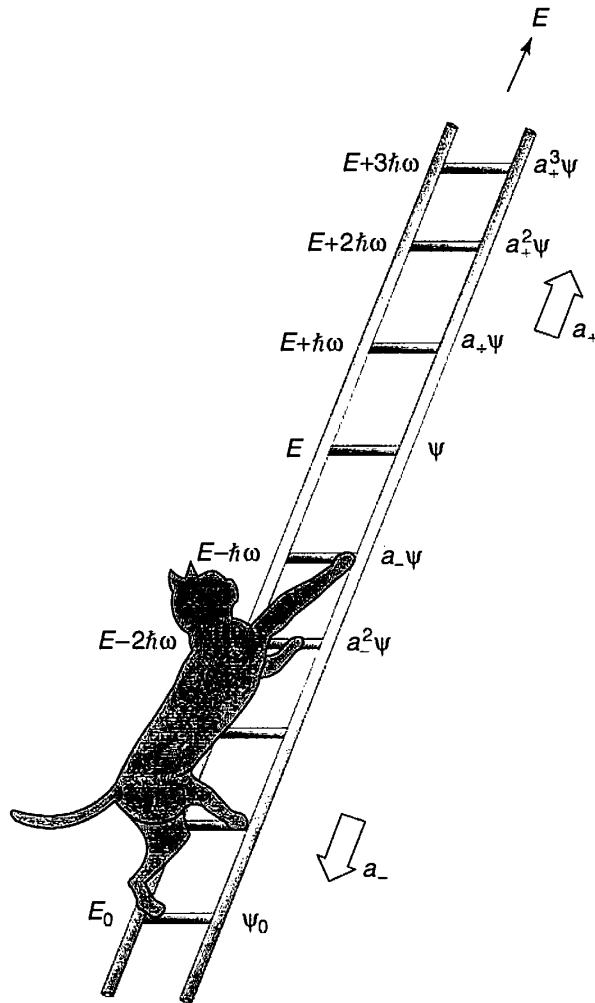
FIGURE 2.5: The "ladder" of states for the harmonic oscillator.

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. In practice it is the former: There occurs a "lowest rung" (call it ψ_0) such that

$$a_- \psi_0 = 0. \qquad [2.58]$$

We can use this to determine $\psi_0(x)$:

$$\frac{1}{\sqrt{2\hbar m\omega}} \left(\hbar \frac{d}{dx} + m\omega x \right) \psi_0 = 0.$$

or

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

This differential equation 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

$$\psi_0(x) = Ae^{-\frac{m\omega}{2\hbar}x^2}.$$

We might as well normalize it right away:

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-m\omega x^2/\hbar}\,dx = |A|^2\sqrt{\frac{\pi\hbar}{m\omega}}.$$

so $A^2 = \sqrt{m\omega/\pi\hbar}$, and hence

$$\boxed{\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}.} \qquad [2.59]$$

To determine the energy of this state we plug it into the Schrödinger equation (in the form of Equation 2.57), $\hbar\omega(a_+a_- + 1/2)\psi_0 = E_0\psi_0$, and exploit the fact that $a_-\psi_0 = 0$:

$$E_0 = \frac{1}{2}\hbar\omega. \qquad [2.60]$$

With our foot now securely planted on the bottom rung (the ground state of the quantum oscillator), we simply apply the raising operator (repeatedly) to generate the excited states,[20] increasing the energy by $\hbar\omega$ with each step:

$$\boxed{\psi_n(x) = A_n(a_+)^n\psi_0(x), \quad \text{with } E_n = \left(n + \frac{1}{2}\right)\hbar\omega,} \qquad [2.61]$$

where A_n is the normalization constant. By applying the raising operator (repeatedly) to ψ_0, then, we can (in principle) construct all[21] the stationary states of

---

[20]In the case of the harmonic oscillator it is customary, for some reason, to depart from the usual practice, and number the states starting with $n = 0$, instead of $n = 1$. Obviously, the lower limit on the sum in a formula such as Equation 2.17 should be altered accordingly.

[21]Note that we obtain all the (normalizable) solutions by this procedure. For if there were some other solution, we could generate from it a second ladder, by repeated application of the raising and lowering operators. But the bottom rung of this new ladder would have to satisfy Equation 2.58, and since that leads inexorably to Equation 2.59, the bottom rungs would be the same, and hence the two ladders would in fact be identical.

the harmonic oscillator. Meanwhile, without ever doing that explicitly, we have determined the allowed energies.

Example 2.4 Find the first excited state of the harmonic oscillator.

Solution: Using Equation 2.61,

$$\psi_1(x) = A_1 a_+ \psi_0 = \frac{A_1}{\sqrt{2\hbar m\omega}} \left(-\hbar\frac{d}{dx} + m\omega x\right) \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}$$

$$= A_1 \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{2m\omega}{\hbar}} x e^{-\frac{m\omega}{2\hbar}x^2}.$$

[2.62]

We can normalize it "by hand":

$$\int |\psi_1|^2 dx = |A_1|^2 \sqrt{\frac{m\omega}{\pi\hbar}} \left(\frac{2m\omega}{\hbar}\right) \int_{-\infty}^{\infty} x^2 e^{-\frac{m\omega}{\hbar}x^2} dx = |A_1|^2,$$

so, as it happens, $A_1 = 1$.

I wouldn't want to calculate ψ_{50} this way (applying the raising operator fifty times!), but never mind: In *principle* Equation 2.61 does the job—except for the normalization.

You can even get the normalization algebraically, but it takes some fancy footwork, so watch closely. We know that $a_{\pm}\psi_n$ is *proportional* to $\psi_{n\pm1}$,

$$a_+\psi_n = c_n\psi_{n+1}, \quad a_-\psi_n = d_n\psi_{n-1}$$

[2.63]

but what are the proportionality factors, c_n and d_n? First note that for "any"[22] functions $f(x)$ and $g(x)$,

$$\int_{-\infty}^{\infty} f^*(a_{\pm}g) dx = \int_{-\infty}^{\infty} (a_{\mp}f)^* g dx.$$

[2.64]

(In the language of linear algebra, $a_{\mp}$ is the **hermitian conjugate** of $a_{\pm}$.)

Proof:

$$\int_{-\infty}^{\infty} f^*(a_{\pm}g) dx = \frac{1}{\sqrt{2\hbar m\omega}} \int_{-\infty}^{\infty} f^* \left(\mp\hbar\frac{d}{dx} + m\omega x\right) g dx.$$

---

[22]Of course, the integrals must *exist*, and this means that $f(x)$ and $g(x)$ must go to zero at $\pm\infty$.

and integration by parts takes $\int f^*(dg/dx)\,dx$ to $-\int (df/dx)^* g\,dx$ (the boundary terms vanish, for the reason indicated in footnote 22), so

$$\int_{-\infty}^{\infty} f^*(a_{\pm}\,g)\,dx = \frac{1}{\sqrt{2\hbar m\omega}} \int_{-\infty}^{\infty} \left[\left(\pm\hbar\frac{d}{dx} + m\omega x\right)f\right]^* g\,dx = \int_{-\infty}^{\infty} (a_{\mp}f)^* g\,dx.$$

QED

In particular,

$$\int_{-\infty}^{\infty} (a_{\pm}\,\psi_n)^*(a_{\pm}\,\psi_n)\,dx = \int_{-\infty}^{\infty} (a_{\mp}a_{\pm}\,\psi_n)^*\,\psi_n\,dx.$$

But (invoking Equations 2.57 and 2.61)

$$a_+a_-\psi_n = n\psi_n, \qquad a_-a_+\psi_n = (n+1)\psi_n. \tag{2.65}$$

so

$$\int_{-\infty}^{\infty} (a_+\psi_n)^*(a_+\psi_n)\,dx = |c_n|^2 \int_{-\infty}^{\infty} |\psi_{n+1}|^2\,dx = (n+1)\int_{-\infty}^{\infty} |\psi_n|^2\,dx.$$

$$\int_{-\infty}^{\infty} (a_-\psi_n)^*(a_-\psi_n)\,dx = |d_n|^2 \int_{-\infty}^{\infty} |\psi_{n-1}|^2\,dx = n\int_{-\infty}^{\infty} |\psi_n|^2\,dx.$$

But since ψ_n and $\psi_{n\pm 1}$ are normalized, it follows that $|c_n|^2 = n+1$ and $|d_n|^2 = n$, and hence

$$\boxed{a_+\psi_n = \sqrt{n+1}\,\psi_{n+1}, \qquad a_-\psi_n = \sqrt{n}\,\psi_{n-1}.} \tag{2.66}$$

Thus

$$\psi_1 = a_+\psi_0, \qquad \psi_2 = \frac{1}{\sqrt{2}}a_+\psi_1 = \frac{1}{\sqrt{2}}(a_+)^2\psi_0,$$

$$\psi_3 = \frac{1}{\sqrt{3}}a_+\psi_2 = \frac{1}{\sqrt{3\cdot 2}}(a_+)^3\psi_0, \qquad \psi_4 = \frac{1}{\sqrt{4}}a_+\psi_3 = \frac{1}{\sqrt{4\cdot 3\cdot 2}}(a_+)^4\psi_0,$$

and so on. Clearly

$$\boxed{\psi_n = \frac{1}{\sqrt{n!}}(a_+)^n\psi_0.} \tag{2.67}$$

which is to say that the normalization factor in Equation 2.61 is $A_n = 1/\sqrt{n!}$ (in particular, $A_1 = 1$, confirming our result in Example 2.4).

As in the case of the infinite square well, the stationary states of the harmonic oscillator are orthogonal:

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx = \delta_{mn}. \tag{2.68}$$

This can be proved using Equation 2.65, and Equation 2.64 twice—first moving a_+ and then moving a_-:

$$\int_{-\infty}^{\infty} \psi_m^*(a_+ a_-)\psi_n \, dx = n \int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx$$

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

$$= m \int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx.$$

Unless $m = n$, then, $\int \psi_m^* \psi_n \, dx$ must be zero. Orthonormality means that we can again use Fourier's trick (Equation 2.34) to evaluate the coefficients, when we expand $\Psi(x, 0)$ as a linear combination of stationary states (Equation 2.16), and $|c_n|^2$ is again the probability that a measurement of the energy would yield the value E_n.

Example 2.5   Find the expectation value of the potential energy in the nth state of the harmonic oscillator.

Solution:

$$\langle V \rangle = \left\langle \frac{1}{2} m\omega^2 x^2 \right\rangle = \frac{1}{2} m\omega^2 \int_{-\infty}^{\infty} \psi_n^* x^2 \psi_n \, dx.$$

There's a beautiful device for evaluating integrals of this kind (involving powers of x or p): Use the definition (Equation 2.47) to express x and p in terms of the raising and lowering operators:

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a_+ + a_-); \quad p = i\sqrt{\frac{\hbar m\omega}{2}}(a_+ - a_-). \tag{2.69}$$

In this example we are interested in x^2:

$$x^2 = \frac{\hbar}{2m\omega} \left[(a_+)^2 + (a_+ a_-) + (a_- a_+) + (a_-)^2 \right].$$

So

$$\langle V \rangle = \frac{\hbar\omega}{4} \int \psi_n^* \left[(a_+)^2 + (a_+ a_-) + (a_- a_+) + (a_-)^2 \right] \psi_n \, dx.$$

But $(a_+)^2\psi_n$ is (apart from normalization) ψ_{n+2}, which is orthogonal to ψ_n, and the same goes for $(a_-)^2\psi_n$, which is proportional to ψ_{n-2}. So those terms drop out, and we can use Equation 2.65 to evaluate the remaining two:

$$\langle V \rangle = \frac{\hbar\omega}{4}(n + n + 1) = \frac{1}{2}\hbar\omega\left(n + \frac{1}{2}\right).$$

As it happens, the expectation value of the potential energy is exactly *half* the total (the other half, of course, is kinetic). This is a peculiarity of the harmonic oscillator, as we'll see later on.

---

*Problem 2.10

(a) Construct $\psi_2(x)$.

(b) Sketch ψ_0, ψ_1, and ψ_2.

(c) Check the orthogonality of ψ_0, ψ_1, and ψ_2, by explicit integration. *Hint:* If you exploit the even-ness and odd-ness of the functions, there is really only one integral left to do.

---

*Problem 2.11

(a) Compute $\langle x \rangle$, $\langle p \rangle$, $\langle x^2 \rangle$, and $\langle p^2 \rangle$, for the states ψ_0 (Equation 2.59) and ψ_1 (Equation 2.62), by explicit integration. *Comment:* In this and other problems involving the harmonic oscillator it simplifies matters 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 $\langle T \rangle$ (the average kinetic energy) and $\langle V \rangle$ (the average potential energy) for these states. (No new integration allowed!) Is their sum what you would expect?

---

*Problem 2.12 Find $\langle x \rangle$, $\langle p \rangle$, $\langle x^2 \rangle$, $\langle p^2 \rangle$, and $\langle T \rangle$, for the nth stationary state of the harmonic oscillator, using the method of Example 2.5. Check that the uncertainty principle is satisfied.

Problem 2.13 A particle in the harmonic oscillator potential starts out in the state

$$\Psi(x, 0) = A[3\psi_0(x) + 4\psi_1(x)].$$

(a) Find A.

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

(c) Find $\langle x \rangle$ and $\langle p \rangle$. Don't get too excited if they oscillate at the classical frequency; what would it have been had I specified $\psi_2(x)$, instead of $\psi_1(x)$? Check that Ehrenfest's theorem (Equation 1.38) holds for this wave function.

(d) If you measured the energy of this particle, what values might you get, and with what probabilities?

Problem 2.14 A particle is in the ground state of the harmonic oscillator with classical frequency ω, when suddenly the spring constant quadruples, so $\omega' = 2\omega$, without initially changing the wave function (of course, Ψ will now *evolve* differently, because the Hamiltonian has changed). What is the probability that a measurement of the energy would still return the value $\hbar\omega/2$? What is the probability of getting $\hbar\omega$? [*Answer:* 0.943.]

2.3.2 Analytic Method

We return now to the Schrödinger equation for the harmonic oscillator,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi = E\psi. \tag{2.70}$$

and solve it directly, by the series method. Things look a little cleaner if we introduce the dimensionless variable

$$\xi \equiv \sqrt{\frac{m\omega}{\hbar}}x; \tag{2.71}$$

in terms of ξ the Schrödinger equation reads

$$\frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi, \tag{2.72}$$

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

$$K \equiv \frac{2E}{\hbar\omega}. \tag{2.73}$$

Our problem is to solve Equation 2.72, 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

$$\frac{d^2\psi}{d\xi^2} \approx \xi^2\psi, \tag{2.74}$$

which has the approximate solution (check it!)

$$\psi(\xi) \approx Ae^{-\xi^2/2} + Be^{+\xi^2/2}. \tag{2.75}$$

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

$$\psi(\xi) \rightarrow (\quad)e^{-\xi^2/2}, \quad \text{at large } \xi. \tag{2.76}$$

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

$$\psi(\xi) = h(\xi)e^{-\xi^2/2}, \tag{2.77}$$

in hopes that what remains, $h(\xi)$, has a simpler functional form than $\psi(\xi)$ itself.[23] Differentiating Equation 2.77,

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

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 2.72) becomes

$$\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (K - 1)h = 0. \tag{2.78}$$

I propose to look for solutions to Equation 2.78 in the form of *power series* in ξ:[24]

$$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \cdots = \sum_{j=0}^{\infty} a_j\xi^j. \tag{2.79}$$

Differentiating the series term by term,

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

and

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

---

[23]Note that although we invoked some approximations to *motivate* Equation 2.77, 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 (footnote 11). Chapter 12.

[24]This is known as the **Frobenius method** for solving a differential equation. According to Taylor's theorem. *any* reasonably well-behaved function can be expressed as a power series, so Equation 2.79 ordinarily involves no loss of generality. For conditions on the applicability of the method. see Boas (footnote 11) or George B. Arfken and Hans-Jurgen Weber, *Mathematical Methods for Physicists*, 5th ed., Academic Press. Orlando (2000). Section 8.5.

Putting these into Equation 2.78, we find

$$\sum_{j=0}^{\infty} \left[(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j \right] \xi^j = 0. \qquad [2.80]$$

It follows (from the uniqueness of power series expansions[25]) 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

$$a_{j+2} = \frac{(2j+1-K)}{(j+1)(j+2)} a_j. \qquad [2.81]$$

This **recursion formula** is entirely equivalent to the Schrödinger equation. Starting with a_0, it generates all the even-numbered coefficients:

$$a_2 = \frac{(1-K)}{2} a_0, \quad a_4 = \frac{(5-K)}{12} a_2 = \frac{(5-K)(1-K)}{24} a_0, \quad \cdots,$$

and starting with a_1, it generates the odd coefficients:

$$a_3 = \frac{(3-K)}{6} a_1, \quad a_5 = \frac{(7-K)}{20} a_3 = \frac{(7-K)(3-K)}{120} a_1, \quad \cdots.$$

We write the complete solution as

$$h(\xi) = h_{\text{even}}(\xi) + h_{\text{odd}}(\xi), \qquad [2.82]$$

where

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

is an even function of ξ, 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 2.81 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)

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

---

[25]See. for example. Arfken (footnote 24). 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)

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

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 2.77), which is precisely the asymptotic behavior we *didn't* want.[26] 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: $a_1 = 0$ if n is even, and $a_0 = 0$ if n is odd). For physically acceptable solutions, then, Equation 2.81 requires that

$$K = 2n + 1,$$

for some non-negative integer n, which is to say (referring to Equation 2.73) that the *energy* must be

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega, \quad \text{for } n = 0, 1, 2. \ldots . \qquad [2.83]$$

Thus we recover, by a completely different method, the fundamental quantization condition we found algebraically in Equation 2.61.

It seems at first rather surprising that the quantization of energy should emerge from a technical detail in the power series solution to the Schrödinger equation, but let's look at it from a different perspective. Equation 2.70 has solutions, of course, for *any* value of E (in fact, it has *two* linearly independent solutions for every E). But almost all of these solutions blow up exponentially at large x, and hence are not normalizable. Imagine, for example, using an E that is slightly *less* than one of the allowed values (say, $0.49\hbar\omega$), and plotting the solution (Figure 2.6(a)); the "tails" fly off to infinity. Now try an E slightly *larger* (say, $0.51\hbar\omega$); the "tails" now blow up in the *other* direction (Figure 2.6(b)). As you tweak the parameter in tiny increments from 0.49 to 0.51, the tails flip over when you pass through 0.5—only at *precisely* 0.5 do the tails go to zero, leaving a normalizable solution.[27]

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[26] It's no surprise that the ill-behaved solutions are still contained in Equation 2.81: this recursion relation is equivalent to the Schrödinger equation, so it's *got* to include both the asymptotic forms we found in Equation 2.75.

[27] It is possible to set this up on a computer, and discover the allowed energies "experimentally." You might call it the **wag the dog** method: When the tail wags, you know you've just passed over an allowed value. See Problems 2.54–2.56.
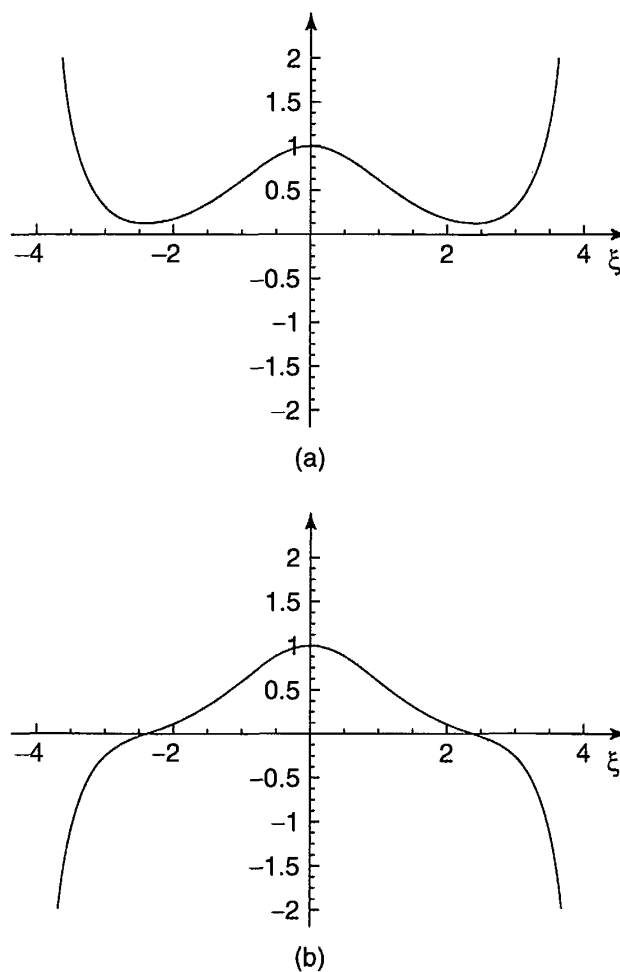
(a)

(b)

FIGURE 2.6: Solutions to the Schrödinger equation for (a) $E = 0.49\,\hbar\omega$, and (b) $E = 0.51\,\hbar\omega$.

For the allowed values of K, the recursion formula reads

$$a_{j+2} = \frac{-2(n-j)}{(j+1)(j+2)}a_j. \qquad [2.84]$$

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 2.84 yields $a_2 = 0$):

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

and hence

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

(which, apart from the normalization, reproduces Equation 2.59). For $n = 1$ we take $a_0 = 0$,[28] and Equation 2.84 with $j = 1$ yields $a_3 = 0$, so

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

and hence

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

(confirming Equation 2.62). 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 2.10, where this last 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**, $H_n(\xi)$.[29] 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[30] stationary states for the harmonic oscillator are

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}H_n(\xi)e^{-\xi^2/2}. \qquad [2.85]$$

They are identical (of course) to the ones we obtained algebraically in Equation 2.67.

TABLE 2.1:   The first few Hermite polynomials, $H_n(\xi)$.

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

---

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

[29]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 2.17.

[30]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., McGraw-Hill, New York (1968), Section 13.

In Figure 2.7(a) 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 finding the particle at the center is zero. Only at large n do we begin to see some resemblance to the classical case. In Figure 2.7(b) I have superimposed the classical position distribution on the quantum one (for $n = 100$); if you smoothed out the bumps, 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).[31]

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:* Classically, the energy of an oscillator is $E = (1/2)ka^2 = (1/2)m\omega^2 a^2$, where a is the amplitude. So the "classically allowed region" for an oscillator of energy E extends from $-\sqrt{2E/m\omega^2}$ to $+\sqrt{2E/m\omega^2}$. Look in a math table under "Normal Distribution" or "Error Function" for the numerical value of the integral.

Problem 2.16 Use the recursion formula (Equation 2.84) to work out $H_5(\xi)$ and $H_6(\xi)$. Invoke the convention that the coefficient of the highest power of ξ is 2^n to fix the overall constant.

$*$ $*$**Problem 2.17** In this problem we explore some of the more useful theorems (stated without proof) involving Hermite polynomials.

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

$$H_n(\xi) = (-1)^n e^{\xi^2} \left(\frac{d}{d\xi} \right)^n e^{-\xi^2}. \qquad [2.86]$$

Use it to derive H_3 and H_4.

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

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2n H_{n-1}(\xi). \qquad [2.87]$$

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

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[31]The parallel is perhaps more direct if you interpret the classical distribution as an ensemble of oscillators all with the same energy, but with random starting times.
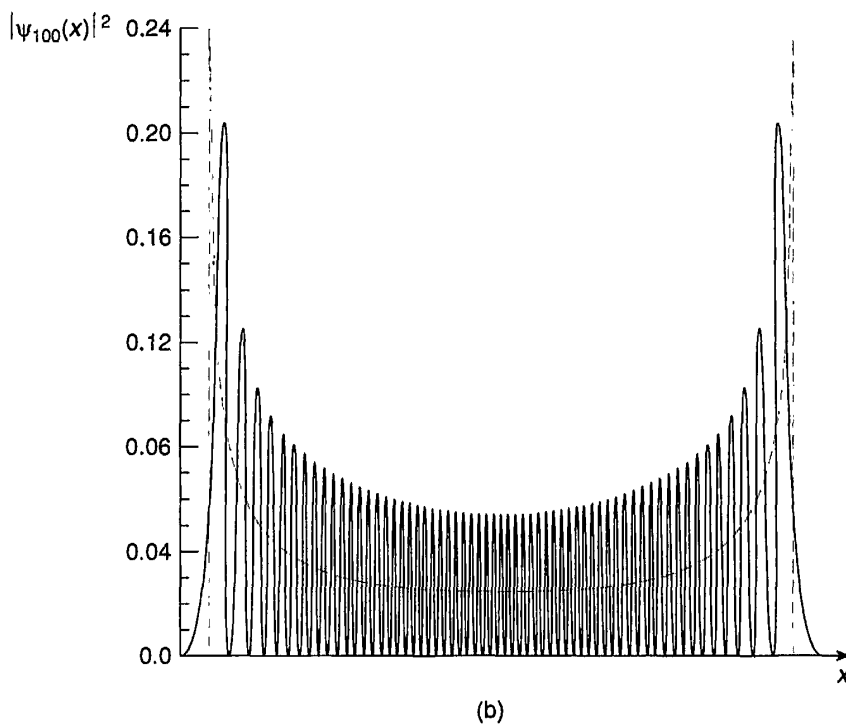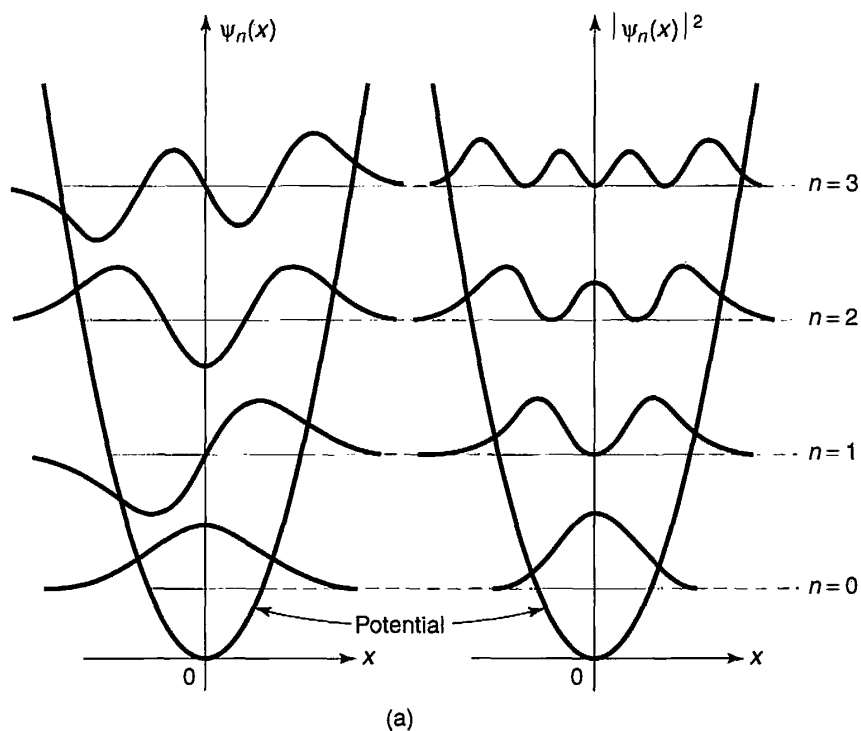
(a)

(b)

FIGURE 2.7: (a) The first four stationary states of the harmonic oscillator. This material is used by permission of John Wiley & Sons, Inc.; Stephen Gasiorowicz, *Quantum Physics*, John Wiley & Sons, Inc., 1974. (b) Graph of $|\psi_{100}|^2$, with the classical distribution (dashed curve) superimposed.

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

$$\frac{dH_n}{d\xi} = 2nH_{n-1}(\xi). \qquad [2.88]$$

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:

$$e^{-z^2+2z\xi} = \sum_{n=0}^{\infty} \frac{z^n}{n!} H_n(\xi). \qquad [2.89]$$

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). Classically this would just mean motion at constant velocity, but in quantum mechanics the problem is surprisingly subtle and tricky. The time-independent Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi. \qquad [2.90]$$

or

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}. \qquad [2.91]$$

So far, it's the same as inside the infinite square well (Equation 2.21), 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:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}. \qquad [2.92]$$

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, $\exp(-iEt/\hbar)$,

$$\Psi(x, t) = Ae^{ik\left(x-\frac{\hbar k}{2m}t\right)} + Be^{-ik\left(x+\frac{\hbar k}{2m}t\right)}. \qquad [2.93]$$

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

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

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 2.93 represents a wave traveling to the *right*, and the second 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

$$\Psi_k(x, t) = A e^{i\left(kx - \frac{\hbar k^2}{2m} t\right)}, \qquad [2.94]$$

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

$$k \equiv \pm \frac{\sqrt{2mE}}{\hbar}, \quad \text{with} \quad \begin{cases} k > 0 \Rightarrow & \text{traveling to the right,} \\ k < 0 \Rightarrow & \text{traveling to the left.} \end{cases} \qquad [2.95]$$

Evidently the "stationary states" of the free particle are propagating waves; their wavelength is $\lambda = 2\pi/|k|$, and, according to the de Broglie formula (Equation 1.39), they carry momentum

$$p = \hbar k. \qquad [2.96]$$

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

$$v_{\text{quantum}} = \frac{\hbar|k|}{2m} = \sqrt{\frac{E}{2m}}. \qquad [2.97]$$

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

$$v_{\text{classical}} = \sqrt{\frac{2E}{m}} = 2v_{\text{quantum}}. \qquad [2.98]$$

Apparently 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

$$\int_{-\infty}^{+\infty} \Psi_k^* \Psi_k \, dx = |A|^2 \int_{-\infty}^{+\infty} dx = |A|^2(\infty). \qquad [2.99]$$

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):

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m}t)} \, dk. \qquad [2.100]$$

(The quantity $1/\sqrt{2\pi}$ is factored out for convenience; what plays the role of the coefficient c_n in Equation 2.17 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**.[32]

In the generic quantum problem, we are *given* $\Psi(x, 0)$, and we are asked to *find* $\Psi(x, t)$. For a free particle the solution takes the form of Equation 2.100; the only question is how to determine $\phi(k)$ so as to match the initial wave function:

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{ikx} \, dk. \qquad [2.101]$$

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

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(k) e^{ikx} \, dk \Longleftrightarrow F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{-ikx} \, dx. \qquad [2.102]$$

$F(k)$ 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*.[33] For our purposes this is guaranteed by the physical requirement that $\Psi(x, 0)$ itself

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[32] Sinusoidal waves extend out to infinity, and they are not normalizable. But *superpositions* of such waves lead to interference, which allows for localization and normalizability.

[33] 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 24), Section 15.5.

be normalized. So the solution to the generic quantum problem, for the free particle, is Equation 2.100, with

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

[2.103]

Example 2.6   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. Find $\Psi(x, t)$.

Solution: First we need to normalize $\Psi(x, 0)$:

$$1 = \int_{-\infty}^{\infty} |\Psi(x, 0)|^2 \, dx = |A|^2 \int_{-a}^{a} dx = 2a|A|^2 \quad \Rightarrow \quad A = \frac{1}{\sqrt{2a}}.$$

Next we calculate $\phi(k)$, using Equation 2.103:

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2a}} \int_{-a}^{a} e^{-ikx} \, dx = \frac{1}{2\sqrt{\pi a}} \frac{e^{-ikx}}{-ik} \Big|_{-a}^{a}$$

$$= \frac{1}{k\sqrt{\pi a}} \left(\frac{e^{ika} - e^{-ika}}{2i} \right) = \frac{1}{\sqrt{\pi a}} \frac{\sin(ka)}{k}.$$

Finally, we plug this back into Equation 2.100:

$$\Psi(x, t) = \frac{1}{\pi\sqrt{2a}} \int_{-\infty}^{\infty} \frac{\sin(ka)}{k} e^{i(kx - \frac{\hbar k^2}{2m}t)} \, dk.$$

[2.104]

Unfortunately, this integral cannot be solved in terms of elementary functions, though it can of course be evaluated numerically (Figure 2.8). (There are, in fact, precious few cases in which the integral for $\Psi(x, t)$ (Equation 2.100) *can* be calculated explicitly; see Problem 2.22 for a particularly beautiful example.)

It is illuminating to explore the limiting cases. If a is very small, the starting wave function is a nicely localized spike (Figure 2.9(a)). In this case we can use the small angle approximation to write $\sin(ka) \approx ka$, and hence

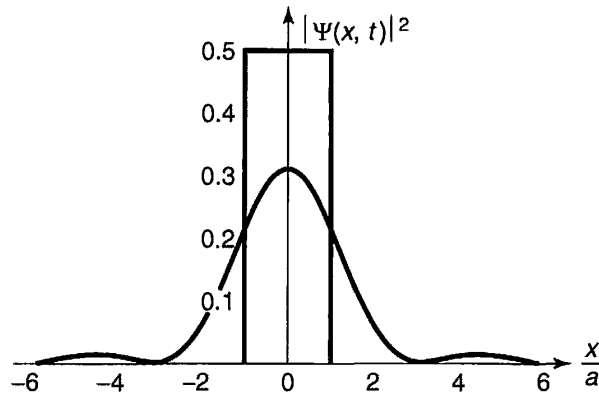$$\phi(k) \approx \sqrt{\frac{a}{\pi}};$$

FIGURE 2.8: Graph of $|\Psi(x, t)|^2$ (Equation 2.104) at $t = 0$ (the rectangle) and at $t = ma^2/\hbar$ (the curve).
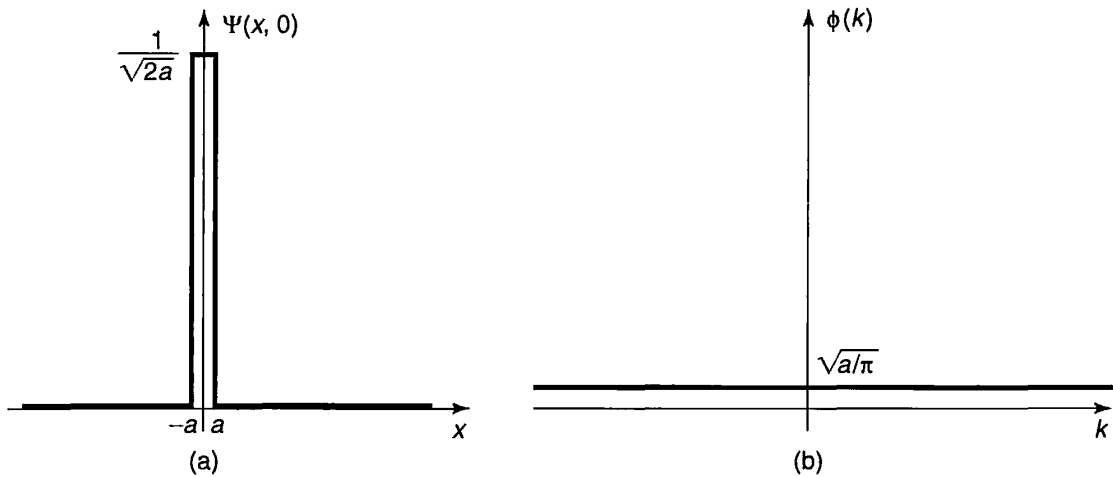

FIGURE 2.9: Example 2.6, for small a. (a) Graph of $\Psi(x, 0)$. (b) Graph of $\phi(k)$.

it's *flat*, since the k's cancelled out (Figure 2.9(b)). This is an example of the uncertainty principle: If the spread in *position* is small, the spread in *momentum* (and hence in k—see Equation 2.96) must be large. At the other extreme (*large* a) the spread in position is broad (Figure 2.10(a)) and

$$\phi(k) = \sqrt{\frac{a}{\pi}} \frac{\sin(ka)}{ka}.$$

Now, $\sin z/z$ has its maximum at $z = 0$, and drops to zero at $z = \pm \pi$ (which, in this context, means $k = \pm \pi/a$). So for large a, $\phi(k)$ is a sharp spike about $k = 0$ (Figure 2.10(b)). This time it's got a well-defined momentum but an ill-defined position.
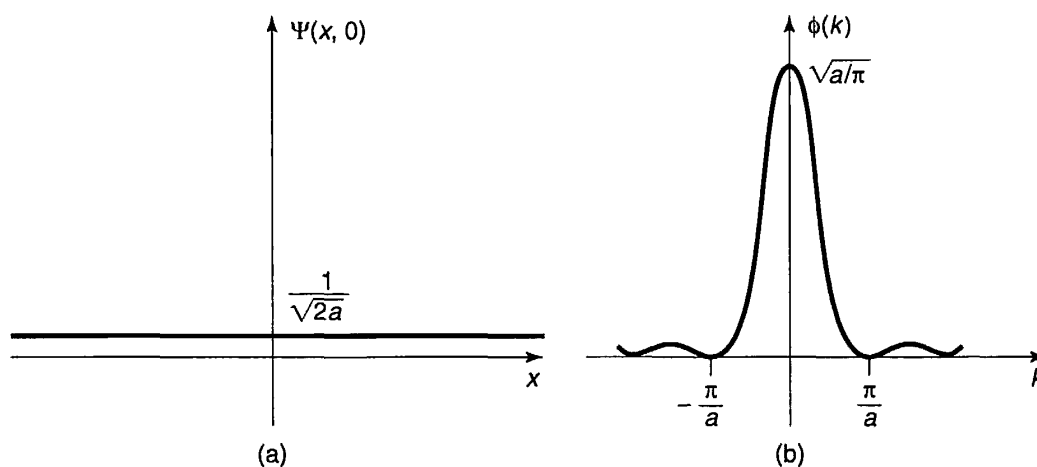
FIGURE 2.10:   Example 2.6, for large *a*. (a) Graph of Ψ(*x*, 0). (b) Graph of φ(*k*).

I return now to the paradox noted earlier: the fact that the separable solution $\Psi_k(x, t)$ in Equation 2.94 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 realizable state. Nevertheless, it is of interest to discover how information about velocity *is* contained in the free particle wave function (Equation 2.100). The essential idea is this: A wave packet is a superposition of sinusoidal functions whose amplitude is modulated by φ (Figure 2.11); 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
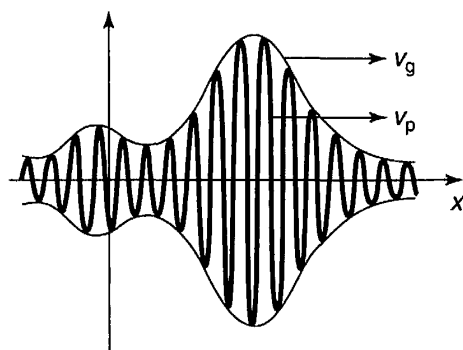

FIGURE 2.11:   A wave packet. The "envelope" travels at the group velocity; the "ripples" travel at the phase velocity.

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 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

$$\Psi(x, t) \cong e^{-i(\omega_0 - k_0\omega_0')t} \Psi(x - \omega_0't, 0). \qquad [2.105]$$

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 ω_0':

$$v_{\text{group}} = \frac{d\omega}{dk} \qquad [2.106]$$

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

$$v_{\text{phase}} = \frac{\omega}{k}. \qquad [2.107]$$

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:

$$v_{\text{classical}} = v_{\text{group}} = 2v_{\text{phase}}.$$ [2.108]

Problem 2.18 Show that $[Ae^{ikx} + Be^{-ikx}]$ and $[C \cos kx + D \sin kx]$ are equivalent ways of writing the same function of x, and determine the constants C and D in terms of A and B, and vice versa. *Comment:* In quantum mechanics, when $V = 0$, the exponentials represent *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.

Problem 2.19 Find the probability current, J (Problem 1.14) for the free particle wave function Equation 2.94. Which direction does the probability current flow?

**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 $F(k) = \sqrt{2/\pi}\, ac_n$. 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. *Comment:* 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 A free particle has the initial wave function

$$\Psi(x, 0) = Ae^{-a|x|},$$

where A and a are positive real constants.

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

(b) Find $\phi(k)$.

(c) Construct $\Psi(x, t)$, in the form of an integral.

(d) Discuss the limiting cases (a very large, and a very small).

∗Problem 2.22 The gaussian wave packet. 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

$$w \equiv \sqrt{\frac{a}{1 + (2\hbar at/m)^2}}.$$

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

2.5.1 Bound States and Scattering States

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 particle 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 2.12(a)), then the particle is "stuck" in the potential well—it rocks back and forth between the **turning points**, but it cannot escape (unless, 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 2.12(b)). (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.

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 2.12(c)):

$$\begin{cases} E < [V(-\infty) & \text{and } V(+\infty)] \Rightarrow & \text{bound state,} \\ E > [V(-\infty) & \text{or } \quad V(+\infty)] \Rightarrow & \text{scattering state.} \end{cases} \qquad [2.109]$$

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

$$\begin{cases} E < 0 \Rightarrow & \text{bound state,} \\ E > 0 \Rightarrow & \text{scattering state.} \end{cases} \qquad [2.110]$$

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
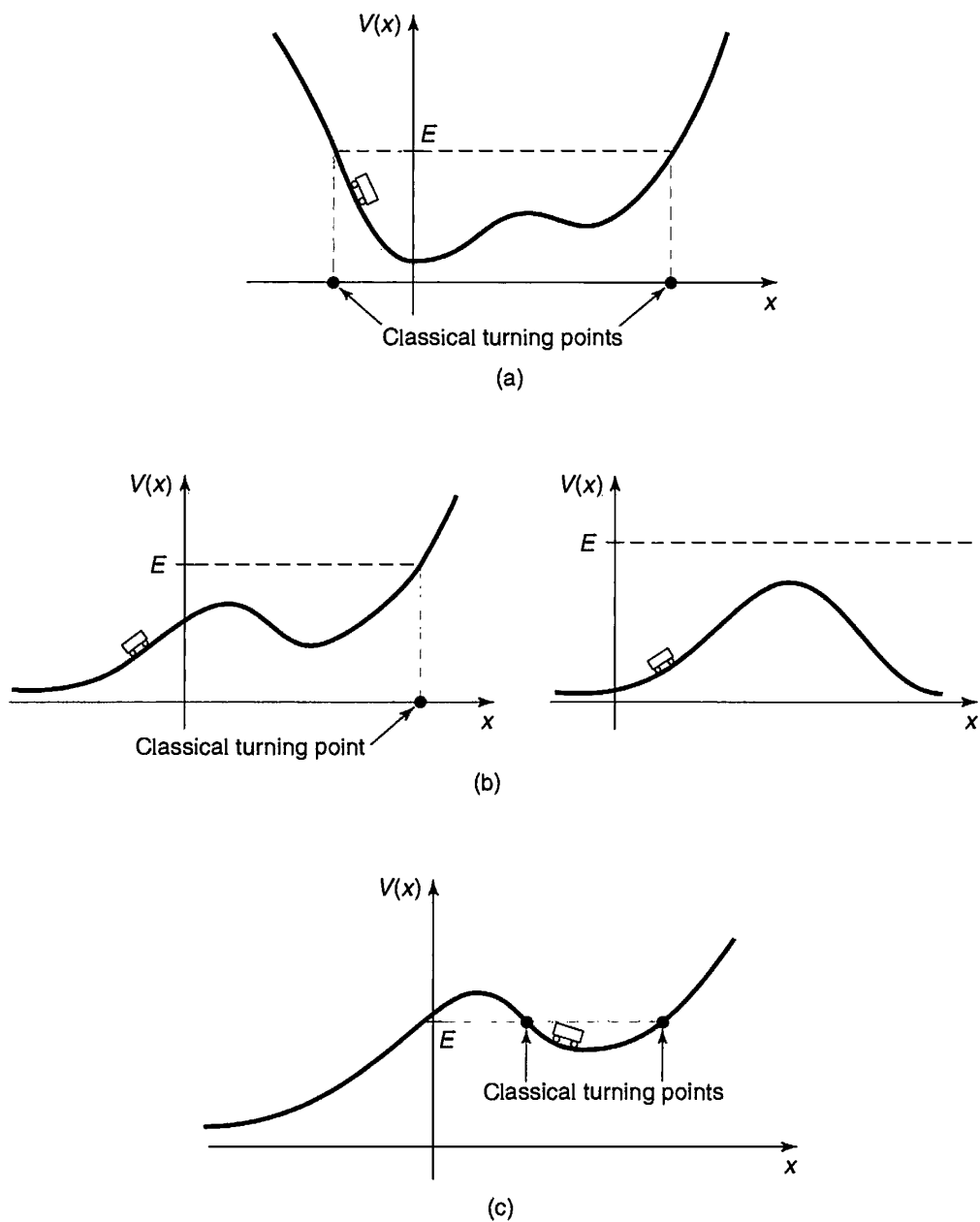
FIGURE 2.12: (a) A bound state. (b) Scattering states. (c) A *classical* bound state, but a quantum scattering state.

everywhere, it only allows scattering states.[34] In this section (and the following one) we shall explore potentials that give rise to both kinds of states.

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[34]If you are irritatingly observant, 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 $E \leq 0$, for the free particle, and
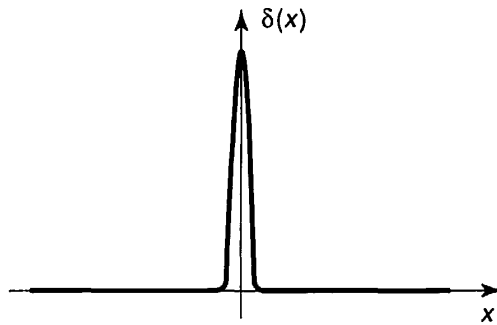
FIGURE 2.13: The Dirac delta function (Equation 2.111).

2.5.2 The Delta-Function Well

The **Dirac delta function** is an infinitely high, infinitesimally narrow spike at the origin, whose *area* is 1 (Figure 2.13):

$$\delta(x) \equiv \begin{cases} 0, & \text{if } x \neq 0 \\ \infty, & \text{if } x = 0 \end{cases}, \quad \text{with} \quad \int_{-\infty}^{+\infty} \delta(x)\,dx = 1. \qquad [2.111]$$

Technically, it isn't a function at all, since it is not finite at $x = 0$ (mathematicians call it a **generalized function**, or **distribution**).[35] 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 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 $f(a)$,

$$f(x)\delta(x - a) = f(a)\delta(x - a), \qquad [2.112]$$

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

$$\int_{-\infty}^{+\infty} f(x)\delta(x - a)\,dx = f(a) \int_{-\infty}^{+\infty} \delta(x - a)\,dx = f(a). \qquad [2.113]$$

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

$$V(x) = -\alpha\delta(x), \qquad [2.114]$$

---

note that *even linear combinations* of these solutions cannot be normalized. The positive energy solutions by themselves constitute a complete set.

[35]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.

where α is some positive constant.[36] This is an artificial potential, to be sure (so was the infinite square well), but it's delightfully simple to work with, and illuminates the basic theory with a minimum of analytical clutter. The Schrödinger equation for the delta-function well reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - \alpha\delta(x)\psi = E\psi;$$ [2.115]

it 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

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = \kappa^2\psi,$$ [2.116]

where

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}.$$ [2.117]

(E is negative, by assumption, so κ is real and positive.) The general solution to Equation 2.116 is

$$\psi(x) = Ae^{-\kappa x} + Be^{\kappa x},$$ [2.118]

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

$$\psi(x) = Be^{\kappa x}. \quad (x < 0).$$ [2.119]

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

$$\psi(x) = Fe^{-\kappa x}. \quad (x > 0).$$ [2.120]

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:

$$\left\{\begin{array}{ll} 1. \ \psi & \text{is always continuous;} \\ 2. \ d\psi/dx & \text{is continuous except at points where the potential is infinite.} \end{array}\right.$$ [2.121]

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

$$\psi(x) = \left\{\begin{array}{ll} Be^{\kappa x}, & (x \leq 0). \\ Be^{-\kappa x}, & (x \geq 0); \end{array}\right.$$ [2.122]

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[36]The delta function itself carries units of $1/length$ (see Equation 2.111), so α has the dimensions *energy × length*.
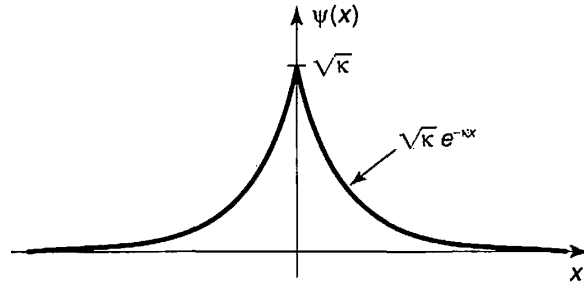
FIGURE 2.14:   Bound state wave function for the delta-function potential (Equation 2.122).

$\psi(x)$ is plotted in Figure 2.14. 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 by-product 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 $\epsilon \to 0$:

$$-\frac{\hbar^2}{2m} \int_{-\epsilon}^{+\epsilon} \frac{d^2\psi}{dx^2} \, dx + \int_{-\epsilon}^{+\epsilon} V(x)\psi(x) \, dx = E \int_{-\epsilon}^{+\epsilon} \psi(x) \, dx. \qquad [2.123]$$

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

$$\Delta\left(\frac{d\psi}{dx}\right) \equiv \lim_{\epsilon \to 0} \left(\frac{d\psi}{dx}\bigg|_{+\epsilon} - \frac{d\psi}{dx}\bigg|_{-\epsilon}\right) = \frac{2m}{\hbar^2} \lim_{\epsilon \to 0} \int_{-\epsilon}^{+\epsilon} V(x)\psi(x) \, dx. \qquad [2.124]$$

Typically, the limit on the right is again zero, and that's why $d\psi/dx$ is ordinarily continuous. But when $V(x)$ is *infinite* at the boundary, this argument fails. In particular, if $V(x) = -\alpha\delta(x)$, Equation 2.113 yields

$$\Delta\left(\frac{d\psi}{dx}\right) = -\frac{2m\alpha}{\hbar^2}\psi(0). \qquad [2.125]$$

For the case at hand (Equation 2.122),

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

and hence $\Delta(d\psi/dx) = -2B\kappa$. And $\psi(0) = B$. So Equation 2.125 says

$$\kappa = \frac{m\alpha}{\hbar^2}. \qquad [2.126]$$

and the allowed energy (Equation 2.117) is

$$E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{m\alpha^2}{2\hbar^2}.$$ [2.127]

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):

$$B = \sqrt{\kappa} = \frac{\sqrt{m\alpha}}{\hbar}.$$ [2.128]

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

$$\boxed{\psi(x) = \frac{\sqrt{m\alpha}}{\hbar} e^{-m\alpha|x|/\hbar^2}; \quad E = -\frac{m\alpha^2}{2\hbar^2}.}$$ [2.129]

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

$$k \equiv \frac{\sqrt{2mE}}{\hbar}$$ [2.130]

is real and positive. The general solution is

$$\psi(x) = Ae^{ikx} + Be^{-ikx},$$ [2.131]

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

$$\psi(x) = Fe^{ikx} + Ge^{-ikx}.$$ [2.132]

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

$$F + G = A + B.$$ [2.133]

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 2.125) says

$$ik(F - G - A + B) = -\frac{2m\alpha}{\hbar^2}(A + B),\qquad\qquad [2.134]$$

or, more compactly,

$$F - G = A(1 + 2i\beta) - B(1 - 2i\beta),\quad \text{where } \beta \equiv \frac{m\alpha}{\hbar^2 k}.\qquad [2.135]$$

Having imposed both boundary conditions, we are left with two equations (Equations 2.133 and 2.135) 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 2.131) is the amplitude of a wave coming in from the left, B is the amplitude of a wave returning to the left, F (Equation 2.132) is the amplitude of a wave traveling off to the right, and G is the amplitude of a wave coming in from the right (see Figure 2.15). 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*:

$$G = 0, \quad \text{(for scattering from the left)};\qquad\qquad [2.136]$$

A is 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 2.133 and 2.135 for B and F, we find

$$B = \frac{i\beta}{1 - i\beta}A, \quad F = \frac{1}{1 - i\beta}A.\qquad\qquad [2.137]$$

(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.)
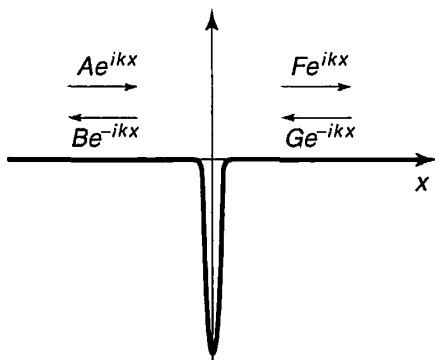

FIGURE 2.15: Scattering from a delta function well.

Now, the probability of finding the particle at a specified location is given by $|\Psi|^2$, so the *relative*[37] probability that an incident particle will be reflected back is

$$R \equiv \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2}.$$ [2.138]

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**

$$T \equiv \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2}.$$ [2.139]

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

$$R + T = 1.$$ [2.140]

Notice that R and T are functions of β, and hence (Equations 2.130 and 2.135) of E:

$$R = \frac{1}{1 + (2\hbar^2 E/m\alpha^2)}, \quad T = \frac{1}{1 + (m\alpha^2/2\hbar^2 E)}.$$ [2.141]

The higher the energy, the greater the probability of transmission (which certainly 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.[38] 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 the *vicinity* of E.

Incidentally, it might strike you as peculiar that we were able to analyze a quintessentially time-dependent problem (particle comes in, scatters off a potential,

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[37]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 the incident and reflected waves *is* meaningful. More on this in the next paragraph.

[38]Numerical studies of wave packets scattering off wells and barriers reveal extraordinarily rich structure. The classic analysis is A. Goldberg, H. M. Schey, and J. L. Schwartz, *Am. J. Phys.* **35**, 177 (1967); more recent work can be found on the Web.
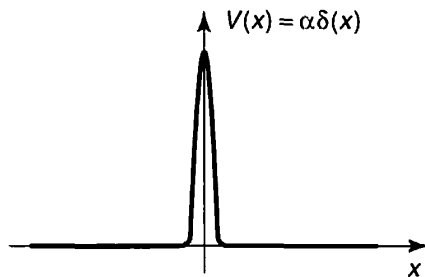
FIGURE 2.16:   The delta-function barrier.

and flies off to infinity) using *stationary* states. After all, ψ (in Equations 2.131 and 2.132) 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 2.43).

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 2.16). Formally, all we have to do is change the sign of α. This kills the bound state, of course (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, a particle cannot make it over an infinitely high barrier, regardless of its energy. In fact, classical scattering problems are pretty dull: If $E > V_{max}$, then $T = 1$ and $R = 0$—the particle certainly makes it over; if $E < V_{max}$ then $T = 0$ and $R = 1$—it rides up the hill until it runs out of steam, and then returns the same way it came. *Quantum* scattering problems are 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 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 hope that quantum mechanics will save you (see Problem 2.35).

∗**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 Delta functions live under integral signs, and 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 every (ordinary) function $f(x)$.

(a) Show that

$$\delta(cx) = \frac{1}{|c|}\delta(x), \qquad\qquad [2.142]$$

where c is a real constant. (Be sure to check the case where c is negative.)

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

$$\theta(x) \equiv \begin{cases} 1, & \text{if } x > 0. \\ 0, & \text{if } x < 0. \end{cases} \qquad\qquad [2.143]$$

(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** Check the uncertainty principle for the wave function in Equation 2.129. *Hint:* Calculating $\langle p^2 \rangle$ is tricky, because the derivative of ψ has a step discontinuity at $x = 0$. Use the result in Problem 2.24(b). *Partial answer:* $\langle p^2 \rangle = (m\alpha/\hbar)^2$.

***Problem 2.26** What is the Fourier transform of $\delta(x)$? Using Plancherel's theorem, show that

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{ikx}\, dk. \qquad\qquad [2.144]$$

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 Equation 2.144 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 33). In spite of this, Equation 2.144 can be extremely useful, if handled with care.

***Problem 2.27** 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 2.28 Find the transmission coefficient for the potential in Problem 2.27.

2.6 THE FINITE SQUARE WELL

As a last example, consider the *finite* square well potential

$$V(x) = \begin{cases} -V_0, & \text{for } -a \le x \le a, \\ 0, & \text{for } |x| > a, \end{cases} \qquad [2.145]$$

where V_0 is a (positive) constant (Figure 2.17). Like the delta-function well, this potential 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

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

where

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar} \qquad [2.146]$$

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 admissible solution (as before—see Equation 2.119) is

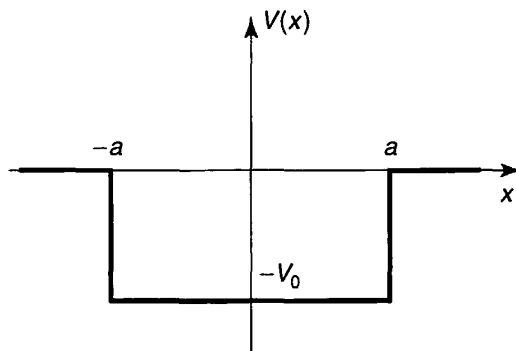$$\psi(x) = Be^{\kappa x}, \quad \text{for } x < -a. \qquad [2.147]$$

FIGURE 2.17: The finite square well (Equation 2.145).

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

$$l \equiv \frac{\sqrt{2m(E + V_0)}}{\hbar}. \qquad [2.148]$$

Although E is negative, for bound states, it must be greater than $-V_0$, by the old theorem $E > V_{\min}$ (Problem 2.2); so l is also real and positive. The general solution is[39]

$$\psi(x) = C\sin(lx) + D\cos(lx), \quad \text{for } -a < x < a, \qquad [2.149]$$

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

$$\psi(x) = Fe^{-\kappa x}, \quad \text{for } x > a. \qquad [2.150]$$

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 2.1(c)). 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 2.29. The cosine is even (and the sine is odd), so I'm looking for solutions of the form

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, & \text{for } x > a, \\ D\cos(lx), & \text{for } 0 < x < a, \\ \psi(-x), & \text{for } x < 0. \end{cases} \qquad [2.151]$$

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

$$Fe^{-\kappa a} = D\cos(la), \qquad [2.152]$$

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

$$-\kappa Fe^{-\kappa a} = -lD\sin(la). \qquad [2.153]$$

Dividing Equation 2.153 by Equation 2.152, we find that

$$\kappa = l\tan(la). \qquad [2.154]$$

---

[39]You can, if you like, write the general solution in exponential form $(C'e^{ilx} + D'e^{-ilx})$. This leads to the same final result, but since the potential is symmetric we know the solutions will be either even or odd, and the sine/cosine notation allows us to exploit this directly.
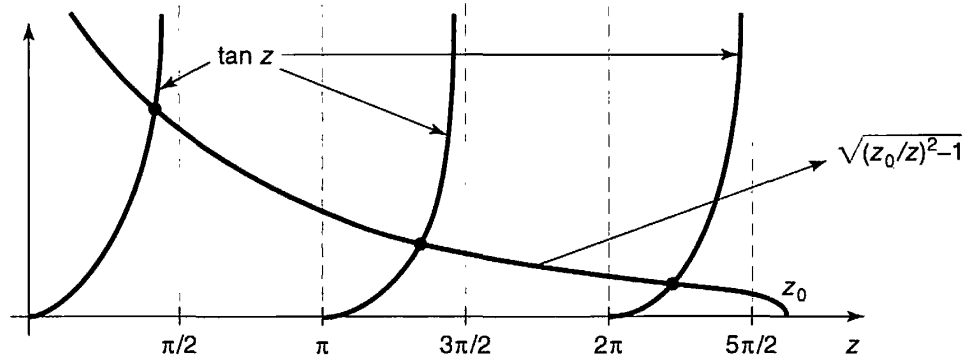
FIGURE 2.18:   Graphical solution to Equation 2.156, for $z_0 = 8$ (*even* states).

This is a formula for the allowed energies, since κ and l are both functions of E. To solve for E, we first adopt some nicer notation: Let

$$z \equiv la, \quad \text{and} \quad z_0 \equiv \frac{a}{\hbar}\sqrt{2mV_0}. \tag{2.155}$$

According to Equations 2.146 and 2.148, $(\kappa^2 + l^2) = 2mV_0/\hbar^2$, so $\kappa a = \sqrt{z_0^2 - z^2}$, and Equation 2.154 reads

$$\tan z = \sqrt{(z_0/z)^2 - 1}. \tag{2.156}$$

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 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 2.18). 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

$$E_n + V_0 \cong \frac{n^2\pi^2\hbar^2}{2m(2a)^2}. \tag{2.157}$$

But $E + V_0$ is the energy *above the bottom of the well*, and on the right side we have precisely the infinite square well energies, for a well of width $2a$ (see Equation 2.27)—or rather, *half* of them, since this n is odd. (The other ones, of course, come from the *odd* wave functions, as you'll discover in Problem 2.29.) 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 a finite number of 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 2.151), if you're interested (Problem 2.30), but I'm going to move on now to the scattering states ($E > 0$). To the left, where $V(x) = 0$, we have

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad \text{for } (x < -a). \qquad [2.158]$$

where (as usual)

$$k \equiv \frac{\sqrt{2mE}}{\hbar}. \qquad [2.159]$$

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

$$\psi(x) = C\sin(lx) + D\cos(lx), \quad \text{for } (-a < x < a), \qquad [2.160]$$

where, as before,

$$l \equiv \frac{\sqrt{2m(E + V_0)}}{\hbar}. \qquad [2.161]$$

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

$$\psi(x) = Fe^{ikx}. \qquad [2.162]$$

Here A is the incident amplitude, B is the reflected amplitude, and F is the transmitted amplitude.[40]

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

$$Ae^{-ika} + Be^{ika} = -C\sin(la) + D\cos(la), \qquad [2.163]$$

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

$$ik[Ae^{-ika} - Be^{ika}] = l[C\cos(la) + D\sin(la)] \qquad [2.164]$$

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

$$C\sin(la) + D\cos(la) = Fe^{ika}. \qquad [2.165]$$

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

$$l[C\cos(la) - D\sin(la)] = ikFe^{ika}. \qquad [2.166]$$

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[40] We *could* look for even and odd functions, as we did in the case of bound states, but the scattering problem is inherently asymmetric, since the waves come in from one side only, and the exponential notation (representing traveling waves) is more natural in this context.
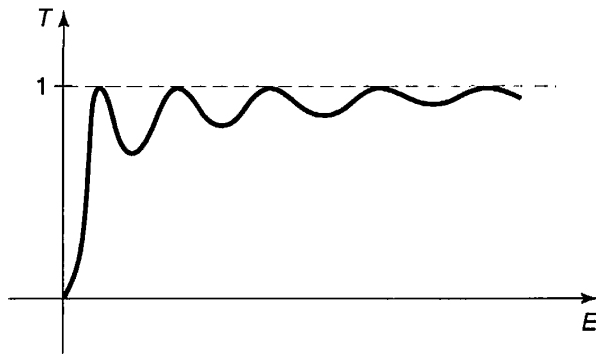
FIGURE 2.19: Transmission coefficient as a function of energy (Equation 2.169).

We can use two of these to eliminate C and D, and solve the remaining two for B and F (see Problem 2.32):

$$B = i \frac{\sin(2la)}{2kl}(l^2 - k^2)F.$$ [2.167]

$$F = \frac{e^{-2ika}A}{\cos(2la) - i \frac{(k^2+l^2)}{2kl}\sin(2la)}.$$ [2.168]

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

$$T^{-1} = 1 + \frac{V_0^2}{4E(E + V_0)} \sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E + V_0)}\right).$$ [2.169]

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

$$\frac{2a}{\hbar}\sqrt{2m(E_n + V_0)} = n\pi,$$ [2.170]

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

$$E_n + V_0 = \frac{n^2\pi^2\hbar^2}{2m(2a)^2},$$ [2.171]

which happen to be precisely the allowed energies for the *infinite* square well. T is plotted in Figure 2.19, as a function of energy.[41]

∗**Problem 2.29** 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 an odd bound state?

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[41] This remarkable phenomenon has been observed in the laboratory, in the form of the **Ramsauer-Townsend effect**. For an illuminating discussion see Richard W. Robinett, *Quantum Mechanics*, Oxford U.P., 1997, Section 12.4.1.

Problem 2.30 Normalize $\psi(x)$ in Equation 2.151, to determine the constants D and F.

Problem 2.31 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 2.114) 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 2.129. Also show that Equation 2.169 reduces to Equation 2.141 in the appropriate limit.

Problem 2.32 Derive Equations 2.167 and 2.168. *Hint:* Use Equations 2.165 and 2.166 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 2.163 and 2.164. Obtain the transmission coefficient, and confirm Equation 2.169.

∗∗Problem 2.33 Determine the transmission coefficient for a rectangular *barrier* (same as Equation 2.145, only with $V(x) = +V_0 > 0$ 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 $E < V_0$,[42]

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

∗Problem 2.34 Consider the "step" 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, which 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

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[42]This is a good example of tunneling—*classically* the particle would bounce back.
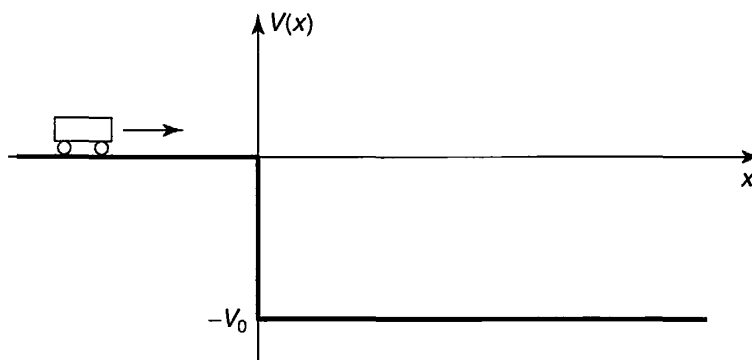
FIGURE 2.20:   Scattering from a "cliff" (Problem 2.35).

incident amplitude and F the transmitted amplitude), because the transmitted wave travels at a different *speed*. Show that

$$T = \sqrt{\frac{E - V_0}{E}} \frac{|F|^2}{|A|^2},$$ [2.172]

for $E > V_0$. *Hint:* You can figure it out using Equation 2.98, or—more elegantly, but less informatively—from the probability current (Problem 2.19). What is T, for $E < V_0$?

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

Problem 2.35 A particle of mass m and kinetic energy $E > 0$ approaches an abrupt potential drop V_0 (Figure 2.20).

(a)   What is the probability that it will "reflect" back, if $E = V_0/3$? *Hint:* This is just like Problem 2.34, except that the step now goes *down*, instead of up.

(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. *Hint:* In Figure 2.20 the potential energy of the car drops *discontinuously* to $-V_0$, as it passes $x = 0$; would this be true for a falling car?

(c)   When a free neutron enters a nucleus, it experiences a sudden drop in potential energy, from $V = 0$ outside to around -12 MeV (million electron volts) inside. Suppose a neutron, emitted with kinetic energy 4 MeV by a fission event, strikes such a nucleus. What is the probability it will be absorbed, thereby initiating another fission? *Hint:* You calculated the probability of *reflection* in part (a); use $T = 1 - R$ to get the probability of transmission through the surface.

FURTHER PROBLEMS FOR CHAPTER 2

Problem 2.36 Solve the time-independent Schrödinger equation with appropriate boundary conditions for the "centered" infinite square well: $V(x) = 0$ (for $-a < x < +a$), $V(x) = \infty$ (otherwise). Check that your allowed energies are consistent with mine (Equation 2.27), and confirm that your ψ's can be obtained from mine (Equation 2.28) by the substitution $x \to (x + a)/2$ (and appropriate renormalization). Sketch your first three solutions, and compare Figure 2.2. Note that the width of the well is now $2a$.

Problem 2.37 A particle in the infinite square well (Equation 2.19) has the initial wave function

$$\Psi(x, 0) = A \sin^3(\pi x/a) \quad (0 \le x \le a).$$

Determine A, find $\Psi(x, t)$, and calculate $\langle x \rangle$, as a function of time. What is the expectation value of the energy? *Hint:* $\sin^n \theta$ and $\cos^n \theta$ can be reduced, by repeated application of the trigonometric sum formulas, to linear combinations of $\sin(m\theta)$ and $\cos(m\theta)$, with $m = 0, 1, 2, \ldots, n$.

∗Problem 2.38 A particle of mass m is in the ground state of the infinite square well (Equation 2.19). Suddenly the well expands to twice its original size—the right wall moving from a to $2a$—leaving the wave function (momentarily) undisturbed. The energy of the particle is now measured.

(a) What is the most probable result? What is the probability of getting that result?

(b) What is the *next* most probable result, and what is its probability?

(c) What is the *expectation value* of the energy? *Hint:* If you find yourself confronted with an infinite series, try another method.

Problem 2.39

(a) Show that the wave function of a particle in the infinite square well returns to its original form after a quantum **revival time** $T = 4ma^2/\pi\hbar$. That is: $\Psi(x, T) = \Psi(x, 0)$ for any state (*not* just a stationary state).

(b) What is the *classical* revival time, for a particle of energy E bouncing back and forth between the walls?

(c) For what energy are the two revival times equal?[43]

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[43]The fact that the classical and quantum revival times bear no obvious relation to one another (and the quantum one doesn't even depend on the energy) is a curious paradox; see Daniel Styer, *Am. J. Phys.* **69**, 56 (2001).

Problem 2.40 A particle of mass m is in the potential

$$V(x) = \begin{cases} \infty & (x < 0), \\ -32\hbar^2/ma^2 & (0 \le x \le a), \\ 0 & (x > a). \end{cases}$$

(a) How many bound states are there?

(b) In the highest-energy bound state, what is the probability that the particle would be found *outside* the well ($x > a$)? *Answer:* 0.542, so even though it is "bound" by the well, it is more likely to be found outside than inside!

Problem 2.41 A particle of mass m in the harmonic oscillator potential (Equation 2.43) starts out in the state

$$\Psi(x, 0) = A \left(1 - 2\sqrt{\frac{m\omega}{\hbar}}x \right)^2 e^{-\frac{m\omega}{2\hbar}x^2},$$

for some constant A.

(a) What is the expectation value of the energy?

(b) At some later time T the wave function is

$$\Psi(x, T) = B \left(1 + 2\sqrt{\frac{m\omega}{\hbar}}x \right)^2 e^{-\frac{m\omega}{2\hbar}x^2},$$

for some constant B. What is the smallest possible value of T?

Problem 2.42 Find the allowed energies of the *half* harmonic oscillator

$$V(x) = \begin{cases} (1/2)m\omega^2 x^2, & \text{for } x > 0, \\ \infty, & \text{for } x < 0. \end{cases}$$

(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 2.43** 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 2.44 Solve the time-independent Schrödinger equation for a centered infinite square well with a delta-function barrier in the middle:

$$V(x) = \begin{cases} \alpha\delta(x), & \text{for } -a < x < +a, \\ \infty, & \text{for } |x| \geq a. \end{cases}$$

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? Explain why the odd solutions are not affected by the delta function. Comment on the limiting cases $\alpha \to 0$ and $\alpha \to \infty$.

Problem 2.45 If two (or more) distinct[44] 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 never encountered *normalizable* degenerate solutions, and this is no accident. Prove the following theorem: *In one dimension*[45] *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 2.46 Imagine a bead of mass m that slides frictionlessly around a circular wire ring of circumference L. (This is just like a free particle, except that $\psi(x + L) = \psi(x)$.) 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 counter-clockwise circulation; call them $\psi_n^+(x)$ and $\psi_n^-(x)$. How do you account for this degeneracy, in view of the theorem in Problem 2.45 (why does the theorem fail, in this case)?

∗∗Problem 2.47 *Attention:* This is a *strictly qualitative* problem—no calculations allowed! Consider the "double square well" potential (Figure 2.21). Suppose the

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[44] If 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 sense they are *not* distinct solutions. Technically, by "distinct" I mean "linearly independent."

[45] 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.
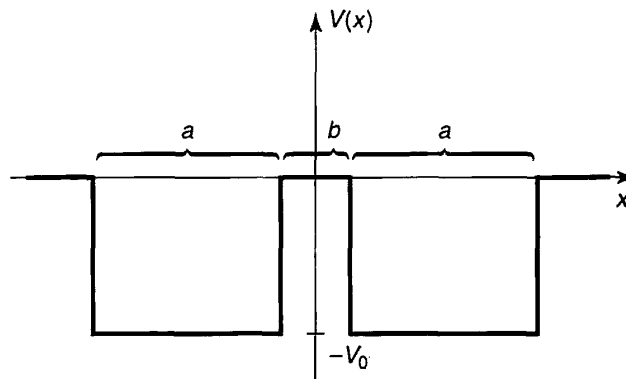
FIGURE 2.21:   The double square well (Problem 2.47).

depth V_0 and the width a are fixed, and large 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 2.48 In Problem 2.7(d) you got the expectation value of the energy by summing the series in Equation 2.39, but I warned you (in footnote 15) not to try it the "old fashioned way," $\langle H \rangle = \int \Psi(x, 0)^* H \Psi(x, 0) \, dx$, because the discontinuous first derivative of $\Psi(x, 0)$ renders the second derivative problematic. Actually, you *could* have done it using integration by parts, but the Dirac delta function affords a much cleaner way to handle such anomalies.

(a) Calculate the first derivative of $\Psi(x, 0)$ (in Problem 2.7), and express the answer in terms of the step function, $\theta(x - a/2)$, defined in Equation 2.143. (Don't worry about the end points—just the interior region $0 < x < a$.)

(b) Exploit the result of Problem 2.24(b) to write the second derivative of $\Psi(x, 0)$ in terms of the delta function.

(c) Evaluate the integral $\int \Psi(x, 0)^* H \Psi(x, 0) \, dx$, and check that you get the same answer as before.

✳ ✳ ✳Problem 2.49

(a) Show that

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

satisfies the time-*dependent* Schrödinger equation for the harmonic oscillator potential (Equation 2.43). Here a is any real constant with the dimensions of length.[46]

(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 2.50 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 the result of Problem 2.24(b).

(b) Find the expectation value of the Hamiltonian in this state, and comment on the result.

✳ ✳ ✳Problem 2.51 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) Graph this potential.

(b) Check that this potential has the ground state

$$\psi_0(x) = A\,\text{sech}(ax),$$

and find its energy. Normalize ψ_0, and sketch its graph.

---

[46]This rare example of an exact closed-form solution to the time-dependent Schrödinger equation was discovered by Schrödinger himself, in 1926.

(c) 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? *Comment:* This is a famous example of a **reflectionless potential**—every incident particle, regardless of its energy, passes right through.[47]

Problem 2.52 The scattering matrix. The theory of scattering generalizes in a pretty obvious way to arbitrary localized potentials (Figure 2.22). To the left (Region I), $V(x) = 0$, so

$$\psi(x) = Ae^{ikx} + Be^{-ikx}.\quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}. \tag{2.173}$$

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

$$\psi(x) = Fe^{ikx} + Ge^{-ikx}. \tag{2.174}$$

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

$$\psi(x) = Cf(x) + Dg(x).$$

where $f(x)$ and $g(x)$ are two linearly independent particular solutions.[48] There will be four boundary conditions (two joining Regions I and II, and two joining
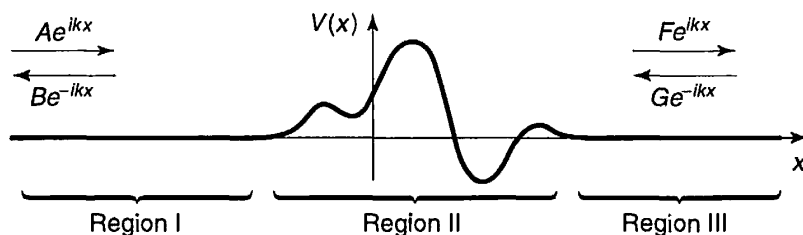

FIGURE 2.22:   Scattering from an arbitrary localized potential ($V(x) = 0$ except in Region II); Problem 2.52.

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[47]R. E. Crandall and B. R. Litt. *Annals of Physics.* **146.** 458 (1983).

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

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:

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

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

$$\begin{pmatrix} B \\ F \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} A \\ G \end{pmatrix}. \quad\quad [2.175]$$

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

$$R_l = \frac{|B|^2}{|A|^2}\bigg|_{G=0} = |S_{11}|^2. \quad T_l = \frac{|F|^2}{|A|^2}\bigg|_{G=0} = |S_{21}|^2. \quad\quad [2.176]$$

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

$$R_r = \frac{|F|^2}{|G|^2}\bigg|_{A=0} = |S_{22}|^2. \quad T_r = \frac{|B|^2}{|G|^2}\bigg|_{A=0} = |S_{12}|^2. \quad\quad [2.177]$$

(a) Construct the S-matrix for scattering from a delta-function well (Equation 2.114).

(b) Construct the S-matrix for the finite square well (Equation 2.145). *Hint:* This requires no new work, if you carefully exploit the symmetry of the problem.

∗ ∗ ∗**Problem 2.53 The transfer matrix.** The S-matrix (Problem 2.52) tells you the *outgoing* amplitudes (B and F) in terms of the *incoming* amplitudes (A and G)—Equation 2.175. 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):

$$\begin{pmatrix} F \\ G \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix}. \quad\quad [2.178]$$

(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 2.176 and 2.177) in terms of elements of the M-matrix.

(b) Suppose you have a potential consisting of two isolated pieces (Figure 2.23). Show that the M-matrix for the combination is the *product* of the two M-matrices for each section separately:

$$\mathbf{M} = \mathbf{M_2 M_1}. \quad\quad [2.179]$$

(This obviously generalizes to any number of pieces, and accounts for the usefulness of the M-matrix.)
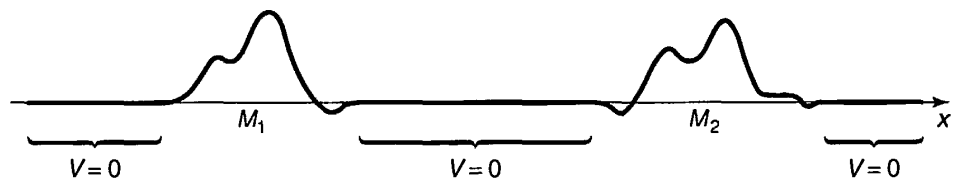
FIGURE 2.23:   A potential consisting of two isolated pieces (Problem 2.53).

(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?

Problem 2.54 Find the ground state energy of the harmonic oscillator, to five significant digits, by the "wag-the-dog" method. That is, solve Equation 2.72 numerically, varying K until you get a wave function that goes to zero at large ξ. In Mathematica, appropriate input code would be

**Plot[Evaluate[u[x]/.NDSolve[{u″[x] -(x² - K)*u[x] == 0, u[0] == 1,
u′[0] == 0}, u[x], {x, 10⁻⁸, 10}, MaxSteps -> 10000]], {x, a, b},
PlotRange -> {c, d}];**

(Here (a, b) is the horizontal range of the graph, and (c, d) is the vertical range—start with $a = 0$, $b = 10$, $c = -10$, $d = 10$.) We know that the correct solution is $K = 1$, so you might start with a "guess" of $K = 0.9$. Notice what the "tail" of the wave function does. Now try $K = 1.1$, and note that the tail flips over. Somewhere in between those values lies the correct solution. Zero in on it by bracketing K ˙ tighter and tighter. As you do so, you may want to adjust a, b, c, and d, to zero in on the cross-over point.

Problem 2.55 Find the first three excited state energies (to five significant digits) for the harmonic oscillator, by wagging the dog (Problem 2.54). For the first (and third) excited state you will need to set $u[0] == 0$. $u'[0] == 1$.

Problem 2.56 Find the first four allowed energies (to five significant digits) for the infinite square well, by wagging the dog. *Hint:* Refer to Problem 2.54, making appropriate changes to the differential equation. This time the condition you are looking for is $u(1) = 0$.

CHAPTER 3

FORMALISM

3.1 HILBERT SPACE

In the last two chapters we have stumbled on a number of interesting properties of simple quantum systems. Some of these are "accidental" features of specific potentials (the even spacing of energy levels for the harmonic oscillator, for example), but others seem to be more general, and it would be nice to prove them once and for all (the uncertainty principle, for instance, and the orthogonality of stationary states). The purpose of this chapter is to recast the theory in a more powerful form, with that in mind. There is not much here that is genuinely *new*; the idea, rather, is to make coherent sense of what we have already discovered in particular cases.

Quantum theory is based on two constructs: *wave functions* and *operators*. The state of a system is represented by its wave function, observables are represented by operators. Mathematically, wave functions satisfy the defining conditions for abstract **vectors**, and operators act on them as **linear transformations**. So the natural language of quantum mechanics is **linear algebra**.[1]

But it is not, I suspect, a form of linear algebra with which you are immediately familiar. In an N-dimensional space it is simplest to represent a vector, $|\alpha\rangle$, by the N-tuple of its components, $\{a_n\}$, with respect to a specified orthonormal basis:

$$|\alpha\rangle \rightarrow \mathbf{a} = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix}.$$
[3.1]

---

[1] If you have never studied linear algebra, you should read the Appendix before continuing.

The **inner product**, $\langle \alpha | \beta \rangle$, of two vectors (generalizing the dot product in three dimensions) is the complex number,

$$\langle \alpha | \beta \rangle = a_1^* b_1 + a_2^* b_2 + \cdots + a_N^* b_N.$$ [3.2]

Linear transformations, T, are represented by **matrices** (with respect to the specified basis), which act on vectors (to produce new vectors) by the ordinary rules of matrix multiplication:

$$|\beta\rangle = T|\alpha\rangle \rightarrow \mathbf{b} = \mathbf{Ta} = \begin{pmatrix} t_{11} & t_{12} & \cdots & t_{1N} \\ t_{21} & t_{22} & \cdots & t_{2N} \\ \vdots & \vdots & & \vdots \\ t_{N1} & t_{N2} & \cdots & t_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix}.$$ [3.3]

But the "vectors" we encounter in quantum mechanics are (for the most part) *functions*, and they live in *infinite*-dimensional spaces. For them the N-tuple/matrix notation is awkward, at best, and manipulations that are well-behaved in the finite-dimensional case can be problematic. (The underlying reason is that whereas the *finite* sum in Equation 3.2 always exists, an *infinite* sum—or an integral—may not converge, in which case the inner product does not exist, and any argument involving inner products is immediately suspect.) So even though most of the terminology and notation should be familiar, it pays to approach this subject with caution.

The collection of *all* functions of x constitutes a vector space, but for our purposes it is much too large. To represent a possible physical state, the wave function Ψ must be *normalized*:

$$\int |\Psi|^2 \, dx = 1.$$

The set of all **square-integrable functions**, on a specified interval,[2]

$$f(x) \quad \text{such that} \quad \int_a^b |f(x)|^2 \, dx < \infty,$$ [3.4]

constitutes a (much smaller) vector space (see Problem 3.1(a)). Mathematicians call it $L_2(a, b)$; physicists call it **Hilbert space**.[3] In quantum mechanics, then,

Wave functions live in Hilbert space.

    [3.5]

---

[2]For us. the limits (a and b) will almost always be $\pm\infty$. but we might as well keep things more general for the moment.

[3]Technically. a Hilbert space is a **complete inner product space**, and the collection of square-integrable functions is only *one example* of a Hilbert space—indeed, every finite-dimensional vector space is trivially a Hilbert space. But since L_2 is the arena of quantum mechanics, it's what physicists generally *mean* when they say "Hilbert space." By the way, the word **complete** here means that any Cauchy sequence of functions in Hilbert space converges to a function that is also in the space: it has no "holes" in it. just as the set of all real numbers has no holes (by contrast, the space of all *polynomials*, for example, like the set of all *rational* numbers, certainly *does* have holes in it). The completeness of a *space* has nothing to do with the completeness (same word, unfortunately) of a *set of functions*, which is the property that any other function can be expressed as a linear combination of them.

We define the **inner product of two functions**, $f(x)$ and $g(x)$, as follows:

$$\langle f | g \rangle \equiv \int_a^b f(x)^* g(x)\, dx. \tag{3.6}$$

If f and g are both square-integrable (that is, if they are both in Hilbert space), their inner product is guaranteed to exist (the integral in Equation 3.6 converges to a finite number).[4] This follows from the integral **Schwarz inequality**:[5]

$$\left| \int_a^b f(x)^* g(x)\, dx \right| \le \sqrt{\int_a^b |f(x)|^2\, dx \int_a^b |g(x)|^2\, dx}. \tag{3.7}$$

You can check for yourself that Equation 3.6 satisfies all the conditions for an inner product (Problem 3.1(b)). Notice in particular that

$$\langle g | f \rangle = \langle f | g \rangle^*. \tag{3.8}$$

Moreover, the inner product of $f(x)$ with *itself*,

$$\langle f | f \rangle = \int_a^b |f(x)|^2\, dx, \tag{3.9}$$

is *real* and non-negative; it's *zero* only[6] when $f(x) = 0$.

A function is said to be **normalized** if its inner product with itself is 1; two functions are **orthogonal** if their inner product is 0; and a *set* of functions, $\{f_n\}$, is **orthonormal** if they are normalized and mutually orthogonal:

$$\langle f_m | f_n \rangle = \delta_{mn}. \tag{3.10}$$

Finally, a set of functions is **complete** if any *other* function (in Hilbert space) can be expressed as a linear combination of them:

$$f(x) = \sum_{n=1}^{\infty} c_n\, f_n(x). \tag{3.11}$$

---

[4] In Chapter 2 we were obliged on occasion to work with functions that were *not* normalizable. Such functions lie *outside* Hilbert space, and we are going to have to handle them with special care, as you will see shortly. For the moment, I shall assume that all the functions we encounter *are* in Hilbert space.

[5] For a proof, see F. Riesz and B. Sz.-Nagy, *Functional Analysis* (Unger, New York, 1955), Section 21. In a *finite* dimensional vector space the Schwarz inequality, $|\langle \alpha | \beta \rangle|^2 \le \langle \alpha | \alpha \rangle \langle \beta | \beta \rangle$, is easy to prove (see Problem A.5). But that proof *assumes* the existence of the inner products, which is precisely what we are trying to *establish* here.

[6] What about a function that is zero everywhere except at a few isolated points? The integral (Equation 3.9) would still vanish, even though the function itself does not. If this bothers you, you should have been a math major. In physics such pathological functions do not occur, but in any case, in Hilbert space two functions that have the same square integral are considered equivalent. Technically, vectors in Hilbert space represent **equivalence classes** of functions.

If the functions $\{f_n(x)\}$ are orthonormal, the coefficients are given by Fourier's trick:

$$c_n = \langle f_n | f \rangle.$$ [3.12]

as you can check for yourself. I anticipated this terminology, of course, back in Chapter 2. (The stationary states for the infinite square well (Equation 2.28) constitute a complete orthonormal set on the interval $(0, a)$; the stationary states for the harmonic oscillator (Equation 2.67 or 2.85) are a complete orthonormal set on the interval $(-\infty, \infty)$.)

Problem 3.1

(a) Show that the set of all square-integrable functions is a vector space (refer to Section A.1 for the definition). *Hint:* The main problem is to show that the sum of two square-integrable functions is itself square-integrable. Use Equation 3.7. Is the set of all *normalized* functions a vector space?

(b) Show that the integral in Equation 3.6 satisfies the conditions for an inner product (Section A.2).

∗Problem 3.2

(a) For what range of ν is the function $f(x) = x^\nu$ in Hilbert space, on the interval $(0, 1)$? Assume ν is real, but not necessarily positive.

(b) For the specific case $\nu = 1/2$, is $f(x)$ in this Hilbert space? What about $xf(x)$? How about $(d/dx)f(x)$?

3.2 OBSERVABLES

3.2.1 Hermitian Operators

The expectation value of an observable $Q(x, p)$ can be expressed very neatly in inner-product notation:[7]

$$\langle Q \rangle = \int \Psi^* \hat{Q} \Psi \, dx = \langle \Psi | \hat{Q} \Psi \rangle.$$ [3.13]

---

[7]Remember that $\hat{Q}$ is the operator constructed from Q by the replacement $p \to \hat{p} \equiv (\hbar/i)d/dx$. These operators are **linear**, in the sense that

$$\hat{Q}[af(x) + bg(x)] = a\hat{Q}f(x) + b\hat{Q}g(x),$$

for any functions f and g and any complex numbers a and b. They constitute *linear transformations* (Section A.3) on the space of all functions. However, they sometimes carry a function *inside* Hilbert

Now, the outcome of a measurement has got to be *real*, and so, *a fortiori*, is the *average* of many measurements:

$$\langle Q \rangle = \langle Q \rangle^*. \qquad [3.14]$$

But the complex conjugate of an inner product reverses the order (Equation 3.8), so

$$\langle \Psi | \hat{Q}\Psi \rangle = \langle \hat{Q}\Psi | \Psi \rangle. \qquad [3.15]$$

and this must hold true for any wave function Ψ. Thus operators representing *observables* have the very special property that

$$\langle f | \hat{Q}f \rangle = \langle \hat{Q}f | f \rangle \quad \text{for all } f(x). \qquad [3.16]$$

We call such operators **hermitian**.

Actually, most books require an ostensibly stronger condition:

$$\langle f | \hat{Q}g \rangle = \langle \hat{Q}f | g \rangle \quad \text{for all } f(x) \text{ and all } g(x). \qquad [3.17]$$

But it turns out, in spite of appearances, that this is perfectly equivalent to my definition (Equation 3.16), as you will prove in Problem 3.3. So use whichever you like. The essential point is that a hermitian operator can be applied either to the first member of an inner product or to the second, with the same result, and hermitian operators naturally arise in quantum mechanics because their expectation values are real:

> **Observables are represented by hermitian operators.**   [3.18]

Well, let's *check* this. Is the momentum operator, for example, hermitian?

$$\langle f | \hat{p}g \rangle = \int_{-\infty}^{\infty} f^* \frac{\hbar}{i} \frac{dg}{dx} dx = \frac{\hbar}{i} f^* g \Big|_{-\infty}^{\infty} + \int_{-\infty}^{\infty} \left(\frac{\hbar}{i} \frac{df}{dx} \right)^* g \, dx = \langle \hat{p}f | g \rangle. \qquad [3.19]$$

I used integration by parts, of course, and threw away the boundary term for the usual reason: If $f(x)$ and $g(x)$ are square integrable, they must go to zero at $\pm\infty$.[8]

---

space into a function *outside* it (see Problem 3.2(b)), and in this case the domain of the operator may have to be restricted.

[8]Actually, this is not quite true. As I mention in Chapter 1, there exist pathological functions that are square-integrable but do *not* go to zero at infinity. However, such functions do not arise in physics, and if you are worried about it we will simply restrict the domain of our operators to exclude them. On *finite* intervals, though, you really *do* have to be more careful with the boundary terms, and an operator that is hermitian on $(-\infty, \infty)$ may *not* be hermitian on $(0, \infty)$ or $(-\pi, \pi)$. If you're wondering about the infinite square well, it's safest to think of those wave functions as residing on the infinite line—they just happen to be *zero* outside $(0, a)$.

Notice how the complex conjugation of i compensates for the minus sign picked up from integration by parts—the operator d/dx (without the i) is *not* hermitian, and it does not represent a possible observable.

---

*Problem 3.3 Show that if $\langle h|\hat{Q}h\rangle = \langle \hat{Q}h|h\rangle$ for all functions h (in Hilbert space), then $\langle f|\hat{Q}g\rangle = \langle \hat{Q}f|g\rangle$ for all f and g (i.e., the two definitions of "hermitian"—Equations 3.16 and 3.17—are equivalent). *Hint:* First let $h = f + g$, and then let $h = f + ig$.

Problem 3.4

(a) Show that the *sum* of two hermitian operators is hermitian.

(b) Suppose $\hat{Q}$ is hermitian, and α is a complex number. Under what condition (on α) is $\alpha\hat{Q}$ hermitian?

(c) When is the *product* of two hermitian operators hermitian?

(d) Show that the position operator ($\hat{x} = x$) and the hamiltonian operator ($\hat{H} = -(\hbar^2/2m)d^2/dx^2 + V(x)$) are hermitian.

Problem 3.5 The **hermitian conjugate** (or **adjoint**) of an operator $\hat{Q}$ is the operator $\hat{Q}^\dagger$ such that

$$\langle f|\hat{Q}g\rangle = \langle \hat{Q}^\dagger f|g\rangle \quad \text{(for all } f \text{ and } g\text{).} \quad [3.20]$$

(A hermitian operator, then, is equal to its hermitian conjugate: $\hat{Q} = \hat{Q}^\dagger$.)

(a) Find the hermitian conjugates of x, i, and d/dx.

(b) Construct the hermitian conjugate of the harmonic oscillator raising operator, a_+ (Equation 2.47).

(c) Show that $(\hat{Q}\hat{R})^\dagger = \hat{R}^\dagger\hat{Q}^\dagger$.

3.2.2 Determinate States

Ordinarily, when you measure an observable Q on an ensemble of identically prepared systems, all in the same state Ψ, you do *not* get the same result each time—this is the *indeterminacy* of quantum mechanics.[9] *Question:* Would it be possible to prepare a state such that *every* measurement of Q is certain to return the *same* value (call it q)? This would be, if you like, a **determinate state**, for the observable Q. (Actually, we already know one example: Stationary states are determinate states of the Hamiltonian; a measurement of the total energy, on a

---

[9] I'm talking about *competent* measurements, of course—it's always possible to make a *mistake*, and simply get the wrong answer, but that's not the fault of quantum mechanics.

particle in the stationary state Ψ_n, is certain to yield the corresponding "allowed" energy E_n.)

Well, the standard deviation of Q, in a determinate state, would be *zero*, which is to say,

$$\sigma^2 = \langle (\hat{Q} - \langle Q \rangle)^2 \rangle = \langle \Psi | (\hat{Q} - q)^2 \Psi \rangle = \langle (\hat{Q} - q) \Psi | (\hat{Q} - q) \Psi \rangle = 0. \quad [3.21]$$

(Of course, if every measurement gives q, their average is also q: $\langle Q \rangle = q$. I also used the fact that $\hat{Q}$, and hence also $\hat{Q} - q$, is a *hermitian* operator, to move one factor over to the first term in the inner product.) But the only function whose inner product with itself vanishes is 0, so

$$\hat{Q} \Psi = q \Psi. \quad [3.22]$$

This is the **eigenvalue equation** for the operator $\hat{Q}$; Ψ is an **eigenfunction** of $\hat{Q}$, and q is the corresponding **eigenvalue**. Thus

> **Determinate states are eigenfunctions of $\hat{Q}$.**   [3.23]

Measurement of Q on such a state is certain to yield the eigenvalue, q.

Note that the eigen*value* is a *number* (not an operator or a function). You can multiply any eigenfunction by a constant, and it is still an eigenfunction, with the same eigenvalue. Zero does not count as an eigenfunction (we exclude it by definition—otherwise *every* number would be an eigenvalue, since $\hat{Q} 0 = q 0 = 0$ for any operator $\hat{Q}$ and all q). But there's nothing wrong with zero as an eigen*value*. The collection of all the eigenvalues of an operator is called its **spectrum**. Sometimes two (or more) linearly independent eigenfunctions share the same eigenvalue; in that case the spectrum is said to be **degenerate**.

For example, determinate states of the total energy are eigenfunctions of the Hamiltonian:

$$\hat{H} \psi = E \psi, \quad [3.24]$$

which is precisely the time-independent Schrödinger equation. In this context we use the letter E for the eigenvalue, and the lower case ψ for the eigenfunction (tack on the factor $\exp(-iEt/\hbar)$ to make it Ψ, if you like; it's still an eigenfunction of H).

Example 3.1   Consider the operator

$$\hat{Q} \equiv i \frac{d}{d\phi}, \quad [3.25]$$

where ϕ is the usual polar coordinate in two dimensions. (This operator might arise in a physical context if we were studying the bead-on-a-ring; see Problem 2.46.) Is $\hat{Q}$ hermitian? Find its eigenfunctions and eigenvalues.

Solution: Here we are working with functions $f(\phi)$ on the *finite* interval $0 \le \phi \le 2\pi$, and stipulate that

$$f(\phi + 2\pi) = f(\phi). \tag{3.26}$$

since ϕ and $\phi + 2\pi$ describe the same physical point. Using integration by parts,

$$\langle f | \hat{Q} g \rangle = \int_0^{2\pi} f^* \left(i \frac{dg}{d\phi} \right) d\phi = i f^* g \Big|_0^{2\pi} - \int_0^{2\pi} i \left(\frac{df^*}{d\phi} \right) g \, d\phi = \langle \hat{Q} f | g \rangle,$$

so $\hat{Q}$ *is* hermitian (this time the boundary term disappears by virtue of Equation 3.26).
The eigenvalue equation,

$$i \frac{d}{d\phi} f(\phi) = q f(\phi), \tag{3.27}$$

has the general solution

$$f(\phi) = A e^{-iq\phi}. \tag{3.28}$$

Equation 3.26 restricts the possible values of the q:

$$e^{-iq2\pi} = 1 \quad \Rightarrow \quad q = 0. \pm 1. \pm 2, \ldots \tag{3.29}$$

The spectrum of this operator is the set of all integers, and it is nondegenerate.

Problem 3.6 Consider the operator $\hat{Q} = d^2/d\phi^2$, where (as in Example 3.1) ϕ is the azimuthal angle in polar coordinates, and the functions are subject to Equation 3.26. Is $\hat{Q}$ hermitian? Find its eigenfunctions and eigenvalues. What is the spectrum of $\hat{Q}$? Is the spectrum degenerate?

3.3 EIGENFUNCTIONS OF A HERMITIAN OPERATOR

Our attention is thus directed to the *eigenfunctions of hermitian operators* (physically: determinate states of observables). These fall into two categories: If the spectrum is **discrete** (i.e., the eigenvalues are separated from one another) then the eigenfunctions lie in Hilbert space and they constitute physically realizable states. If the spectrum is **continuous** (i.e., the eigenvalues fill out an entire range) then the eigenfunctions are not normalizable, and they do not represent possible wave functions (though *linear combinations* of them—involving necessarily a spread in eigenvalues—may be normalizable). Some operators have a discrete spectrum only (for example, the Hamiltonian for the harmonic oscillator), some have only a continuous spectrum (for example, the free particle Hamiltonian), and some have both a discrete part and a continuous part (for example, the Hamiltonian for a

finite square well). The discrete case is easier to handle, because the relevant inner products are guaranteed to exist—in fact, it is very similar to the finite-dimensional theory (the eigenvectors of a hermitian *matrix*). I'll treat the discrete case first, and then the continuous one.

3.3.1 Discrete Spectra

Mathematically, the normalizable eigenfunctions of a hermitian operator have two important properties:

Theorem 1: Their eigen*values* are *real*.

Proof: Suppose

$$\hat{Q}f = qf,$$

(i.e., $f(x)$ is an eigenfunction of $\hat{Q}$, with eigenvalue q), and[10]

$$\langle f|\hat{Q}f\rangle = \langle\hat{Q}f|f\rangle$$

($\hat{Q}$ is hermitian). Then

$$q\langle f|f\rangle = q^*\langle f|f\rangle$$

(q is a *number*, so it comes outside the integral, and because the first function in the inner product is complex conjugated (Equation 3.6), so too is the q on the right). But $\langle f|f\rangle$ cannot be zero ($f(x) = 0$ is not a legal eigenfunction), so $q = q^*$, and hence q is real. **QED**

This is comforting: If you measure an observable on a particle in a determinate state, you will at least get a real number.

Theorem 2: Eigenfunctions belonging to distinct eigenvalues are *orthogonal*.

Proof: Suppose

$$\hat{Q}f = qf, \quad \text{and} \quad \hat{Q}g = q'g,$$

and $\hat{Q}$ is hermitian. Then $\langle f|\hat{Q}g\rangle = \langle\hat{Q}f|g\rangle$, so

$$q'\langle f|g\rangle = q^*\langle f|g\rangle$$

(again, the inner products exist because the eigenfunctions are in Hilbert space by assumption). But q is real (from Theorem 1), so if $q' \neq q$ it must be that $\langle f|g\rangle = 0$. **QED**

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[10]It is here that we assume the eigenfunctions are in Hilbert space—otherwise the inner product might not exist at all.

That's why the stationary states of the infinite square well, for example, or the harmonic oscillator, are orthogonal—they are eigenfunctions of the Hamiltonian with distinct eigenvalues. But this property is not peculiar to them, or even to the Hamiltonian—the same holds for determinate states of *any* observable.

Unfortunately, Theorem 2 tells us nothing about degenerate states ($q' = q$). However, if two (or more) eigenfunctions share the same eigenvalue, any linear combination of them is itself an eigenfunction, with the same eigenvalue (Problem 3.7(a)), and we can use the **Gram-Schmidt orthogonalization procedure** (Problem A.4) to *construct* orthogonal eigenfunctions within each degenerate subspace. It is almost never necessary to do this explicitly (thank God!), but it can always be done in principle. So *even in the presence of degeneracy* the eigenfunctions can be *chosen* to be orthogonal, and in setting up the formalism of quantum mechanics we shall assume that this has already been done. That licenses the use of Fourier's trick, which depends on the orthonormality of the basis functions.

In a *finite*-dimensional vector space the eigenvectors of a hermitian matrix have a third fundamental property: They span the space (every vector can be expressed as a linear combination of them). Unfortunately, the proof does not generalize to infinite-dimensional spaces. But the property itself is essential to the internal consistency of quantum mechanics, so (following Dirac[11]) we will take it as an *axiom* (or, more precisely, as a restriction on the class of hermitian operators that can represent observables):

> **Axiom:** The eigenfunctions of an observable operator are *complete*: Any function (in Hilbert space) can be expressed as a linear combination of them.[12]

Problem 3.7

(a) Suppose that $f(x)$ and $g(x)$ are two eigenfunctions of an operator $\hat{Q}$, with the same eigenvalue q. Show that any linear combination of f and g is itself an eigenfunction of $\hat{Q}$, with eigenvalue q.

(b) Check that $f(x) = \exp(x)$ and $g(x) = \exp(-x)$ are eigenfunctions of the operator d^2/dx^2, with the same eigenvalue. Construct two linear combinations of f and g that are *orthogonal* eigenfunctions on the interval $(-1, 1)$.

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[11]P. A. M. Dirac. *The Principles of Quantum Mechanics*. Oxford University Press, New York (1958).

[12]In some specific cases completeness is provable (we know that the stationary states of the infinite square well, for example, are complete, because of Dirichlet's theorem). It is a little awkward to call something an "axiom" that is *provable* in some cases, but I don't know a better way to handle it.

Problem 3.8

(a) Check that the eigenvalues of the hermitian operator in Example 3.1 are real. Show that the eigenfunctions (for distinct eigenvalues) are orthogonal.

(b) Do the same for the operator in Problem 3.6.

3.3.2 Continuous Spectra

If the spectrum of a hermitian operator is *continuous*, the eigenfunctions are not normalizable, and the proofs of Theorems 1 and 2 fail, because the inner products may not exist. Nevertheless, there is a sense in which the three essential properties (reality, orthogonality, and completeness) still hold. I think it's best to approach this subtle case through specific examples.

Example 3.2   Find the eigenfunctions and eigenvalues of the momentum operator.

Solution: Let $f_p(x)$ be the eigenfunction and p the eigenvalue:

$$\frac{\hbar}{i}\frac{d}{dx}f_p(x) = pf_p(x).$$ [3.30]

The general solution is

$$f_p(x) = Ae^{ipx/\hbar}.$$

This is not square-integrable, for *any* (complex) value of p—the momentum operator has *no* eigenfunctions in Hilbert space. And yet, if we restrict ourselves to *real* eigenvalues, we do recover a kind of *ersatz* "orthonormality." Referring to Problems 2.24(a) and 2.26,

$$\int_{-\infty}^{\infty} f_{p'}^*(x)\, f_p(x)\, dx = |A|^2 \int_{-\infty}^{\infty} e^{i(p-p')x/\hbar}\, dx = |A|^2 2\pi\hbar\,\delta(p - p').$$ [3.31]

If we pick $A = 1/\sqrt{2\pi\hbar}$, so that

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar},$$ [3.32]

then

$$\langle f_{p'}|f_p \rangle = \delta(p - p').$$ [3.33]

which is strikingly reminiscent of *true* orthonormality (Equation 3.10)—the indices are now continuous variables, and the Kronecker delta has become a Dirac delta, but otherwise it looks just the same. I'll call Equation 3.33 **Dirac orthonormality**.

Most important, the eigenfunctions are *complete*, with the sum (in Equation 3.11) replaced by an integral: Any (square-integrable) function $f(x)$ can be written in the form

$$f(x) = \int_{-\infty}^{\infty} c(p)\, f_p(x)\, dp = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} c(p) e^{ipx/\hbar}\, dp. \qquad [3.34]$$

The expansion coefficient (now a *function*, $c(p)$) is obtained, as always, by Fourier's trick:

$$\langle f_{p'} | f \rangle = \int_{-\infty}^{\infty} c(p)\langle f_{p'} | f_p \rangle\, dp = \int_{-\infty}^{\infty} c(p)\delta(p - p')\, dp = c(p'). \qquad [3.35]$$

Alternatively, you can get them from Plancherel's theorem (Equation 2.102), for the expansion (Equation 3.34) is nothing but a Fourier transform.

The eigenfunctions of momentum (Equation 3.32) are sinusoidal, with wavelength

$$\lambda = \frac{2\pi\hbar}{p}. \qquad [3.36]$$

This is the old de Broglie formula (Equation 1.39), which I promised to prove at the appropriate time. It turns out to be a little more subtle than de Broglie imagined, because we now know that there is actually *no such thing* as a particle with determinate momentum. But we could make a normalizable wave *packet* with a narrow range of momenta, and it is to such an object that the de Broglie relation applies.

What are we to make of Example 3.2? Although none of the eigenfunctions of $\hat{p}$ lives in Hilbert space, a certain family of them (those with real eigenvalues) reside in the nearby "suburbs," with a kind of quasi-normalizability. They do not represent possible physical states, but they are still very useful (as we have already seen, in our study of one-dimensional scattering).[13]

Example 3.3   Find the eigenfunctions and eigenvalues of the position operator.

Solution: Let $g_y(x)$ be the eigenfunction and y the eigenvalue:

$$x\, g_y(x) = y\, g_y(x). \qquad [3.37]$$

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[13]What about the eigenfunctions with *non*real eigenvalues? These are not merely non-normalizable—they actually blow up at $\pm\infty$. Functions in what I called the "suburbs" of Hilbert space (the entire metropolitan area is sometimes called a "rigged Hilbert space": see, for example, Leslie Ballentine's *Quantum Mechanics: A Modern Development*, World Scientific, 1998) have the property that although they have no (finite) inner product with *themselves*, they *do* admit inner products with all members of Hilbert space. This is *not* true for eigenfunctions of $\hat{p}$ with nonreal eigenvalues. In particular, I showed that the momentum operator is hermitian *for functions in Hilbert space*, but the argument depended on dropping the boundary term (in Equation 3.19). That term is still zero if g is an eigenfunction of $\hat{p}$ with a real eigenvalue (as long as f is in Hilbert space), but not if the eigenvalue has an imaginary part. In this sense *any* complex number is an eigenvalue of the operator $\hat{p}$, but only *real* numbers are eigenvalues of the *hermitian* operator $\hat{p}$—the others lie outside the space over which $\hat{p}$ is hermitian.

Here y is a fixed number (for any given eigenfunction), but x is a continuous variable. What function of x has the property that multiplying it by x is the same as multiplying it by the constant y? Obviously it's got to be *zero*, except at the one point $x = y$; in fact, it is nothing but the Dirac delta function:

$$g_y(x) = A\delta(x - y).$$

This time the eigenvalue *has* to be real; the eigenfunctions are not square-integrable, but again they admit *Dirac* orthonormality:

$$\int_{-\infty}^{\infty} g_{y'}^*(x)\, g_y(x)\, dx = |A|^2 \int_{-\infty}^{\infty} \delta(x - y')\delta(x - y)\, dx = |A|^2 \delta(y - y'). \quad [3.38]$$

If we pick $A = 1$, so

$$g_y(x) = \delta(x - y). \quad [3.39]$$

then

$$\langle g_{y'}|g_y \rangle = \delta(y - y'). \quad [3.40]$$

These eigenfunctions are also *complete*:

$$f(x) = \int_{-\infty}^{\infty} c(y)\, g_y(x)\, dy = \int_{-\infty}^{\infty} c(y)\delta(x - y)\, dy, \quad [3.41]$$

with

$$c(y) = f(y) \quad [3.42]$$

(trivial, in this case, but you can get it from Fourier's trick if you insist).

If the spectrum of a hermitian operator is *continuous* (so the eigenvalues are labeled by a continuous variable—p or y, in the examples; z, generically, in what follows), the eigenfunctions are not normalizable, they are not in Hilbert space and they do not represent possible physical states; nevertheless, the eigenfunctions with real eigenvalues are *Dirac* orthonormalizable and complete (with the sum now an integral). Luckily, this is all we really require.

Problem 3.9

(a) Cite a Hamiltonian from Chapter 2 (*other* than the harmonic oscillator) that has only a *discrete* spectrum.

(b) Cite a Hamiltonian from Chapter 2 (*other* than the free particle) that has only a *continuous* spectrum.

(c) Cite a Hamiltonian from Chapter 2 (*other* than the finite square well) that has both a discrete and a continuous part to its spectrum.

Problem 3.10 Is the ground state of the infinite square well an eigenfunction of momentum? If so, what is its momentum? If not, *why* not?

3.4 GENERALIZED STATISTICAL INTERPRETATION

In Chapter 1 I showed you how to calculate the probability that a particle would be found in a particular location, and how to determine the expectation value of any observable quantity. In Chapter 2 you learned how to find the possible outcomes of an energy measurement and their probabilities. I am now in a position to state the **generalized statistical interpretation**, which subsumes all of this and enables you to figure out the possible results of *any* measurement, and their probabilities. Together with the Schrödinger equation (which tells you how the wave function evolves in time) it is the foundation of quantum mechanics.

Generalized statistical interpretation: If you measure an observable $Q(x, p)$ on a particle in the state $\Psi(x, t)$, you are certain to get *one of the eigenvalues* of the hermitian operator $\hat{Q}(x, -i\hbar d/dx)$. If the spectrum of $\hat{Q}$ is discrete, the probability of getting the particular eigenvalue q_n associated with the orthonormalized eigenfunction $f_n(x)$ is

$$|c_n|^2, \quad \text{where} \quad c_n = \langle f_n | \Psi \rangle. \tag{3.43}$$

If the spectrum is continuous, with real eigenvalues $q(z)$ and associated Dirac-orthonormalized eigenfunctions $f_z(x)$, the probability of getting a result in the range dz is

$$|c(z)|^2 dz \quad \text{where} \quad c(z) = \langle f_z | \Psi \rangle. \tag{3.44}$$

Upon measurement, the wave function "collapses" to the corresponding eigenstate.[14]

The statistical interpretation is radically different from anything we encounter in classical physics. A somewhat different perspective helps to make it plausible: The eigenfunctions of an observable operator are *complete*, so the wave function can be written as a linear combination of them:

$$\Psi(x, t) = \sum_n c_n f_n(x). \tag{3.45}$$

---

[14] In the case of continuous spectra the collapse is to a narrow *range* about the measured value, depending on the precision of the measuring device.

(For simplicity, I'll assume that the spectrum is discrete; it's easy to generalize this argument to the continuous case.) Because the eigenfunctions are *orthonormal*, the coefficients are given by Fourier's trick:[15]

$$c_n = \langle f_n | \Psi \rangle = \int f_n(x)^* \Psi(x, t) \, dx. \qquad [3.46]$$

Qualitatively, c_n tells you "how much f_n is contained in Ψ," and given that a measurement has to return one of the eigenvalues of $\hat{Q}$, it seems reasonable that the probability of getting the particular eigenvalue q_n would be determined by the "amount of f_n" in Ψ. But because probabilities are determined by the absolute *square* of the wave function, the precise measure is actually $|c_n|^2$. That's the essential burden of the generalized statistical interpretation.[16]

Of course, the *total* probability (summed over all possible outcomes) has got to be *one*:

$$\sum_n |c_n|^2 = 1. \qquad [3.47]$$

and sure enough, this follows from the normalization of the wave function:

$$1 = \langle \Psi | \Psi \rangle = \left\langle \left(\sum_{n'} c_{n'} f_{n'} \right) \middle| \left(\sum_n c_n f_n \right) \right\rangle = \sum_{n'} \sum_n c_{n'}^* c_n \langle f_{n'} | f_n \rangle$$

$$= \sum_{n'} \sum_n c_{n'}^* c_n \delta_{n'n} = \sum_n c_n^* c_n = \sum_n |c_n|^2. \qquad [3.48]$$

Similarly, the expectation value of Q should be the sum over all possible outcomes of the eigenvalue times the probability of getting that eigenvalue:

$$\langle Q \rangle = \sum_n q_n |c_n|^2. \qquad [3.49]$$

Indeed,

$$\langle Q \rangle = \langle \Psi | \hat{Q} \Psi \rangle = \left\langle \left(\sum_{n'} c_{n'} f_{n'} \right) \middle| \left(\hat{Q} \sum_n c_n f_n \right) \right\rangle, \qquad [3.50]$$

---

[15]Notice that the time dependence—which is not at issue here—is carried by the coefficients; to make this explicit, we should really write $c_n(t)$.

[16]Again, I am scrupulously avoiding the all-too-common assertion "$|c_n|^2$ is the probability that the particle is in the state f_n." This is nonsense. The particle is in the state Ψ, *period*. Rather, $|c_n|^2$ is the probability that a *measurement* of Q would yield the value q_n. It is true that such a measurement will collapse the state to the eigenfunction f_n, so one could correctly say "$|c_n|^2$ is the probability that a particle which is *now* in the state Ψ *will be* in the state f_n subsequent to a measurement of Q" ... but that's a completely different assertion.

but $\hat{Q}f_n = q_n f_n$, so

$$\langle Q \rangle = \sum_{n'}\sum_{n} c_{n'}^* c_n q_n \langle f_{n'}|f_n\rangle = \sum_{n'}\sum_{n} c_{n'}^* c_n q_n \delta_{n'n} = \sum_n q_n |c_n|^2. \qquad [3.51]$$

So far, at least, everything looks consistent.

Can we reproduce, in this language, the original statistical interpretation for position measurements? Sure—it's real overkill, but worth checking. A measurement of x on a particle in state Ψ must return one of the eigenvalues of the position operator. Well, in Example 3.3 we found that every (real) number y is an eigenvalue of x, and the corresponding (Dirac-orthonormalized) eigenfunction is $g_y(x) = \delta(x - y)$. Evidently

$$c(y) = \langle g_y|\Psi\rangle = \int_{-\infty}^{\infty} \delta(x - y)\Psi(x, t)\,dx = \Psi(y, t), \qquad [3.52]$$

so the probability of getting a result in the range dy is $|\Psi(y, t)|^2\,dy$, which is precisely the original statistical interpretation.

What about momentum? In Example 3.2 we found that the eigenfunctions of the momentum operator are $f_p(x) = (1/\sqrt{2\pi\hbar})\exp(ipx/\hbar)$, so

$$c(p) = \langle f_p|\Psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipx/\hbar}\Psi(x, t)\,dx. \qquad [3.53]$$

This is such an important quantity that we give it a special name and symbol: the **momentum space wave function**, $\Phi(p, t)$. It is essentially the *Fourier transform* of the **(position space)** wave function $\Psi(x, t)$—which, by Plancherel's theorem, is its *inverse* Fourier transform:

$$\Phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipx/\hbar}\Psi(x, t)\,dx; \qquad [3.54]$$

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{ipx/\hbar}\Phi(p, t)\,dp. \qquad [3.55]$$

According to the generalized statistical interpretation, the probability that a measurement of momentum would yield a result in the range dp is

$$|\Phi(p, t)|^2\,dp. \qquad [3.56]$$

Example 3.4 A particle of mass m is bound in the delta function well $V(x) = -\alpha\delta(x)$. What is the probability that a measurement of its momentum would yield a value greater than $p_0 = m\alpha/\hbar$?

Solution: The (position space) wave function is (Equation 2.129)

$$\Psi(x, t) = \frac{\sqrt{m\alpha}}{\hbar} e^{-m\alpha|x|/\hbar^2} e^{-iEt/\hbar}$$

(where $E = -m\alpha^2/2\hbar^2$). The momentum space wave function is therefore

$$\Phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \frac{\sqrt{m\alpha}}{\hbar} e^{-iEt/\hbar} \int_{-\infty}^{\infty} e^{-ipx/\hbar} e^{-m\alpha|x|/\hbar^2} dx = \sqrt{\frac{2}{\pi}} \frac{p_0^{3/2} e^{-iEt/\hbar}}{p^2 + p_0^2}$$

(I looked up the integral). The probability, then, is

$$\frac{2}{\pi} p_0^3 \int_{p_0}^{\infty} \frac{1}{(p^2 + p_0^2)^2} dp = \frac{1}{\pi} \left[\frac{pp_0}{p^2 + p_0^2} + \tan^{-1}\left(\frac{p}{p_0}\right) \right]\Big|_{p_0}^{\infty}$$

$$= \frac{1}{4} - \frac{1}{2\pi} = 0.0908$$

(again, I looked up the integral).

Problem 3.11 Find the momentum-space wave function, $\Phi(p, t)$, for a particle in the ground state of the harmonic oscillator. What is the probability (to 2 significant digits) that a measurement of p on a particle in this state would yield a value outside the classical range (for the same energy)? *Hint:* Look in a math table under "Normal Distribution" or "Error Function" for the numerical part—or use Mathematica.

Problem 3.12 Show that

$$\langle x \rangle = \int \Phi^* \left(-\frac{\hbar}{i} \frac{\partial}{\partial p} \right) \Phi \, dp. \tag{3.57}$$

Hint: Notice that $x \exp(ipx/\hbar) = -i\hbar(d/dp)\exp(ipx/\hbar)$.

In momentum space, then, the position operator is $i\hbar\partial/\partial p$. More generally,

$$\langle Q(x, p) \rangle = \begin{cases} \int \Psi^* \hat{Q}\left(x, \frac{\hbar}{i}\frac{\partial}{\partial x}\right) \Psi \, dx, & \text{in position space;} \\[4mm] \int \Phi^* \hat{Q}\left(-\frac{\hbar}{i}\frac{\partial}{\partial p}, p\right) \Phi \, dp, & \text{in momentum space.} \end{cases} \tag{3.58}$$

In principle you can do all calculations in momentum space just as well (though not always as *easily*) as in position space.

3.5 THE UNCERTAINTY PRINCIPLE

I stated the uncertainty principle (in the form $\sigma_x \sigma_p \geq \hbar/2$), back in Section 1.6, and you have checked it several times, in the problems. But we have never actually *proved* it. In this section I will prove a more general version of the uncertainty principle, and explore some of its implications. The argument is beautiful, but rather abstract, so watch closely.

3.5.1 Proof of the Generalized Uncertainty Principle

For any observable A, we have (Equation 3.21):

$$\sigma_A^2 = \langle (\hat{A} - \langle A \rangle)\Psi | (\hat{A} - \langle A \rangle)\Psi \rangle = \langle f | f \rangle,$$

where $f \equiv (\hat{A} - \langle A \rangle)\Psi$. Likewise, for any *other* observable, B,

$$\sigma_B^2 = \langle g | g \rangle, \quad \text{where } g \equiv (\hat{B} - \langle B \rangle)\Psi.$$

Therefore (invoking the Schwarz inequality, Equation 3.7),

$$\sigma_A^2 \sigma_B^2 = \langle f | f \rangle \langle g | g \rangle \geq |\langle f | g \rangle|^2. \tag{3.59}$$

Now, for any complex number z,

$$|z|^2 = [\text{Re}(z)]^2 + [\text{Im}(z)]^2 \geq [\text{Im}(z)]^2 = \left[\frac{1}{2i}(z - z^*) \right]^2. \tag{3.60}$$

Therefore, letting $z = \langle f | g \rangle$,

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i}[\langle f | g \rangle - \langle g | f \rangle] \right)^2. \tag{3.61}$$

But

$$\langle f | g \rangle = \langle (\hat{A} - \langle A \rangle)\Psi | (\hat{B} - \langle B \rangle)\Psi \rangle = \langle \Psi | (\hat{A} - \langle A \rangle)(\hat{B} - \langle B \rangle)\Psi \rangle$$

$$= \langle \Psi | (\hat{A}\hat{B} - \hat{A}\langle B \rangle - \hat{B}\langle A \rangle + \langle A \rangle \langle B \rangle)\Psi \rangle$$

$$= \langle \Psi | \hat{A}\hat{B}\Psi \rangle - \langle B \rangle \langle \Psi | \hat{A}\Psi \rangle - \langle A \rangle \langle \Psi | \hat{B}\Psi \rangle + \langle A \rangle \langle B \rangle \langle \Psi | \Psi \rangle$$

$$= \langle \hat{A}\hat{B} \rangle - \langle B \rangle \langle A \rangle - \langle A \rangle \langle B \rangle + \langle A \rangle \langle B \rangle$$

$$= \langle \hat{A}\hat{B} \rangle - \langle A \rangle \langle B \rangle.$$

Similarly,

$$\langle g | f \rangle = \langle \hat{B}\hat{A} \rangle - \langle A \rangle \langle B \rangle,$$

so

$$\langle f|g \rangle - \langle g|f \rangle = \langle \hat{A}\hat{B} \rangle - \langle \hat{B}\hat{A} \rangle = \langle [\hat{A}, \hat{B}] \rangle,$$

where

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

is the commutator of the two operators (Equation 2.48). *Conclusion:*

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

[3.62]

This is the (generalized) **uncertainty principle**. You might think the i makes it trivial—isn't the right side *negative*? No, for the commutator of two hermitian operators carries its own factor of i, and the two cancel out.[17]

As an example, suppose the first observable is position ($\hat{A} = x$), and the second is momentum ($\hat{B} = (\hbar/i)d/dx$). We worked out their commutator back in Chapter 2 (Equation 2.51):

$$[\hat{x}, \hat{p}] = i\hbar.$$

So

$$\sigma_x^2 \sigma_p^2 \geq \left(\frac{1}{2i} i\hbar \right)^2 = \left(\frac{\hbar}{2} \right)^2,$$

or, since standard deviations are by their nature positive,

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}.$$

[3.63]

That's the original Heisenberg uncertainty principle, but we now see that it is just one application of a much more general theorem.

There is, in fact, an "uncertainty principle" for *every pair of observables whose operators do not commute*—we call them **incompatible observables**. Incompatible observables do not have shared eigenfunctions—at least, they cannot have a *complete set* of common eigenfunctions (see Problem 3.15). By contrast, *compatible* (commuting) observables *do* admit complete sets of simultaneous eigenfunctions.[18]

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[17]More precisely, the commutator of two hermitian operators is itself *anti*-hermitian ($\hat{Q}^\dagger = -\hat{Q}$), and its expectation value is imaginary (Problem 3.26).

[18]This corresponds to the fact that noncommuting matrices cannot be simultaneously diagonalized (that is, they cannot both be brought to diagonal form by the same similarity transformation), whereas commuting hermitian matrices *can* be simultaneously diagonalized. See Section A.5.

For example, in the hydrogen atom (as we shall see in Chapter 4) the Hamiltonian, the magnitude of the angular momentum, and the z component of angular momentum are mutually compatible observables, and we will construct simultaneous eigenfunctions of all three, labeled by their respective eigenvalues. But there is *no* eigenfunction of position that is also an eigenfunction of momentum, because these operators are *in*compatible.

Note that the uncertainty principle is not an *extra* assumption in quantum theory, but rather a *consequence* of the statistical interpretation. You might wonder how it is enforced in the laboratory—*why* can't you determine (say) both the position and the momentum of a particle? You can certainly measure the position of the particle, but the act of measurement collapses the wave function to a narrow spike, which necessarily carries a broad range of wavelengths (hence momenta) in its Fourier decomposition. If you now measure the momentum, the state will collapse to a long sinusoidal wave, with (now) a well-defined wavelength—but the particle no longer has the position you got in the first measurement.[19] The problem, then, is that the second measurement renders the outcome of the first measurement obsolete. Only if the wave function were simultaneously an eigenstate of both observables would it be possible to make the second measurement without disturbing the state of the particle (the second collapse wouldn't change anything, in that case). But this is only possible, in general, if the two observables are compatible.

∗Problem 3.13

(a) Prove the following commutator identity:

$$[AB, C] = A[B, C] + [A, C]B. \tag{3.64}$$

(b) Show that

$$[x^n, p] = i\hbar n x^{n-1}.$$

(c) Show more generally that

$$[f(x), p] = i\hbar \frac{df}{dx}, \tag{3.65}$$

for any function $f(x)$.

---

[19]Niels Bohr was at pains to track down the *mechanism* by which the measurement of x (for instance) destroys the previously existing value of p. The crux of the matter is that in order to determine the position of a particle you have to poke it with something—shine light on it, say. But these photons impart to the particle a momentum you cannot control. You now know the position, but you no longer know the momentum. His famous debates with Einstein include many delightful examples, showing in detail how experimental constraints enforce the uncertainty principle. For an inspired account see Bohr's article in *Albert Einstein: Philosopher-Scientist*, edited by P. A. Schilpp, Tudor, New York (1949).

∗Problem 3.14 Prove the famous "(your name) uncertainty principle," relating the uncertainty in position ($A = x$) to the uncertainty in energy ($B = p^2/2m + V$):

$$\sigma_x \sigma_H \geq \frac{\hbar}{2m}|\langle p \rangle|.$$

For stationary states this doesn't tell you much—why not?

Problem 3.15 Show that two noncommuting operators cannot have a complete set of common eigenfunctions. *Hint:* Show that if $\hat{P}$ and $\hat{Q}$ have a complete set of common eigenfunctions, then $[\hat{P}, \hat{Q}]f = 0$ for any function in Hilbert space.

3.5.2 The Minimum-Uncertainty Wave Packet

We have twice encountered wave functions that *hit* the position-momentum uncertainty limit ($\sigma_x \sigma_p = \hbar/2$): the ground state of the harmonic oscillator (Problem 2.11) and the Gaussian wave packet for the free particle (Problem 2.22). This raises an interesting question: What is the *most general* minimum-uncertainty wave packet? Looking back at the proof of the uncertainty principle, we note that there were two points at which *in*equalities came into the argument: Equation 3.59 and Equation 3.60. Suppose we require that each of these be an *equality*, and see what this tells us about Ψ.

The Schwarz inequality becomes an equality when one function is a multiple of the other: $g(x) = cf(x)$, for some complex number c (see Problem A.5). Meanwhile, in Equation 3.60 I threw away the real part of z; equality results if $\text{Re}(z) = 0$, which is to say, if $\text{Re}\langle f|g \rangle = \text{Re}(c\langle f|f \rangle) = 0$. Now, $\langle f|f \rangle$ is certainly real, so this means the constant c must be purely imaginary—let's call it ia. The necessary and sufficient condition for minimum uncertainty, then, is

$$g(x) = iaf(x), \quad \text{where } a \text{ is real.} \tag{3.66}$$

For the position-momentum uncertainty principle this criterion becomes:

$$\left(\frac{\hbar}{i}\frac{d}{dx} - \langle p \rangle\right)\Psi = ia(x - \langle x \rangle)\Psi. \tag{3.67}$$

which is a differential equation for Ψ as a function of x. Its general solution (Problem 3.16) is

$$\Psi(x) = Ae^{-a(x-\langle x \rangle)^2/2\hbar}e^{i\langle p \rangle x/\hbar}. \tag{3.68}$$

Evidently the minimum-uncertainty wave packet is a *gaussian*—and the two examples we encountered earlier *were* gaussians.[20]

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[20]Note that it is only the dependence of Ψ on x that is at issue here—the "constants" A, a, $\langle x \rangle$. and $\langle p \rangle$ may all be functions of time, and for that matter Ψ may evolve away from the minimal form. All I'm asserting is that if, at some instant. the wave function is gaussian in x. then (at that instant) the uncertainty product is minimal.

Problem 3.16 Solve Equation 3.67 for $\Psi(x)$. Note that $\langle x \rangle$ and $\langle p \rangle$ are *constants*.

3.5.3 The Energy-Time Uncertainty Principle

The position-momentum uncertainty principle is often written in the form

$$\Delta x \, \Delta p \geq \frac{\hbar}{2}; \tag{3.69}$$

Δx (the "uncertainty" in x) is loose notation (and sloppy language) for the standard deviation of the results of repeated measurements on identically prepared systems.[21] Equation 3.69 is often paired with the **energy-time uncertainty principle**,

$$\Delta t \, \Delta E \geq \frac{\hbar}{2}. \tag{3.70}$$

Indeed, in the context of special relativity the energy-time form might be thought of as a *consequence* of the position-momentum version, because x and t (or rather, ct) go together in the position-time four-vector, while p and E (or rather, E/c) go together in the energy-momentum four-vector. So in a relativistic theory Equation 3.70 would be a necessary concomitant to Equation 3.69. But we're not doing relativistic quantum mechanics. The Schrödinger equation is explicitly non-relativistic: It treats t and x on a very unequal footing (as a differential equation it is *first*-order in t, but *second*-order in x), and Equation 3.70 is emphatically *not* implied by Equation 3.69. My purpose now is to *derive* the energy-time uncertainty principle, and in the course of that derivation to persuade you that it is really an altogether different beast, whose superficial resemblance to the position-momentum uncertainty principle is actually quite misleading.

After all, position, momentum, and energy are all dynamical variables—measurable characteristics of the system, at any given time. But time itself is not a dynamical variable (not, at any rate, in a nonrelativistic theory): You don't go out and measure the "time" of a particle, as you might its position or its energy. Time is the *independent* variable, of which the dynamical quantities are *functions*. In particular, the Δt in the energy-time uncertainty principle is not the standard deviation of a collection of time measurements; roughly speaking (I'll make this more precise in a moment) it is the *time it takes the system to change substantially*.

---

[21] Many casual applications of the uncertainty principle are actually based (often inadvertently) on a completely different—and sometimes quite unjustified—measure of "uncertainty." Conversely, some perfectly rigorous arguments use other definitions of "uncertainty." See Jan Hilgevoord, *Am. J. Phys.* **70**, 983 (2002).

As a measure of how fast the system is changing, let us compute the time derivative of the expectation value of some observable, $Q(x, p, t)$:

$$\frac{d}{dt}\langle Q \rangle = \frac{d}{dt}\langle \Psi | \hat{Q}\Psi \rangle = \left\langle \frac{\partial \Psi}{\partial t} \bigg| \hat{Q}\Psi \right\rangle + \left\langle \Psi \bigg| \frac{\partial \hat{Q}}{\partial t} \Psi \right\rangle + \left\langle \Psi \bigg| \hat{Q}\frac{\partial \Psi}{\partial t} \right\rangle.$$

Now, the Schrödinger equation says

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

(where $H = p^2/2m + V$ is the Hamiltonian). So

$$\frac{d}{dt}\langle Q \rangle = -\frac{1}{i\hbar}\langle \hat{H}\Psi | \hat{Q}\Psi \rangle + \frac{1}{i\hbar}\langle \Psi | \hat{Q}\hat{H}\Psi \rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle.$$

But $\hat{H}$ is hermitian, so $\langle \hat{H}\Psi | \hat{Q}\Psi \rangle = \langle \Psi | \hat{H}\hat{Q}\Psi \rangle$, and hence

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

[3.71]

This is an interesting and useful result in its own right (see Problems 3.17 and 3.31). In the typical case where the operator does not depend explicitly on time,[22] it tells us that the rate of change of the expectation value is determined by the commutator of the operator with the Hamiltonian. In particular, if $\hat{Q}$ *commutes* with $\hat{H}$, then $\langle Q \rangle$ is constant, and in this sense Q is a *conserved* quantity.

Now, suppose we pick $A = H$ and $B = Q$, in the generalized uncertainty principle (Equation 3.62), and assume that Q does not depend explicitly on t:

$$\sigma_H^2 \sigma_Q^2 \geq \left(\frac{1}{2i}\langle [\hat{H}, \hat{Q}] \rangle\right)^2 = \left(\frac{1}{2i}\frac{\hbar}{i}\frac{d\langle Q \rangle}{dt}\right)^2 = \left(\frac{\hbar}{2}\right)^2 \left(\frac{d\langle Q \rangle}{dt}\right)^2.$$

Or, more simply,

$$\sigma_H \sigma_Q \geq \frac{\hbar}{2}\left|\frac{d\langle Q \rangle}{dt}\right|.$$

[3.72]

Let's define $\Delta E \equiv \sigma_H$, and

$$\Delta t \equiv \frac{\sigma_Q}{|d\langle Q \rangle/dt|}.$$

[3.73]

---

[22]Operators that depend explicitly on t are quite rare, so *almost always* $\partial \hat{Q}/\partial t = 0$. As an example of *explicit* time dependence, consider the potential energy of a harmonic oscillator whose spring constant is changing (perhaps the temperature is rising, so the spring becomes more flexible): $Q = (1/2)m[\omega(t)]^2 x^2$.

Then

$$\Delta E \, \Delta t \geq \frac{\hbar}{2},$$ [3.74]

and that's the energy-time uncertainty principle. But notice what is meant by Δt, here: Since

$$\sigma_Q = \left| \frac{d\langle Q \rangle}{dt} \right| \Delta t,$$

Δt represents the *amount of time it takes the expectation value of Q to change by one standard deviation.*[23] In particular, Δt depends entirely on what observable (Q) you care to look at—the change might be rapid for one observable and slow for another. But if ΔE is small, then the rate of change of *all* observables must be very gradual; or, to put it the other way around, if *any* observable changes rapidly, the "uncertainty" in the energy must be large.

Example 3.5 In the extreme case of a stationary state, for which the energy is uniquely determined, all expectation values are constant in time ($\Delta E = 0 \Rightarrow \Delta t = \infty$)—as in fact we noticed some time ago (see Equation 2.9). To make something *happen* you must take a linear combination of at least two stationary states—say:

$$\Psi(x, t) = a\psi_1(x)e^{-iE_1 t/\hbar} + b\psi_2(x)e^{-iE_2 t/\hbar}.$$

If a, b, ψ_1, and ψ_2 are real,

$$|\Psi(x, t)|^2 = a^2(\psi_1(x))^2 + b^2(\psi_2(x))^2 + 2ab\psi_1(x)\psi_2(x) \cos\left(\frac{E_2 - E_1}{\hbar} t \right).$$

The period of oscillation is $\tau = 2\pi\hbar/(E_2 - E_1)$. Roughly speaking, $\Delta E = E_2 - E_1$ and $\Delta t = \tau$ (for the *exact* calculation see Problem 3.18), so

$$\Delta E \, \Delta t = 2\pi\hbar,$$

which is indeed $\geq \hbar/2$.

Example 3.6 How long does it take a free-particle wave packet to pass by a particular point (Figure 3.1)? Qualitatively (an exact version is explored in Problem 3.19), $\Delta t = \Delta x/v = m\Delta x/p$, but $E = p^2/2m$, so $\Delta E = p\Delta p/m$. Therefore,

$$\Delta E \, \Delta t = \frac{p\Delta p}{m} \frac{m\Delta x}{p} = \Delta x \Delta p,$$

which is $\geq \hbar/2$ by the position-momentum uncertainty principle.

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[23]This is sometimes called the "Mandelstam-Tamm" formulation of the energy-time uncertainty principle. For a review of alternative approaches see Paul Busch, *Found. Phys.* **20**, 1 (1990).
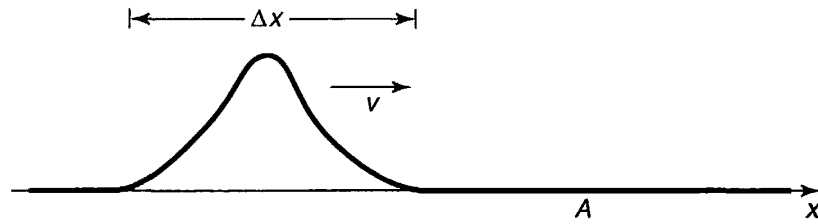
FIGURE 3.1:   A free particle wave packet approaches the point A (Example 3.6).

Example 3.7   The Δ particle lasts about 10^{-23} seconds, before spontaneously disintegrating. If you make a histogram of all measurements of its mass, you get a kind of bell-shaped curve centered at 1232 MeV/c^2, with a width of about 120 MeV/c^2 (Figure 3.2). Why does the rest energy (mc^2) sometimes come out higher than 1232, and sometimes lower? Is this experimental error? No, for

$$\Delta E\, \Delta t = \left(\frac{120}{2}\ \text{MeV} \right) (10^{-23}\ \text{sec}) = 6 \times 10^{-22}\ \text{MeV sec},$$

whereas $\hbar/2 = 3 \times 10^{-22}$ MeV sec. So the spread in m is about as small as the uncertainty principle allows—a particle with so short a lifetime just doesn't *have* a very well-defined mass.[24]
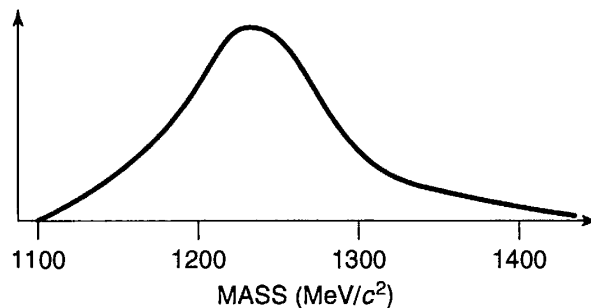

FIGURE 3.2:   Histogram of measurements of the Δ mass (Example 3.7).

[24] Actually, Example 3.7 is a bit of a fraud. You can't measure 10^{-23} sec on a stop-watch, and in practice the lifetime of such a short-lived particle is *inferred* from the width of the mass plot, using the uncertainty principle as *input*. However, the point is valid, even if the logic is backwards. Moreover, if you assume the Δ is about the same size as a proton ($\sim 10^{-15}$ m), then 10^{-23} sec is roughly the time it takes light to cross the particle, and it's hard to imagine that the lifetime could be much *less* than that.

Notice the variety of specific meanings attaching to the term Δt in these examples: In Example 3.5 it's a period of oscillation; in Example 3.6 it's the time it takes a particle to pass a point; in Example 3.7 it's the lifetime of an unstable particle. In every case, however, Δt is the time it takes for the system to undergo "substantial" change.

It is often said that the uncertainty principle means energy is not strictly conserved in quantum mechanics—that you're allowed to "borrow" energy ΔE, as long as you "pay it back" in a time $\Delta t \approx \hbar/(2\Delta E)$; the greater the violation, the briefer the period over which it can occur. Now, there are many legitimate readings of the energy-time uncertainty principle, but this is not one of them. Nowhere does quantum mechanics license violation of energy conservation, and certainly no such authorization entered into the derivation of Equation 3.74. But the uncertainty principle is extraordinarily robust: It can be misused without leading to seriously incorrect results, and as a consequence physicists are in the habit of applying it rather carelessly.

∗**Problem 3.17** Apply Equation 3.71 to the following special cases: (a) $Q = 1$; (b) $Q = H$; (c) $Q = x$; (d) $Q = p$. In each case, comment on the result, with particular reference to Equations 1.27, 1.33, 1.38, and conservation of energy (comments following Equation 2.39).

Problem 3.18 Test the energy-time uncertainty principle for the wave function in Problem 2.5 and the observable x, by calculating σ_H, σ_x, and $d\langle x \rangle/dt$ exactly.

Problem 3.19 Test the energy-time uncertainty principle for the free particle wave packet in Problem 2.43 and the observable x, by calculating σ_H, σ_x, and $d\langle x \rangle/dt$ exactly.

Problem 3.20 Show that the energy-time uncertainty principle reduces to the "your name" uncertainty principle (Problem 3.14), when the observable in question is x.

3.6 DIRAC NOTATION

Imagine an ordinary vector $\mathbf{A}$ in two dimensions (Figure 3.3(a)). How would you describe this vector to someone? The most convenient way is to set up cartesian axes, x and y, and specify the components of $\mathbf{A}$: $A_x = \hat{\imath} \cdot \mathbf{A}$, $A_y = \hat{\jmath} \cdot \mathbf{A}$ (Figure 3.3(b)). Of course, your sister might have drawn a different set of axes, x' and y', and she would report different components: $A'_x = \hat{\imath}' \cdot \mathbf{A}$, $A'_y = \hat{\jmath}' \cdot \mathbf{A}$ (Figure 3.3(c)). But it's all the same *vector*—we're simply expressing it with respect to two different *bases* ($\{\hat{\imath}, \hat{\jmath}\}$ and $\{\hat{\imath}', \hat{\jmath}'\}$). The vector itself lives "out there in space," independent of anybody's (arbitrary) choice of coordinates.
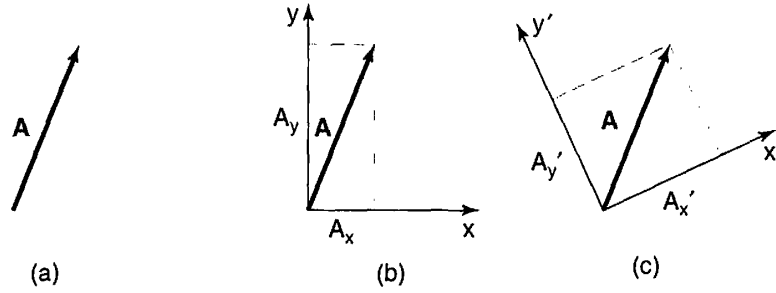
(a)   (b)   (c)

FIGURE 3.3: (a) Vector **A**. (b) Components of **A** with respect to xy axes. (c) Components of **A** with respect to $x'y'$ axes.

The same is true for the state of a system in quantum mechanics. It is represented by a *vector*, $|\mathcal{S}(t)\rangle$, that lives "out there in Hilbert space," but we can *express* it with respect to any number of different *bases*. The wave function $\Psi(x, t)$ is actually the coefficient in the expansion of $|\mathcal{S}\rangle$ in the basis of position eigenfunctions:

$$\Psi(x, t) = \langle x|\mathcal{S}(t)\rangle.$$
[3.75]

(with $|x\rangle$ standing for the eigenfunction of $\hat{x}$ with eigenvalue x),[25] whereas the momentum space wavefunction $\Phi(p, t)$ is the expansion of $|\mathcal{S}\rangle$ in the basis of momentum eigenfunctions:

$$\Phi(p, t) = \langle p|\mathcal{S}(t)\rangle$$
[3.76]

(with $|p\rangle$ standing for the eigenfunction of $\hat{p}$ with eigenvalue p).[26] Or we could expand $|\mathcal{S}\rangle$ in the basis of energy eigenfunctions (supposing for simplicity that the spectrum is discrete):

$$c_n(t) = \langle n|\mathcal{S}(t)\rangle$$
[3.77]

(with $|n\rangle$ standing for the nth eigenfunction of $\hat{H}$)—Equation 3.46. But it's all the same state; the functions Ψ and Φ, and the collection of coefficients $\{c_n\}$, contain exactly the same information—they are simply three different ways of describing the same vector:

$$\Psi(x, t) = \int \Psi(y, t)\delta(x - y)\, dy = \int \Phi(p, t)\frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}\, dp$$

$$= \sum c_n e^{-iE_n t/\hbar}\psi_n(x).$$
[3.78]

---

[25]I don't want to call it g_x (Equation 3.39), because that is its form in the position basis, and the whole point here is to free ourselves from any particular basis. Indeed, when I first defined Hilbert space as the set of square-integrable functions—over x—that was already too restrictive, committing us to a specific representation (the position basis). I want now to think of it as an abstract vector space, whose members can be expressed with respect to any basis you like.

[26]In position space it would be $f_p(x)$ (Equation 3.32).

Operators (representing observables) are linear transformations—they "transform" one vector into another:

$$|\beta\rangle = \hat{Q}|\alpha\rangle. \tag{3.79}$$

Just as vectors are represented, with respect to a particular basis $\{|e_n\rangle\}$,[27] by their components,

$$|\alpha\rangle = \sum_n a_n |e_n\rangle, \text{ with } a_n = \langle e_n|\alpha\rangle; \quad |\beta\rangle = \sum_n b_n |e_n\rangle, \text{ with } b_n = \langle e_n|\beta\rangle, \tag{3.80}$$

operators are represented (with respect to a particular basis) by their **matrix elements**[28]

$$\langle e_m|\hat{Q}|e_n\rangle \equiv Q_{mn}. \tag{3.81}$$

In this notation Equation 3.79 takes the form

$$\sum_n b_n |e_n\rangle = \sum_n a_n \hat{Q}|e_n\rangle, \tag{3.82}$$

or, taking the inner product with $|e_m\rangle$,

$$\sum_n b_n \langle e_m|e_n\rangle = \sum_n a_n \langle e_m|\hat{Q}|e_n\rangle. \tag{3.83}$$

and hence

$$b_m = \sum_n Q_{mn} a_n. \tag{3.84}$$

Thus the matrix elements tell you how the components transform.

Later on we will encounter systems that admit only a finite number (N) of linearly independent states. In that case $|\mathcal{S}(t)\rangle$ lives in an N-dimensional vector space; it can be represented as a column of (N) components (with respect to a given basis), and operators take the form of ordinary $(N \times N)$ matrices. These are the simplest quantum systems—none of the subtleties associated with infinite-dimensional vector spaces arise. Easiest of all is the two-state system, which we explore in the following example.

Example 3.8   Imagine a system in which there are just *two* linearly independent states:[29]

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

---

[27]I'll assume the basis is discrete; otherwise n becomes a continuous index and the sums are replaced by integrals.

[28]This terminology is inspired, obviously, by the finite-dimensional case, but the "matrix" will now typically have an infinite (maybe even uncountable) number of elements.

[29]Technically, the "equals" signs here mean "is represented by," but I don't think any confusion will arise if we adopt the customary informal notation.

The most general state is a normalized linear combination:

$$|\mathcal{S}\rangle = a|1\rangle + b|2\rangle = \begin{pmatrix} a \\ b \end{pmatrix}, \quad \text{with } |a|^2 + |b|^2 = 1.$$

The Hamiltonian can be expressed as a (hermitian) matrix; suppose it has the specific form

$$\mathbf{H} = \begin{pmatrix} h & g \\ g & h \end{pmatrix},$$

where g and h are real constants. If the system starts out (at $t = 0$) in state $|1\rangle$, what is its state at time t?

Solution: The (time-dependent) Schrödinger equation says

$$i\hbar \frac{d}{dt}|\mathcal{S}\rangle = H|\mathcal{S}\rangle. \tag{3.85}$$

As always, we begin by solving the time-*in*dependent Schrödinger equation:

$$H|\mathcal{s}\rangle = E|\mathcal{s}\rangle; \tag{3.86}$$

that is, we look for the eigenvectors and eigenvalues of H. The characteristic equation determines the eigenvalues:

$$\det \begin{pmatrix} h - E & g \\ g & h - E \end{pmatrix} = (h - E)^2 - g^2 = 0 \Rightarrow h - E = \mp g \Rightarrow E_\pm = h \pm g.$$

Evidently the allowed energies are $(h + g)$ and $(h - g)$. To determine the eigenvectors, we write

$$\begin{pmatrix} h & g \\ g & h \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = (h \pm g) \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \Rightarrow h\alpha + g\beta = (h \pm g)\alpha \Rightarrow \beta = \pm \alpha,$$

so the normalized eigenvectors are

$$|\mathcal{s}_\pm\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}.$$

Next we expand the initial state as a linear combination of eigenvectors of the Hamiltonian:

$$|\mathcal{S}(0)\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} (|\mathcal{s}_+\rangle + |\mathcal{s}_-\rangle).$$

Finally, we tack on the standard time-dependence $\exp(-iE_n t/\hbar)$:

$$|\mathcal{S}(t)\rangle = \frac{1}{\sqrt{2}} [e^{-i(h+g)t/\hbar} |\mathcal{s}_+\rangle + e^{-i(h-g)t/\hbar} |\mathcal{s}_-\rangle]$$

$$= \frac{1}{2} e^{-iht/\hbar} \left[e^{-igt/\hbar} \begin{pmatrix} 1 \\ 1 \end{pmatrix} + e^{igt/\hbar} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \right]$$

$$= \frac{1}{2} e^{-iht/\hbar} \begin{pmatrix} e^{-igt/\hbar} + e^{igt/\hbar} \\ e^{-igt/\hbar} - e^{igt/\hbar} \end{pmatrix} = e^{-iht/\hbar} \begin{pmatrix} \cos(gt/\hbar) \\ -i\sin(gt/\hbar) \end{pmatrix}.$$

If you doubt this result, by all means *check* it: Does it satisfy the time-dependent Schrödinger equation? Does it match the initial state when $t = 0$?

This is a crude model for (among other things) **neutrino oscillations**. In that case $|1\rangle$ represents the electron neutrino, and $|2\rangle$ the muon neutrino; if the Hamiltonian has a nonvanishing off-diagonal term (g) then in the course of time the electron neutrino will turn into a muon neutrino (and back again).

Dirac proposed to chop the bracket notation for the inner product, $\langle \alpha | \beta \rangle$, into two pieces, which he called **bra**, $\langle \alpha |$, and **ket**, $|\beta\rangle$ (I don't know what happened to the c). The latter is a vector, but what exactly is the former? It's a *linear function* of vectors, in the sense that when it hits a vector (to its right) it yields a (complex) number—the inner product. (When an *operator* hits a vector, it delivers another vector; when a *bra* hits a vector, it delivers a number.) In a function space, the bra can be thought of as an instruction to integrate:

$$\langle f| = \int f^* [\cdots] \, dx,$$

with the ellipsis $[\cdots]$ waiting to be filled by whatever function the bra encounters in the ket to its right. In a finite-dimensional vector space, with the vectors expressed as columns,

$$|\alpha\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}, \tag{3.87}$$

the corresponding bra is a row vector:

$$\langle \alpha | = \begin{pmatrix} a_1^* & a_2^* & \dots & a_n^* \end{pmatrix}. \tag{3.88}$$

The collection of all bras constitutes another vector space—the so-called **dual space**.

The license to treat bras as separate entities in their own right allows for some powerful and pretty notation (though I shall not exploit it in this book). For example, if $|\alpha\rangle$ is a normalized vector, the operator

$$\hat{P} \equiv |\alpha\rangle\langle\alpha| \tag{3.89}$$

picks out the portion of any other vector that "lies along" $|\alpha\rangle$:

$$\hat{P}|\beta\rangle = \langle\alpha|\beta\rangle|\alpha\rangle;$$

we call it the **projection operator** onto the one-dimensional subspace spanned by $|\alpha\rangle$. If $\{|e_n\rangle\}$ is a discrete orthonormal basis,

$$\langle e_m|e_n\rangle = \delta_{mn}, \qquad\qquad [3.90]$$

then

$$\sum_n |e_n\rangle\langle e_n| = 1 \qquad\qquad [3.91]$$

(the identity operator). For if we let this operator act on any vector $|\alpha\rangle$, we recover the expansion of $|\alpha\rangle$ in the $\{|e_n\rangle\}$ basis:

$$\sum_n |e_n\rangle\langle e_n|\alpha\rangle = |\alpha\rangle. \qquad\qquad [3.92]$$

Similarly, if $\{|e_z\rangle\}$ is a *Dirac* orthonormalized continuous basis,

$$\langle e_z|e_{z'}\rangle = \delta(z - z'), \qquad\qquad [3.93]$$

then

$$\int |e_z\rangle\langle e_z|\, dz = 1. \qquad\qquad [3.94]$$

Equations 3.91 and 3.94 are the tidiest ways to express completeness.

Problem 3.21 Show that projection operators are **idempotent**: $\hat{P}^2 = \hat{P}$. Determine the eigenvalues of $\hat{P}$, and characterize its eigenvectors.

Problem 3.22 Consider a three-dimensional vector space spanned by an orthonormal basis $|1\rangle$, $|2\rangle$, $|3\rangle$. Kets $|\alpha\rangle$ and $|\beta\rangle$ are given by

$$|\alpha\rangle = i|1\rangle - 2|2\rangle - i|3\rangle, \qquad |\beta\rangle = i|1\rangle + 2|3\rangle.$$

(a) Construct $\langle\alpha|$ and $\langle\beta|$ (in terms of the dual basis $\langle1|$, $\langle2|$, $\langle3|$).

(b) Find $\langle\alpha|\beta\rangle$ and $\langle\beta|\alpha\rangle$, and confirm that $\langle\beta|\alpha\rangle = \langle\alpha|\beta\rangle^*$.

(c) Find all nine matrix elements of the operator $\hat{A} \equiv |\alpha\rangle\langle\beta|$, in this basis, and construct the matrix **A**. Is it hermitian?

Problem 3.23 The Hamiltonian for a certain two-level system is

$$\hat{H} = \epsilon \left(|1\rangle\langle 1| - |2\rangle\langle 2| + |1\rangle\langle 2| + |2\rangle\langle 1| \right),$$

where $|1\rangle$, $|2\rangle$ is an orthonormal basis and ϵ is a number with the dimensions of energy. Find its eigenvalues and eigenvectors (as linear combinations of $|1\rangle$ and $|2\rangle$). What is the matrix **H** representing $\hat{H}$ with respect to this basis?

Problem 3.24 Let $\hat{Q}$ be an operator with a complete set of orthonormal eigenvectors:

$$\hat{Q}|e_n\rangle = q_n|e_n\rangle \quad (n = 1, 2, 3, \ldots).$$

Show that $\hat{Q}$ can be written in terms of its **spectral decomposition**:

$$\hat{Q} = \sum_n q_n|e_n\rangle\langle e_n|.$$

Hint: An operator is characterized by its action on all possible vectors, so what you must show is that

$$\hat{Q}|\alpha\rangle = \left\{ \sum_n q_n|e_n\rangle\langle e_n| \right\} |\alpha\rangle,$$

for any vector $|\alpha\rangle$.

FURTHER PROBLEMS FOR CHAPTER 3

Problem 3.25 Legendre polynomials. Use the Gram-Schmidt procedure (Problem A.4) to orthonormalize the functions 1, x, x^2, and x^3, on the interval $-1 \leq x \leq 1$. You may recognize the results—they are (apart from the normalization)[30] **Legendre polynomials** (Table 4.1).

Problem 3.26 An **anti-hermitian** (or **skew-hermitian**) operator is equal to *minus* its hermitian conjugate:

$$\hat{Q}^\dagger = -\hat{Q}. \tag{3.95}$$

(a) Show that the expectation value of an anti-hermitian operator is imaginary.

(b) Show that the commutator of two hermitian operators is anti-hermitian. How about the commutator of two *anti*-hermitian operators?

---

[30]Legendre didn't know what the best convention would be: he picked the overall factor so that all his functions would go to 1 at $x = 1$. and we're stuck with his unfortunate choice.

Problem 3.27 Sequential measurements. An operator $\hat{A}$, representing observable A, has two normalized eigenstates ψ_1 and ψ_2, with eigenvalues a_1 and a_2, respectively. Operator $\hat{B}$, representing observable B, has two normalized eigenstates ϕ_1 and ϕ_2, with eigenvalues b_1 and b_2. The eigenstates are related by

$$\psi_1 = (3\phi_1 + 4\phi_2)/5, \quad \psi_2 = (4\phi_1 - 3\phi_2)/5.$$

(a) Observable A is measured, and the value a_1 is obtained. What is the state of the system (immediately) after this measurement?

(b) If B is now measured, what are the possible results, and what are their probabilities?

(c) Right after the measurement of B, A is measured again. What is the probability of getting a_1? (Note that the answer would be quite different if I had told you the outcome of the B measurement.)

＊＊**Problem 3.28** Find the momentum-space wave function $\Phi_n(p, t)$ for the nth stationary state of the infinite square well. Graph $|\Phi_1(p, t)|^2$ and $|\Phi_2(p, t)|^2$, as functions of p (pay particular attention to the points $p = \pm n\pi\hbar/a$). Use $\Phi_n(p, t)$ to calculate the expectation value of p^2. Compare your answer to Problem 2.4.

Problem 3.29 Consider the wave function

$$\Psi(x, 0) = \begin{cases} \dfrac{1}{\sqrt{2n\lambda}} e^{i2\pi x/\lambda}, & -n\lambda < x < n\lambda, \\ 0, & \text{otherwise,} \end{cases}$$

where n is some positive integer. This function is purely sinusoidal (with wavelength λ) on the interval $-n\lambda < x < n\lambda$, but it still carries a *range* of momenta, because the oscillations do not continue out to infinity. Find the momentum space wave function $\Phi(p, 0)$. Sketch the graphs of $|\Psi(x, 0)|^2$ and $|\Phi(p, 0)|^2$, and determine their widths, w_x and w_p (the distance between zeros on either side of the main peak). Note what happens to each width as $n \to \infty$. Using w_x and w_p as estimates of Δx and Δp, check that the uncertainty principle is satisfied. *Warning:* If you try calculating σ_p, you're in for a rude surprise. Can you diagnose the problem?

Problem 3.30 Suppose

$$\Psi(x, 0) = \frac{A}{x^2 + a^2}. \quad (-\infty < x < \infty)$$

for constants A and a.

(a) Determine A, by normalizing $\Psi(x, 0)$.

(b) Find $\langle x \rangle$, $\langle x^2 \rangle$, and σ_x (at time $t = 0$).

(c) Find the momentum space wave function $\Phi(p, 0)$, and check that it is normalized.

(d) Use $\Phi(p, 0)$ to calculate $\langle p \rangle$, $\langle p^2 \rangle$, and σ_p (at time $t = 0$).

(e) Check the Heisenberg uncertainty principle for this state.

---

*Problem 3.31 **Virial theorem.** Use Equation 3.71 to show that

$$\frac{d}{dt}\langle xp \rangle = 2\langle T \rangle - \left\langle x\frac{dV}{dx} \right\rangle. \qquad [3.96]$$

where T is the kinetic energy ($H = T + V$). In a *stationary* state the left side is zero (why?) so

$$2\langle T \rangle = \left\langle x\frac{dV}{dx} \right\rangle. \qquad [3.97]$$

This is called the **virial theorem.** Use it to prove that $\langle T \rangle = \langle V \rangle$ for stationary states of the harmonic oscillator, and check that this is consistent with the results you got in Problems 2.11 and 2.12.

Problem 3.32 In an interesting version of the energy-time uncertainty principle[31] $\Delta t = \tau/\pi$, where τ is the time it takes $\Psi(x, t)$ to evolve into a state orthogonal to $\Psi(x, 0)$. Test this out, using a wave function that is an equal admixture of two (orthonormal) stationary states of some (arbitrary) potential: $\Psi(x, 0) = (1/\sqrt{2})[\psi_1(x) + \psi_2(x)]$.

Problem 3.33 Find the matrix elements $\langle n|x|n' \rangle$ and $\langle n|p|n' \rangle$ in the (orthonormal) basis of stationary states for the harmonic oscillator (Equation 2.67). You already calculated the "diagonal" elements ($n = n'$) in Problem 2.12; use the same technique for the general case. Construct the corresponding (infinite) matrices, **X** and **P**. Show that $(1/2m)\mathbf{P}^2 + (m\omega^2/2)\mathbf{X}^2 = \mathbf{H}$ is *diagonal*, in this basis. Are its diagonal elements what you would expect? *Partial answer:*

$$\langle n|x|n' \rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n'}\delta_{n,n'-1} + \sqrt{n}\delta_{n',n-1}\right). \qquad [3.98]$$

---

[31] See Lev Vaidman, *Am. J. Phys.* **60.** 182 (1992) for a proof.

Problem 3.34 A harmonic oscillator is in a state such that a measurement of the energy would yield either $(1/2)\hbar\omega$ or $(3/2)\hbar\omega$, with equal probability. What is the largest possible value of $\langle p \rangle$ in such a state? If it assumes this maximal value at time $t = 0$, what is $\Psi(x, t)$?

∗ ∗ ∗Problem 3.35 Coherent states of the harmonic oscillator. Among the stationary states of the harmonic oscillator ($|n\rangle = \psi_n(x)$, Equation 2.67) only $n = 0$ hits the uncertainty limit ($\sigma_x\sigma_p = \hbar/2$); in general, $\sigma_x\sigma_p = (2n + 1)\hbar/2$, as you found in Problem 2.12. But certain *linear combinations* (known as **coherent states**) also minimize the uncertainty product. They are (as it turns out) *eigenfunctions of the lowering operator*:[32]

$$a_- |\alpha\rangle = \alpha |\alpha\rangle$$

(the eigenvalue α can be any complex number).

(a) Calculate $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$, $\langle p^2 \rangle$ in the state $|\alpha\rangle$. *Hint:* Use the technique in Example 2.5, and remember that a_+ is the hermitian conjugate of a_-. Do *not* assume α is real.

(b) Find σ_x and σ_p; show that $\sigma_x\sigma_p = \hbar/2$.

(c) Like any other wave function, a coherent state can be expanded in terms of energy eigenstates:

$$|\alpha\rangle = \sum_{n=0}^{\infty} c_n |n\rangle.$$

Show that the expansion coefficients are

$$c_n = \frac{\alpha^n}{\sqrt{n!}} c_0.$$

(d) Determine c_0 by normalizing $|\alpha\rangle$. *Answer:* $\exp(-|\alpha|^2/2)$.

(e) Now put in the time dependence:

$$|n\rangle \rightarrow e^{-iE_n t/\hbar} |n\rangle,$$

and show that $|\alpha(t)\rangle$ remains an eigenstate of a_-, but the eigen*value* evolves in time:

$$\alpha(t) = e^{-i\omega t}\alpha.$$

So a coherent state *stays* coherent, and continues to minimize the uncertainty product.

---

[32]There are no normalizable eigenfunctions of the *raising* operator.

(f) Is the ground state ($|n = 0\rangle$) itself a coherent state? If so, what is the eigenvalue?

Problem 3.36 Extended uncertainty principle.[33] The generalized uncertainty principle (Equation 3.62) states that

$$\sigma_A^2 \sigma_B^2 \geq \frac{1}{4}\langle C \rangle^2,$$

where $\hat{C} \equiv -i[\hat{A}, \hat{B}]$.

(a) Show that it can be strengthened to read

$$\sigma_A^2 \sigma_B^2 \geq \frac{1}{4}(\langle C \rangle^2 + \langle D \rangle^2), \qquad [3.99]$$

where $\hat{D} \equiv \hat{A}\hat{B} + \hat{B}\hat{A} - 2\langle A \rangle\langle B \rangle$. *Hint:* Keep the Re($z$) term in Equation 3.60.

(b) Check Equation 3.99 for the case $B = A$ (the standard uncertainty principle is trivial, in this case, since $\hat{C} = 0$; unfortunately, the extended uncertainty principle doesn't help much either).

Problem 3.37 The Hamiltonian for a certain three-level system is represented by the matrix

$$\mathbf{H} = \begin{pmatrix} a & 0 & b \\ 0 & c & 0 \\ b & 0 & a \end{pmatrix},$$

where a, b, and c are real numbers (assume $a - c \neq \pm b$).

(a) If the system starts out in the state

$$|\mathcal{S}(0)\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix},$$

what is $|\mathcal{S}(t)\rangle$?

(b) If the system starts out in the state

$$|\mathcal{S}(0)\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix},$$

what is $|\mathcal{S}(t)\rangle$?

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[33]For interesting commentary and references, see R. R. Puri, *Phys. Rev. A* **49**, 2178 (1994).

Problem 3.38 The Hamiltonian for a certain three-level system is represented by the matrix

$$\mathbf{H} = \hbar\omega \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}.$$

Two other observables, A and B, are represented by the matrices

$$\mathbf{A} = \lambda \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \quad \mathbf{B} = \mu \begin{pmatrix} 2 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix},$$

where ω, λ, and μ are positive real numbers.

(a) Find the eigenvalues and (normalized) eigenvectors of **H**, **A**, and **B**.

(b) Suppose the system starts out in the generic state

$$|\mathcal{S}(0)\rangle = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix},$$

with $|c_1|^2 + |c_2|^2 + |c_3|^2 = 1$. Find the expectation values (at $t = 0$) of H, A, and B.

(c) What is $|\mathcal{S}(t)\rangle$? If you measured the energy of this state (at time t), what values might you get, and what is the probability of each? Answer the same questions for A and for B.

★★Problem 3.39

(a) For a function $f(x)$ that can be expanded in a Taylor series, show that

$$f(x + x_0) = e^{i\hat{p}x_0/\hbar} f(x)$$

(where x_0 is any constant distance). For this reason, $\hat{p}/\hbar$ is called the **generator of translations in space**. *Note:* The exponential of an *operator* is defined by the power series expansion: $e^{\hat{Q}} \equiv 1 + \hat{Q} + (1/2)\hat{Q}^2 + (1/3!)\hat{Q}^3 + \ldots$.

(b) If $\Psi(x, t)$ satisfies the (time-dependent) Schrödinger equation, show that

$$\Psi(x, t + t_0) = e^{-i\hat{H}t_0/\hbar}\Psi(x, t)$$

(where t_0 is any constant time); $-\hat{H}/\hbar$ is called the **generator of translations in time**.

(c) Show that the expectation value of a dynamical variable $Q(x, p, t)$, at time $t + t_0$, can be written[34]

$$\langle Q \rangle_{t+t_0} = \langle \Psi(x, t) | e^{i\hat{H}t_0/\hbar} \hat{Q}(\hat{x}, \hat{p}, t + t_0) e^{-i\hat{H}t_0/\hbar} | \Psi(x, t) \rangle.$$

Use this to recover Equation 3.71. *Hint:* Let $t_0 = dt$, and expand to first order in dt.

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* *Problem 3.40

(a) Write down the time-dependent "Schrödinger equation" in momentum space, for a free particle, and solve it. *Answer:* $\exp(-ip^2 t/2m\hbar) \Phi(p, 0)$.

(b) Find $\Phi(p, 0)$ for the traveling gaussian wave packet (Problem 2.43), and construct $\Phi(p, t)$ for this case. Also construct $|\Phi(p, t)|^2$, and note that it is independent of time.

(c) Calculate $\langle p \rangle$ and $\langle p^2 \rangle$ by evaluating the appropriate integrals involving Φ, and compare your answers to Problem 2.43.

(d) Show that $\langle H \rangle = \langle p \rangle^2/2m + \langle H \rangle_0$ (where the subscript 0 denotes the *stationary* gaussian), and comment on this result.

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[34] In particular, if we set $t = 0$. and drop the subscript on t_0,

$$\langle Q(t) \rangle = \langle \Psi(x, t) | \hat{Q} | \Psi(x, t) \rangle = \langle \Psi(x, 0) | \hat{U}^{-1} \hat{Q} \hat{U} | \Psi(x, 0) \rangle.$$

where $\hat{U} \equiv \exp(-i\hat{H}t/\hbar)$. This says that you can calculate expectation values of Q *either* by sandwiching $\hat{Q}$ between $\Psi(x, t)^*$ and $\Psi(x, t)$. as we have always done (letting the wave functions carry the time dependence). or *else* by sandwiching $\hat{U}^{-1} \hat{Q} \hat{U}$ between $\Psi(x, 0)^*$ and $\Psi(x, 0)$. letting the operator carry the time dependence. The former is called the **Schrödinger picture**. and the latter the **Heisenberg picture**.