

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,

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

for a specified potential¹ $V(x, t)$. 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 *products*,

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

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 obtain more than a tiny subset of all solutions in this way. But hang on, because the solutions we *do* get 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 $\psi\varphi$:

$$i\hbar \frac{1}{\varphi} \frac{d\varphi}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2 \psi}{dx^2} + V. \quad (2.3)$$

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

$$\frac{d\varphi}{dt} = -\frac{iE}{\hbar} \varphi, \quad (2.4)$$

and

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

or

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi.} \quad (2.5)$$

Separation of variables has turned a *partial* differential equation into two *ordinary* differential equations (Equations 2.4 and 2.5). The first of these 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 $\psi\varphi$). Then³

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

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 dependent) 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,

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

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

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

does *not*—the time-dependence cancels out.⁴ The same thing happens in calculating the expectation value of any dynamical variable; Equation 1.36 reduces to

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

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 time-dependent wiggle 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**:

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

The corresponding Hamiltonian *operator*, obtained by the canonical substitution $p \rightarrow -i\hbar(\partial/\partial x)$, is therefore⁵

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

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

$$\hat{H}\psi = E\psi, \quad (2.12)$$

and the expectation value of the total energy is

$$\langle H \rangle = \int \psi^* \hat{H} \psi dx = E \int |\psi|^2 dx = E \int |\Psi|^2 dx = E. \quad (2.13)$$

(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

$$\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = E^2 - E^2 = 0. \quad (2.14)$$

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 $(\psi_1(x), \psi_2(x), \psi_3(x), \dots)$, which we write as $\{\psi_n(x)\}$, each with its associated separation constant $(E_1, E_2, E_3, \dots = \{E_n\})$; thus there is a different wave function for each **allowed energy**:

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

Now (as you can easily check for yourself) the (time-dependent) Schrödinger equation (Equation 2.1) has the property that any linear combination⁶ of solutions is itself a solution. Once we have found the separable solutions, then, we can immediately construct a much more general solution, of the form

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

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 $(c_1, c_2, \dots)$ 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-independent Schrödinger equation, you're essentially *done*; getting from there

to the general solution of the time-*dependent* Schrödinger equation is, in principle, simple and straightforward.

A lot has happened in the past 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 is first to solve the time-*independent* Schrödinger equation (Equation 2.5); this yields, in general, an infinite set of solutions, $\{\psi_n(x)\}$, each with its own associated energy, $\{E_n\}$. To fit $\Psi(x, 0)$ you write down the general linear combination of these solutions:

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

the miracle is that you can *always* match the specified initial state⁷ by appropriate choice of the constants $\{c_n\}$. To construct $\Psi(x, t)$ you simply tack onto each term its characteristic time dependence (its “wobble factor”), $\exp(-i E_n t / \hbar)$:⁸

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

The separable solutions themselves,

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

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 construct $|\Psi|^2$.

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

$$\begin{aligned} |\Psi(x, t)|^2 &= (c_1 \psi_1 e^{i E_1 t / \hbar} + c_2 \psi_2 e^{i E_2 t / \hbar}) (c_1 \psi_1 e^{-i E_1 t / \hbar} + c_2 \psi_2 e^{-i E_2 t / \hbar}) \\ &= c_1^2 \psi_1^2 + c_2^2 \psi_2^2 + 2c_1 c_2 \psi_1 \psi_2 \cos[(E_2 - E_1)t / \hbar]. \end{aligned}$$

The probability density *oscillates* sinusoidally, at an angular frequency $\omega = (E_2 - E_1) / \hbar$; this is certainly *not* a stationary state. But notice that it took a *linear combination* of stationary states (with

different energies) to produce motion.⁹

You may be wondering what the coefficients $\{c_n\}$ represent *physically*. I'll tell you the answer, though the explanation will have to await Chapter 3:

$|c_n|^2$ is the *probability* that a measurement of the energy would return the value E_n .

(2.19)

A competent measurement will always yield *one* of the “allowed” values (hence the name), and $|c_n|^2$ is the probability of getting the *particular* value E_n .¹⁰ Of course, the *sum* of these probabilities should be 1:

$$\sum_{n=1}^{\infty} |c_n|^2 = 1,$$

(2.20)

and the expectation value of the energy must be

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

(2.21)

We'll soon see how this works out in some concrete examples. Notice, finally, that because the constants $\{c_n\}$ are independent of time, so too is the probability of getting a particular energy, and, *a fortiori*, the expectation value of H . These are manifestations of **energy conservation** in quantum mechanics.

- * **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 $i(\psi - \psi^*)$.
 - (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

$$V(x) = \begin{cases} 0, & 0 \leq x \leq a, \\ \infty, & \text{otherwise} \end{cases} \quad (2.22)$$

(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.)

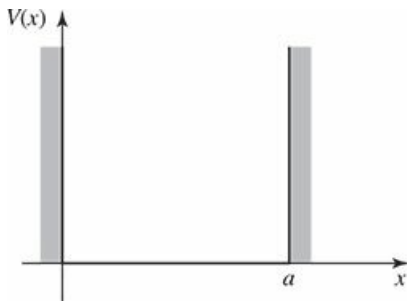


Figure 2.1: The infinite square well potential (Equation 2.22).

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

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi, \quad (2.23)$$

or

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}. \quad (2.24)$$

(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 2.24 is the classical **simple harmonic oscillator** equation; the general solution is

$$\psi(x) = A \sin kx + B \cos kx, \quad (2.25)$$

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*,¹¹ but where the potential goes to infinity only the first of these applies. (I'll *justify* 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

$$\psi(0) = \psi(a) = 0, \quad (2.26)$$

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

$$\psi(x) = A \sin kx. \quad (2.27)$$

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

$$ka = 0, \pm\pi, \pm2\pi, \pm3\pi, \dots \quad (2.28)$$

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

$$k_n = \frac{n\pi}{a}, \quad \text{with } n = 1, 2, 3, \dots \quad (2.29)$$

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 :

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}. \quad (2.30)$$

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.¹² To find A , we *normalize* ψ :¹³

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

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

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right). \quad (2.31)$$

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.¹⁴
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 that¹⁵

$$\int \psi_m(x)^* \psi_n(x) dx = 0, \quad (m \neq n). \quad (2.32)$$

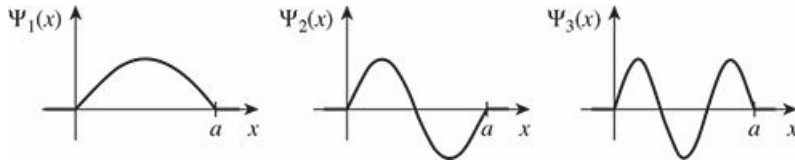


Figure 2.2: The first three stationary states of the infinite square well (Equation 2.31).

Proof:

$$\begin{aligned}
 \int \psi_m(x)^* \psi_n(x) dx &= \frac{2}{a} \int_0^a \sin\left(\frac{m\pi}{a}x\right) \sin\left(\frac{n\pi}{a}x\right) dx \\
 &= \frac{1}{a} \int_0^a \left[\cos\left(\frac{m-n}{a}\pi x\right) - \cos\left(\frac{m+n}{a}\pi x\right) \right] dx \\
 &= \left\{ \frac{1}{(m-n)\pi} \sin\left(\frac{m-n}{a}\pi x\right) - \frac{1}{(m+n)\pi} \sin\left(\frac{m+n}{a}\pi x\right) \right\} \Big|_0^a \\
 &= \frac{1}{\pi} \left\{ \frac{\sin[(m-n)\pi]}{(m-n)} - \frac{\sin[(m+n)\pi]}{(m+n)} \right\} = 0.
 \end{aligned}$$

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:

$$\boxed{\int \psi_m(x)^* \psi_n(x) dx = \delta_{mn}}, \quad (2.33)$$

where δ_{mn} (the so-called **Kronecker delta**) is defined by

$$\delta_{mn} = \begin{cases} 0, & m \neq n, \\ 1, & m = n. \end{cases} \quad (2.34)$$

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:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right). \quad (2.35)$$

I'm not about to *prove* the completeness of the functions $\sqrt{2/a} \sin(n\pi x/a)$, but if you've studied advanced calculus you will recognize that Equation 2.35 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**.¹⁶

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

$$\int \psi_m(x)^* f(x) dx = \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x) dx = \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m. \quad (2.36)$$

(Notice how the Kronecker delta kills every term in the sum except the one for which $n = m$.) Thus the n th coefficient in the expansion of $f(x)$ is¹⁷

$$c_n = \int \psi_n(x)^* f(x) dx. \quad (2.37)$$

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.¹⁸ 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

$$\Psi_n(x, t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}. \quad (2.38)$$

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

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}. \quad (2.39)$$

(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:

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x, 0) dx. \quad (2.40)$$

That *does* it: Given the initial wave function, $\Psi(x, 0)$, we first compute the expansion coefficients c_n , using Equation 2.40, and then plug these into Equation 2.39 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

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

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

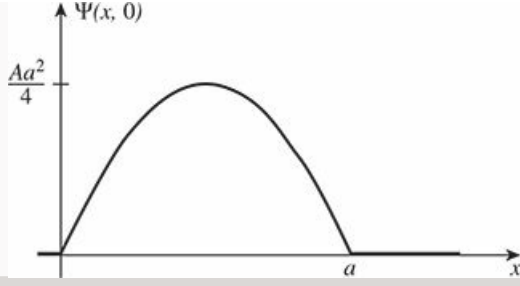


Figure 2.3: The starting wave function in Example 2.2.

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 n th coefficient is (Equation 2.40)

$$\begin{aligned} c_n &= \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \sqrt{\frac{30}{a^5}} x(a-x) dx \\ &= \frac{2\sqrt{15}}{a^3} \left[a \int_0^a x \sin\left(\frac{n\pi}{a}x\right) dx - \int_0^a x^2 \sin\left(\frac{n\pi}{a}x\right) dx \right] \\ &= \frac{2\sqrt{15}}{a^3} \left\{ a \left[\left(\frac{a}{n\pi}\right)^2 \sin\left(\frac{n\pi}{a}x\right) - \frac{ax}{n\pi} \cos\left(\frac{n\pi}{a}x\right) \right] \Big|_0^a \right. \\ &\quad \left. - \left[2 \left(\frac{a}{n\pi}\right)^2 x \sin\left(\frac{n\pi}{a}x\right) - \frac{(n\pi x/a)^2 - 2}{(n\pi/a)^3} \cos\left(\frac{n\pi}{a}x\right) \right] \Big|_0^a \right\} \\ &= \frac{2\sqrt{15}}{a^3} \left[-\frac{a^3}{n\pi} \cos(n\pi) + a^3 \frac{(n\pi)^2 - 2}{(n\pi)^3} \cos(n\pi) + a^3 \frac{2}{(n\pi)^3} \cos(0) \right] \\ &= \frac{4\sqrt{15}}{(n\pi)^3} [\cos(0) - \cos(n\pi)] \\ &= \begin{cases} 0, & n \text{ even,} \\ 8\sqrt{15}/(n\pi)^3, & n \text{ odd.} \end{cases} \end{aligned}$$

Thus (Equation 2.39):

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

Example 2.3

Check that Equation 2.20 is satisfied, for the wave function in Example 2.2. If you measured the energy of a particle in this state, what is the most probable result? What is the expectation value of the energy?

Solution: 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,¹⁹ and in fact

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

The rest of the coefficients make up the difference:²⁰

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

The most likely outcome of an energy measurement is $E_1 = \pi^2 \hbar^2 / 2ma^2$ —more than 99.8% of all measurements will yield this value. The expectation value of the energy (Equation 2.21) is

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

As one would expect, it is very close to E_1 (5 in place of $\pi^2/2 \approx 4.935$)—slightly *larger*, because of the admixture of excited states.

Of course, it's no accident that Equation 2.20 came out right in Example 2.3. 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).

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

(Again, the Kronecker delta picks out the term $m = n$ in the summation over m .) Similarly, the expectation value of the energy (Equation 2.21) can be checked explicitly: The time-independent Schrödinger equation (Equation 2.12) says

$$\hat{H} \psi_n = E_n \psi_n, \tag{2.41}$$

so

$$\begin{aligned}\langle H \rangle &= \int \Psi^* \hat{H} \Psi dx = \int \left(\sum c_m \psi_m \right)^* \hat{H} \left(\sum c_n \psi_n \right) dx \\ &= \sum \sum c_m^* c_n E_n \int \psi_m^* \psi_n dx = \sum |c_n|^2 E_n.\end{aligned}$$

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 satisfy 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 n th 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:

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

- (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 9 of this chapter.)

*

Problem 2.7 A particle in the infinite square well has the initial wave function

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

- Sketch $\Psi(x, 0)$, and determine the constant A .
- Find $\Psi(x, t)$.
- What is the probability that a measurement of the energy would yield the value E_1 ?
- Find the expectation value of the energy, using Equation 2.21.²¹

Problem 2.8 A particle of mass m in the infinite square well (of width a) starts out in the state

$$\Psi(x, 0) = \begin{cases} A, & 0 \leq x \leq a/2, \\ 0, & a/2 \leq x \leq a, \end{cases}$$

for some constant A , so it is (at $t = 0$) equally likely to be found at any point in the left half of the well. What is the probability that a measurement of the energy (at some later time t) 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 we got 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

$$\omega \equiv \sqrt{\frac{k}{m}} \tag{2.42}$$

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

$$V(x) = \frac{1}{2}kx^2; \tag{2.43}$$

its graph is a parabola.

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:

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

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

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

which describes simple harmonic oscillation (about the point x_0), with an effective spring constant $k = V''(x_0)$. 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.²²

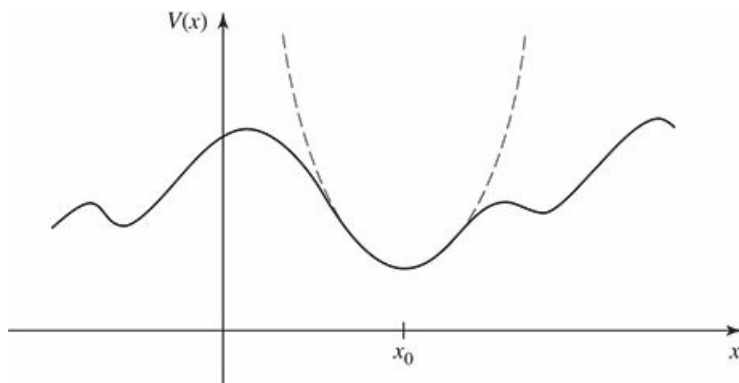


Figure 2.4: Parabolic approximation (dashed curve) to an arbitrary potential, in the neighborhood of a local minimum.

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

$$V(x) = \frac{1}{2}m\omega^2 x^2 \quad (2.44)$$

(it is customary to eliminate the spring constant in favor of the classical frequency, using Equation 2.42). As we have seen, it suffices to solve the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi. \quad (2.45)$$

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 hydrogen atom). 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);²³ 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 2.45 in a more suggestive form:

$$\frac{1}{2m} \left[\hat{p}^2 + (m\omega x)^2 \right] \psi = E\psi, \quad (2.46)$$

where $\hat{p} \equiv -i\hbar d/dx$ is the momentum operator.²⁴ The basic idea is to *factor* the Hamiltonian,

$$\hat{H} = \frac{1}{2m} \left[\hat{p}^2 + (m\omega x)^2 \right]. \quad (2.47)$$

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 $\hat{p}$ and x are *operators*, and operators do not, in general, **commute** ($x\hat{p}$ is not the same as $\hat{p}x$, as we'll see in a moment—though you might want to stop right now and think it through for yourself). Still, this does motivate us to examine the quantities

$$\hat{a}_{\pm} \equiv \frac{1}{\sqrt{2\hbar m\omega}} (\mp i\hat{p} + m\omega x) \quad (2.48)$$

(the factor in front is just there to make the final results look nicer).

Well, what *is* the product $\hat{a}_-\hat{a}_+$?

$$\begin{aligned} \hat{a}_-\hat{a}_+ &= \frac{1}{2\hbar m\omega} (i\hat{p} + m\omega x)(-i\hat{p} + m\omega x) \\ &= \frac{1}{2\hbar m\omega} \left[\hat{p}^2 + (m\omega x)^2 - im\omega (x\hat{p} - \hat{p}x) \right]. \end{aligned}$$

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

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}. \quad (2.49)$$

In this notation,

$$\hat{a}_-\hat{a}_+ = \frac{1}{2\hbar m\omega} \left[\hat{p}^2 + (m\omega x)^2 \right] - \frac{i}{2\hbar} [x, \hat{p}]. \quad (2.50)$$

We need to figure out the commutator of x and $\hat{p}$. *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:

$$\begin{aligned} [x, \hat{p}] f(x) &= \left[x(-i\hbar) \frac{d}{dx}(f) - (-i\hbar) \frac{d}{dx}(xf) \right] = -i\hbar \left(x \frac{df}{dx} - x \frac{df}{dx} - f \right) \\ &= i\hbar f(x). \end{aligned} \quad (2.51)$$

Dropping the test function, which has served its purpose,

$$\boxed{[x, \hat{p}] = i\hbar.} \quad (2.52)$$

This lovely and ubiquitous formula is known as the **canonical commutation relation**.²⁵

With this, Equation 2.50 becomes

$$\hat{a}_- \hat{a}_+ = \frac{1}{\hbar\omega} \hat{H} + \frac{1}{2}, \quad (2.53)$$

or

$$\hat{H} = \hbar\omega \left(\hat{a}_- \hat{a}_+ - \frac{1}{2} \right). \quad (2.54)$$

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

$$\hat{a}_+ \hat{a}_- = \frac{1}{\hbar\omega} \hat{H} - \frac{1}{2}. \quad (2.55)$$

In particular,

$$[\hat{a}_-, \hat{a}_+] = 1. \quad (2.56)$$

Meanwhile, the Hamiltonian can equally well be written

$$\hat{H} = \hbar\omega \left(\hat{a}_+ \hat{a}_- + \frac{1}{2} \right). \quad (2.57)$$

In terms of $\hat{a}_\pm$, then, the Schrödinger equation²⁶ for the harmonic oscillator takes the form

$$\hbar\omega \left(\hat{a}_\pm \hat{a}_\mp \pm \frac{1}{2} \right) \psi = E \psi \quad (2.58)$$

(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: $\hat{H}\psi = E\psi$), then $\hat{a}_+\psi$ satisfies the Schrödinger equation with energy $(E + \hbar\omega)$: $\hat{H}(\hat{a}_+\psi) = (E + \hbar\omega)(\hat{a}_+\psi)$.

Proof:

$$\begin{aligned} \hat{H}(\hat{a}_+\psi) &= \hbar\omega \left(\hat{a}_+ \hat{a}_- + \frac{1}{2} \right) (\hat{a}_+\psi) = \hbar\omega \left(\hat{a}_+ \hat{a}_- \hat{a}_+ + \frac{1}{2} \hat{a}_+ \right) \psi \\ &= \hbar\omega \hat{a}_+ \left(\hat{a}_- \hat{a}_+ + \frac{1}{2} \right) \psi = \hat{a}_+ \left[\hbar\omega \left(\hat{a}_+ \hat{a}_- + 1 + \frac{1}{2} \right) \psi \right] \\ &= \hat{a}_+ \left(\hat{H} + \hbar\omega \right) \psi = \hat{a}_+ (E + \hbar\omega) \psi = (E + \hbar\omega) (\hat{a}_+\psi). \quad \text{QED} \end{aligned}$$

(I used Equation 2.56 to replace $\hat{a}_- \hat{a}_+$ by $(\hat{a}_+ \hat{a}_- + 1)$ in the second line. Notice that whereas the ordering of $\hat{a}_+$ and $\hat{a}_-$ *does* matter, the ordering of $\hat{a}_\pm$ and any *constants*—such as $\hbar$, ω , and E —does *not*; an operator commutes with any constant.)

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

$$\begin{aligned}\hat{H}(\hat{a}_- \psi) &= \hbar\omega \left(\hat{a}_- \hat{a}_+ - \frac{1}{2} \right) (\hat{a}_- \psi) = \hbar\omega \hat{a}_- \left(\hat{a}_+ \hat{a}_- - \frac{1}{2} \right) \psi \\ &= \hat{a}_- \left[\hbar\omega \left(\hat{a}_- \hat{a}_+ - 1 - \frac{1}{2} \right) \psi \right] = \hat{a}_- \left(\hat{H} - \hbar\omega \right) \psi = \hat{a}_- (E - \hbar\omega) \psi \\ &= (E - \hbar\omega) (\hat{a}_- \psi).\end{aligned}$$

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 $\hat{a}_\pm$ **ladder operators**, because they allow us to climb up and down in energy; $\hat{a}_+$ is the **raising operator**, and $\hat{a}_-$ the **lowering operator**. The “ladder” of states is illustrated in Figure 2.5.

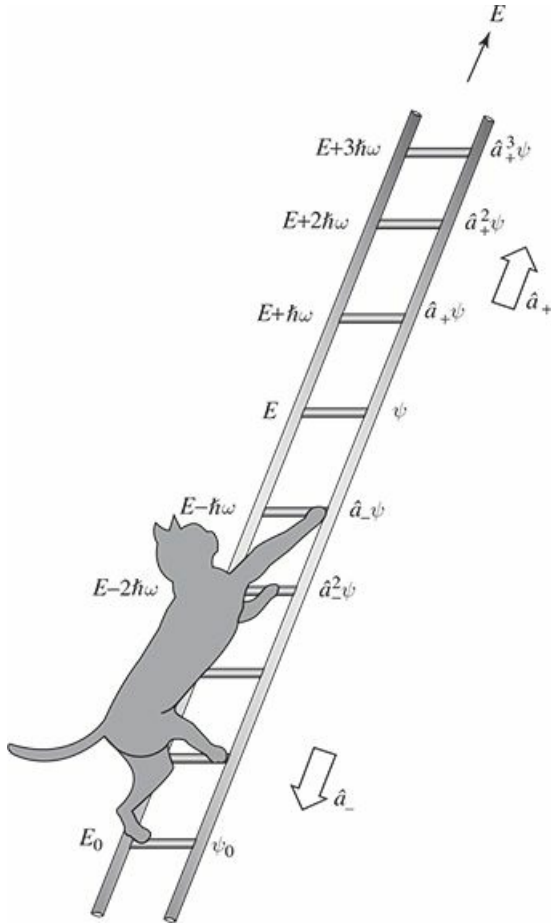


Figure 2.5: The “ladder” of states for the harmonic oscillator.

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 2.3) does not exist! At some point the machine must fail. How can that happen? We know that $\hat{a}_- \psi$ 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

$$\hat{a}_- \psi_0 = 0. \quad (2.59)$$

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:

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

so

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

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

$$\boxed{\psi_0(x) = \left(\frac{m\omega}{\pi \hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar} x^2}.} \quad (2.60)$$

To determine the energy of this state we plug it into the Schrödinger equation (in the form of Equation 2.58), $\hbar\omega (\hat{a}_+ \hat{a}_- + 1/2) \psi_0 = E_0 \psi_0$, and exploit the fact that $\hat{a}_- \psi_0 = 0$:

$$E_0 = \frac{1}{2} \hbar\omega. \quad (2.61)$$

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,²⁷ increasing the energy by $\hbar\omega$ with each step:

$$\boxed{\psi_n(x) = A_n (\hat{a}_+)^n \psi_0(x), \quad \text{with} \quad E_n = \left(n + \frac{1}{2}\right) \hbar\omega,} \quad (2.62)$$

where A_n is the normalization constant. By applying the raising operator (repeatedly) to ψ_0 , then, we can (in principle) construct all²⁸ the stationary states of 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 2.62,

$$\begin{aligned}\psi_1(x) &= A_1 \hat{a}_+ \psi_0 = \frac{A_1}{\sqrt{2\hbar m\omega}} \left(-\hbar \frac{d}{dx} + m\omega x \right) \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar} x^2} \\ &= A_1 \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \sqrt{\frac{2m\omega}{\hbar}} x e^{-\frac{m\omega}{2\hbar} x^2}.\end{aligned}\tag{2.63}$$

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 2.62 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 $\hat{a}_{\pm} \psi_n$ is *proportional* to $\psi_{n\pm 1}$,

$$\hat{a}_+ \psi_n = c_n \psi_{n+1}, \quad \hat{a}_- \psi_n = d_n \psi_{n-1}\tag{2.64}$$

but what are the proportionality factors, c_n and d_n ? First note that for “any”²⁹ functions $f(x)$ and $g(x)$,

$$\int_{-\infty}^{\infty} f^* (\hat{a}_{\pm} g) dx = \int_{-\infty}^{\infty} (\hat{a}_{\mp} f)^* g dx.\tag{2.65}$$

In the language of linear algebra, $\hat{a}_{\mp}$ is the **hermitian conjugate** (or **adjoint**) of $\hat{a}_{\pm}$.

Proof:

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

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 29), so

$$\begin{aligned}\int_{-\infty}^{\infty} f^* (\hat{a}_{\pm} g) dx &= \frac{1}{\sqrt{2\hbar m\omega}} \int_{-\infty}^{\infty} \left[\left(\pm \hbar \frac{d}{dx} + m\omega x \right) f \right]^* g dx \\ &= \int_{-\infty}^{\infty} (\hat{a}_{\pm} f)^* g dx. \quad \text{QED}\end{aligned}$$

In particular,

$$\int_{-\infty}^{\infty} (\hat{a}_{\pm} \psi_n)^* (\hat{a}_{\pm} \psi_n) dx = \int_{-\infty}^{\infty} (\hat{a}_{\mp} \hat{a}_{\pm} \psi_n)^* \psi_n dx.$$

But (invoking Equations 2.58 and 2.62)

$$\hat{a}_+ \hat{a}_- \psi_n = n \psi_n, \quad \hat{a}_- \hat{a}_+ \psi_n = (n+1) \psi_n, \quad (2.66)$$

so

$$\begin{aligned} \int_{-\infty}^{\infty} (\hat{a}_+ \psi_n)^* (\hat{a}_+ \psi_n) dx &= |c_n|^2 \int_{-\infty}^{\infty} |\psi_{n+1}|^2 dx = (n+1) \int_{-\infty}^{\infty} |\psi_n|^2 dx, \\ \int_{-\infty}^{\infty} (\hat{a}_- \psi_n)^* (\hat{a}_- \psi_n) dx &= |d_n|^2 \int_{-\infty}^{\infty} |\psi_{n-1}|^2 dx = n \int_{-\infty}^{\infty} |\psi_n|^2 dx. \end{aligned}$$

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 hence³⁰

$$\boxed{\hat{a}_+ \psi_n = \sqrt{n+1} \psi_{n+1}, \quad \hat{a}_- \psi_n = \sqrt{n} \psi_{n-1}.} \quad (2.67)$$

Thus

$$\begin{aligned} \psi_1 &= \hat{a}_+ \psi_0, \quad \psi_2 = \frac{1}{\sqrt{2}} \hat{a}_+ \psi_1 = \frac{1}{\sqrt{2}} (\hat{a}_+)^2 \psi_0, \\ \psi_3 &= \frac{1}{\sqrt{3}} \hat{a}_+ \psi_2 = \frac{1}{\sqrt{3 \cdot 2}} (\hat{a}_+)^3 \psi_0, \quad \psi_4 = \frac{1}{\sqrt{4}} \hat{a}_+ \psi_3 = \frac{1}{\sqrt{4 \cdot 3 \cdot 2}} (\hat{a}_+)^4 \psi_0, \end{aligned}$$

and so on. Clearly

$$\boxed{\psi_n = \frac{1}{\sqrt{n!}} (\hat{a}_+)^n \psi_0,} \quad (2.68)$$

which is to say that the normalization factor in Equation 2.62 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:

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = \delta_{mn}. \quad (2.69)$$

This can be proved using Equation 2.66, and Equation 2.65 twice—first moving $\hat{a}_+$ and then moving $\hat{a}_-$:

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_m^* (\hat{a}_+ \hat{a}_-) \psi_n dx &= n \int_{-\infty}^{\infty} \psi_m^* \psi_n dx \\ &= \int_{-\infty}^{\infty} (\hat{a}_- \psi_m)^* (\hat{a}_- \psi_n) dx = \int_{-\infty}^{\infty} (\hat{a}_+ \hat{a}_- \psi_m)^* \psi_n dx \\ &= m \int_{-\infty}^{\infty} \psi_m^* \psi_n dx. \end{aligned}$$

Unless $m = n$, then, $\int \psi_m^* \psi_n dx$ must be zero. Orthonormality means that we can again use Fourier's trick (Equation 2.37) to evaluate the coefficients c_n , when we expand $\Psi(x, 0)$ as a linear combination of stationary states (Equation 2.16). As always, $|c_n|^2$ is 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 n th stationary 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 $\hat{p}$): Use the definition (Equation 2.48) to express x and $\hat{p}$ in terms of the raising and lowering operators:

$$x = \sqrt{\frac{\hbar}{2m\omega}} (\hat{a}_+ + \hat{a}_-); \quad \hat{p} = i\sqrt{\frac{\hbar m\omega}{2}} (\hat{a}_+ - \hat{a}_-). \quad (2.70)$$

In this example we are interested in x^2 :

$$x^2 = \frac{\hbar}{2m\omega} [(\hat{a}_+)^2 + (\hat{a}_+ \hat{a}_-) + (\hat{a}_- \hat{a}_+) + (\hat{a}_-)^2].$$

So

$$\langle V \rangle = \frac{\hbar\omega}{4} \int_{-\infty}^{\infty} \psi_n^* [(\hat{a}_+)^2 + (\hat{a}_+ \hat{a}_-) + (\hat{a}_- \hat{a}_+) + (\hat{a}_-)^2] \psi_n dx.$$

But $(\hat{a}_+)^2 \psi_n$ is (apart from normalization) ψ_{n+2} , which is orthogonal to ψ_n , and the same goes for $(\hat{a}_-)^2 \psi_n$, which is proportional to ψ_{n-2} . So those terms drop out, and we can use Equation 2.66 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 3.37).

*

Problem 2.10

- Construct $\psi_2(x)$.
- Sketch ψ_0 , ψ_1 , and ψ_2 .
- 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

- Compute $\langle x \rangle$, $\langle p \rangle$, $\langle x^2 \rangle$, and $\langle p^2 \rangle$, for the states ψ_0 (Equation 2.60) and ψ_1 (Equation 2.63), 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 $\langle T \rangle$ and $\langle V \rangle$ 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 n th 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 $|\Psi(x, t)|^2$. Don't get too excited if $|\Psi(x, t)|^2$ oscillates at exactly the classical frequency; what would it have been had I specified $\psi_2(x)$, instead of $\psi_1(x)$?³¹
- (c) Find $\langle x \rangle$ and $\langle p \rangle$. 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?

2.3.2 Analytic Method

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

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi, \quad (2.71)$$

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

$$\xi \equiv \sqrt{\frac{m\omega}{\hbar}} x; \quad (2.72)$$

in terms of ξ the Schrödinger equation reads

$$\frac{d^2\psi}{d\xi^2} = (\xi^2 - K) \psi, \quad (2.73)$$

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

$$K \equiv \frac{2E}{\hbar\omega}. \quad (2.74)$$

Our problem is to solve Equation 2.73, 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

$$\frac{d^2\psi}{d\xi^2} \approx \xi^2 \psi, \quad (2.75)$$

which has the approximate solution (check it!)

$$\psi(\xi) \approx Ae^{-\xi^2/2} + Be^{+\xi^2/2}. \quad (2.76)$$

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

$$\psi(\xi) \rightarrow () e^{-\xi^2/2}, \quad \text{at large } \xi. \quad (2.77)$$

This suggests that we “peel off” the exponential part,

$$\psi(\xi) = h(\xi) e^{-\xi^2/2}, \quad (2.78)$$

in hopes that what remains, $h(\xi)$, has a simpler functional form than $\psi(\xi)$ itself.³² Differentiating Equation 2.78,

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

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 2.73) becomes

$$\frac{d^2h}{d\xi^2} - 2\xi \frac{dh}{d\xi} + (K - 1)h = 0. \quad (2.79)$$

I propose to look for solutions to Equation 2.79 in the form of *power series* in ξ :³³

$$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \dots = \sum_{j=0}^{\infty} a_j \xi^j. \quad (2.80)$$

Differentiating the series term by term,

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

and

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

Putting these into Equation 2.80, we find

$$\sum_{j=0}^{\infty} [(j+1)(j+2) a_{j+2} - 2j a_j + (K-1) a_j] \xi^j = 0. \quad (2.81)$$

It follows (from the uniqueness of power series expansions³⁴) that the coefficient of *each power* of ξ must vanish,

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

and hence that

$$a_{j+2} = \frac{(2j+1-K)}{(j+1)(j+2)} a_j. \quad (2.82)$$

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

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

and starting with a_1 , it generates the odd coefficients:

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

We write the complete solution as

$$h(\xi) = h_{\text{even}}(\xi) + h_{\text{odd}}(\xi), \quad (2.83)$$

where

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

is an even function of ξ , built on a_0 , and

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

is an odd function, built on a_1 . Thus Equation 2.82 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)

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

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)

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

Now, if h goes like $\exp(\xi^2)$, then ψ (remember ψ ?—that’s what we’re trying to calculate) goes like $\exp(\xi^2/2)$ (Equation 2.78), which is precisely the asymptotic behavior we *didn’t* want.³⁵ 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 2.82 requires that

$$K = 2n + 1,$$

for some positive integer n , which is to say (referring to Equation 2.74) that the *energy* must be

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega, \quad \text{for } n = 0, 1, 2, \dots \quad (2.84)$$

Thus we recover, by a completely different method, the fundamental quantization condition we found algebraically in Equation 2.62.

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 2.71 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). Now try an E slightly *larger* (say, $0.51\hbar\omega$); the “tail” now blows up in the *other* direction (Figure 2.6(b)). As you tweak the parameter in tiny increments from 0.49 to 0.51, the graph

“flips over” at precisely the value 0.5—only here does the solution escape the exponential asymptotic growth that renders it physically unacceptable.³⁶

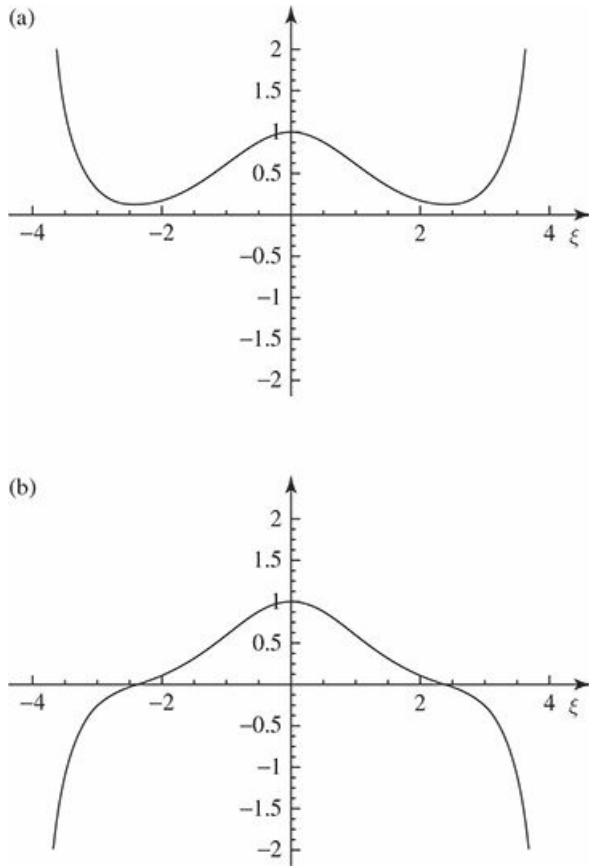


Figure 2.6: Solutions to the Schrödinger equation for (a) $E = 0.49\hbar\omega$, and (b) $E = 0.51\hbar\omega$.

For the allowed values of K , the recursion formula reads

$$a_{j+2} = \frac{-2(n-j)}{(j+1)(j+2)}a_j. \quad (2.85)$$

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 2.85 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 2.60). For $n = 1$ we take $a_0 = 0$,³⁷ and Equation 2.85 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 2.63). 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**, $H_n(\xi)$.³⁸ 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 normalized³⁹ stationary states for the harmonic oscillator are

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}. \quad (2.86)$$

They are identical (of course) to the ones we obtained algebraically in Equation 2.68.

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

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

In Figure 2.7(a) I have plotted $\psi_n(x)$ for the first few ns . 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 2.14), 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 (Problem 1.11) on the quantum one (for $n = 60$); if you smoothed out the bumps, the two would fit pretty well.

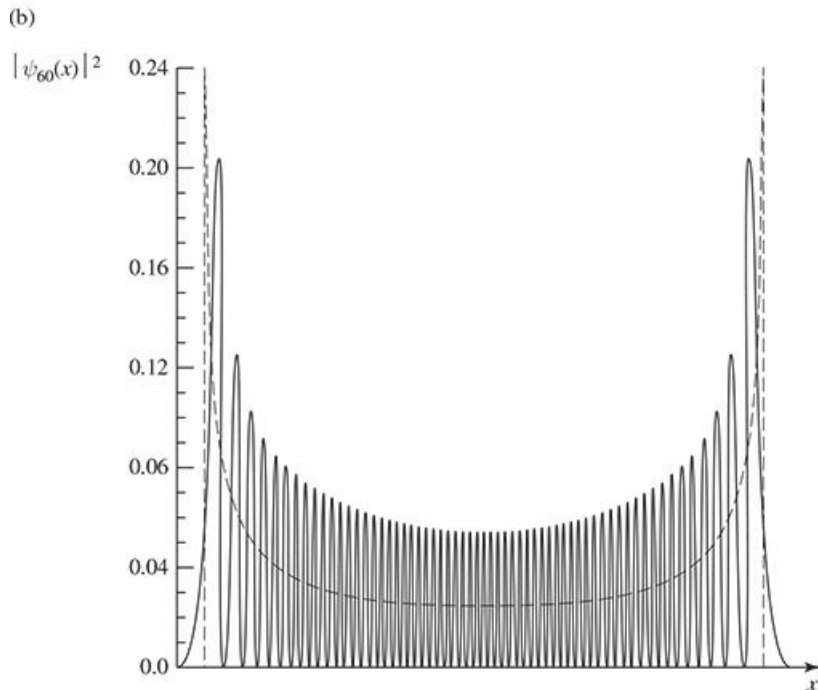
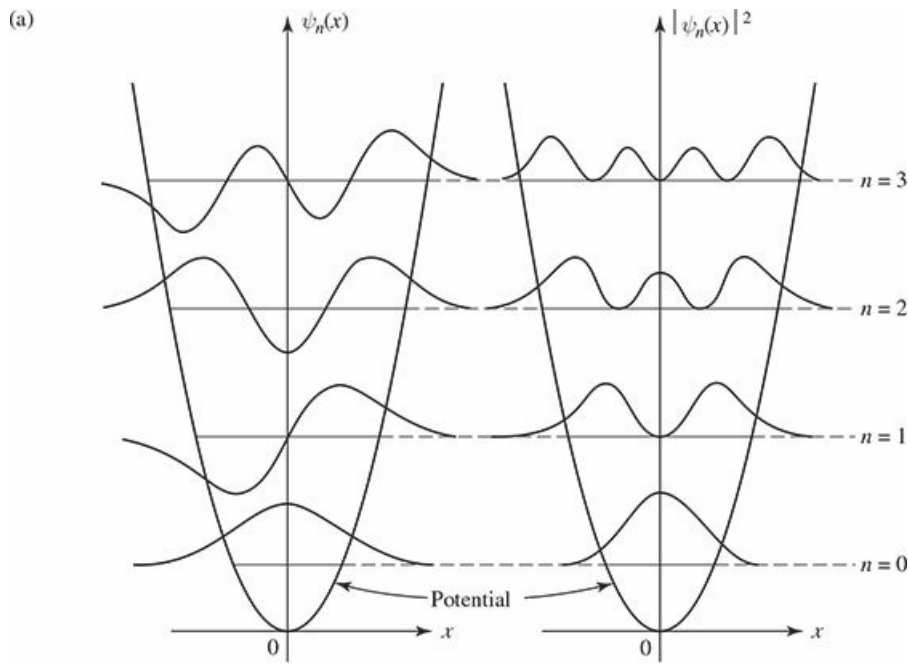


Figure 2.7: (a) The first four stationary states of the harmonic oscillator. (b) Graph of $|\psi_{60}|^2$, with the classical distribution (dashed curve) superimposed.

Problem 2.14 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 $E = (1/2)ka^2 = (1/2)m\omega^2a^2$, 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, or evaluate it by computer.

Problem 2.15 Use the recursion formula (Equation 2.85) 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 2.16 In this problem we explore some of the more useful theorems (stated without proof) involving Hermite polynomials.

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

$$H_n(\xi) = (-1)^n e^{\xi^2} \left(\frac{d}{d\xi} \right)^n e^{-\xi^2}. \quad (2.87)$$

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:

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2n H_{n-1}(\xi). \quad (2.88)$$

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

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

$$\frac{dH_n}{d\xi} = 2n H_{n-1}(\xi). \quad (2.89)$$

Check this, by differentiating H_5 and H_6 .

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

$$e^{-z^2+2z\xi} = \sum_{n=0}^{\infty} \frac{z^n}{n!} H_n(\xi). \quad (2.90)$$

Use this to obtain H_1 , H_2 , and H_3 .

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 be motion at constant velocity, but in quantum mechanics the problem is surprisingly subtle. The time-independent Schrödinger equation reads

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi, \quad (2.91)$$

or

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}. \quad (2.92)$$

So far, it's the same as inside the infinite square well (Equation 2.24), where the potential is also zero; this time, however, I prefer to write the general solution in exponential form (instead of sines and cosines), for reasons that will appear in due course:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}. \quad (2.93)$$

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

$$\Psi(x, t) = Ae^{ik\left(x - \frac{\hbar k}{2m}t\right)} + Be^{-ik\left(x + \frac{\hbar k}{2m}t\right)}. \quad (2.94)$$

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 unchanging shape, 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 moves with the same velocity, its *shape* doesn't change as it propagates. Thus the first term in Equation 2.94 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

$$\Psi_k(x, t) = Ae^{i\left(kx - \frac{\hbar k^2}{2m}t\right)}, \quad (2.95)$$

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

$$k \equiv \pm \frac{\sqrt{2mE}}{\hbar}, \quad \text{with } \begin{cases} k > 0 \Rightarrow & \text{traveling to the right,} \\ k < 0 \Rightarrow & \text{traveling to the left.} \end{cases} \quad (2.96)$$

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

$$p = \hbar k. \quad (2.97)$$

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

$$v_{\text{quantum}} = \frac{\hbar |k|}{2m} = \sqrt{\frac{E}{2m}}. \quad (2.98)$$

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

$$v_{\text{classical}} = \sqrt{\frac{2E}{m}} = 2v_{\text{quantum}}. \quad (2.99)$$

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*:

$$\int_{-\infty}^{+\infty} \Psi_k^* \Psi_k dx = |A|^2 \int_{-\infty}^{+\infty} dx = |A|^2 (\infty). \quad (2.100)$$

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):

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m}t)} dk. \quad (2.101)$$

(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 ks , and hence a range of energies and speeds. We call it a **wave packet**.⁴⁰

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 2.101; the only question is how to determine $\phi(k)$ so as to match the initial wave function:

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{ikx} dk. \quad (2.102)$$

This is a classic problem in Fourier analysis; the answer is provided by **Plancherel's theorem** (see Problem 2.19):

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(k) e^{ikx} dk \iff F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{-ikx} dx. \quad (2.103)$$

$F(k)$ is called the **Fourier transform** of $f(x)$; $f(x)$ is the **inverse Fourier transform** of $F(k)$ (the only difference is the sign in the exponent).⁴¹ There is, of course, some restriction on the allowable functions: The integrals have to *exist*.⁴² For our purposes this is guaranteed by the physical requirement that $\Psi(x, 0)$ itself be normalized. So the solution to the generic quantum problem, for the free particle, is Equation 2.101, with

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \Psi(x, 0) e^{-ikx} dx. \quad (2.104)$$

Example 2.6

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

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

where A and a are positive real constants. Find $\Psi(x, t)$.

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

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

Next we calculate $\phi(k)$, using Equation 2.104:

$$\begin{aligned} \phi(k) &= \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2a}} \int_{-a}^a e^{-ikx} dx = \frac{1}{2\sqrt{\pi a}} \left. \frac{e^{-ikx}}{-ik} \right|_{-a}^a \\ &= \frac{1}{k\sqrt{\pi a}} \left(\frac{e^{ika} - e^{-ika}}{2i} \right) = \frac{1}{\sqrt{\pi a}} \frac{\sin(ka)}{k}. \end{aligned}$$

Finally, we plug this back into Equation 2.101:

$$\Psi(x, t) = \frac{1}{\pi\sqrt{2a}} \int_{-\infty}^{\infty} \frac{\sin(ka)}{k} e^{i\left(kx - \frac{\hbar k^2}{2m}t\right)} dk. \quad (2.105)$$

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 2.101) can be carried out explicitly; see Problem 2.21 for a particularly beautiful example.)

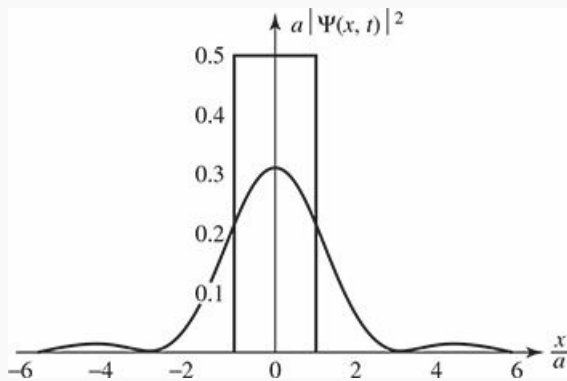


Figure 2.8: Graph of $|\Psi(x, t)|^2$ (Equation 2.105) at $t = 0$ (the rectangle) and at $t = ma^2/\hbar$ (the curve).

In Figure 2.9 I have plotted $\Psi(x, 0)$ and $\phi(k)$. Note that for small a , $\Psi(x, 0)$ is narrow (in x), while $\phi(k)$ is broad (in k), and vice versa for large a . But k is related to momentum, by Equation 2.97, so this is a manifestation of the uncertainty principle: the position can be well defined (small a), or the momentum (large a), but not both.

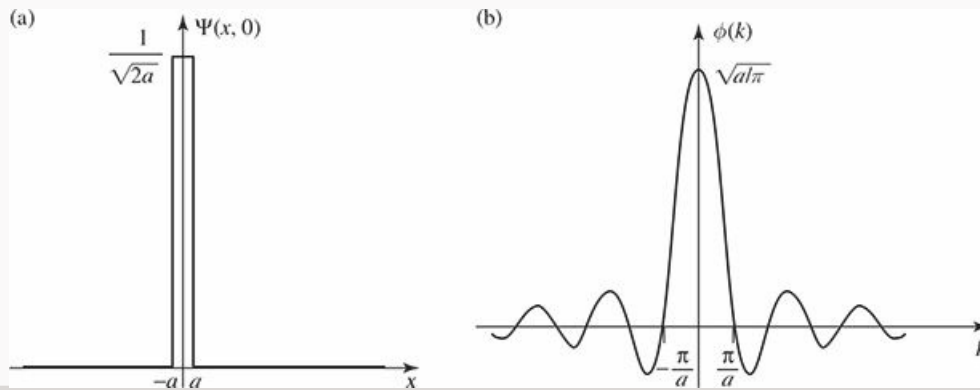


Figure 2.9: (a) Graph of $\Psi(x, 0)$. (b) Graph of $\phi(k)$.

I return now to the paradox noted earlier: the fact that the separable solution $\Psi_k(x, t)$ travels at the “wrong” speed for the particle it ostensibly represents. Strictly speaking, the problem evaporated when we discovered that Ψ_k is not a physically realizable state. Nevertheless, it is of interest to figure out how information about the particle velocity *is* contained in the wave function (Equation 2.101). The essential idea is this: A wave packet is a superposition of sinusoidal functions whose amplitude is modulated by ϕ (Figure 2.10); 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 that speed). What I need to show is that for the wave function of a free particle in quantum mechanics the group velocity is *twice* the phase velocity—just right to match the classical particle speed.

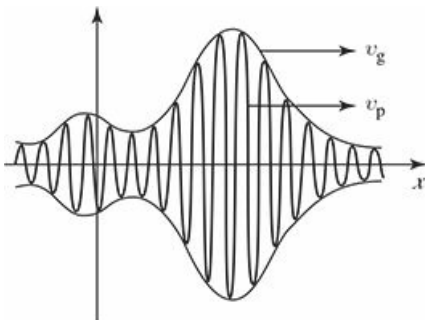


Figure 2.10: A wave packet. The “envelope” travels at the group velocity; the “ripples” travel at the phase velocity.

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

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{i(kx - \omega t)} dk. \quad (2.106)$$

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—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:

$$\omega(k) \approx \omega_0 + \omega'_0 (k - k_0),$$

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

$$\begin{aligned} \Psi(x, t) &\approx \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k_0 + s) e^{i[(k_0 + s)x - (\omega_0 + \omega'_0 s)t]} ds \\ &= \frac{1}{\sqrt{2\pi}} e^{i(k_0 x - \omega_0 t)} \int_{-\infty}^{+\infty} \phi(k_0 + s) e^{is(x - \omega'_0 t)} ds. \end{aligned} \quad (2.107)$$

The term in front is a sinusoidal wave (the “ripples”), traveling at speed ω_0/k_0 . It is modulated by the integral (the “envelope”), which is a function of $x - \omega'_0 t$, and therefore propagates at the speed ω'_0 . Thus the *phase* velocity is

$$v_{\text{phase}} = \frac{\omega}{k}, \quad (2.108)$$

while the *group* velocity is

$$v_{\text{group}} = \frac{d\omega}{dk} \quad (2.109)$$

(both of them evaluated at $k = k_0$).

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 the group velocity of the wave packet matches the classical particle velocity:

$$v_{\text{classical}} = v_{\text{group}} = 2v_{\text{phase}}. \quad (2.110)$$

* **Problem 2.17** 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 2.18 Find the probability current, J (Problem 1.14) for the free particle wave function Equation 2.95. Which direction does the probability flow?

**

Problem 2.19 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:

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

Show that this can be written equivalently as

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

What is c_n , in terms of a_n and b_n ?

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

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

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

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

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

- (d) Take the limit $a \rightarrow \infty$ 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 $a \rightarrow \infty$.

Problem 2.20 A free particle has the initial wave function

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

where A and a are positive real constants.

- Normalize $\Psi(x, 0)$.
- Find $\phi(k)$.
- Construct $\Psi(x, t)$, in the form of an integral.
- Discuss the limiting cases (a very large, and a very small).

- * **Problem 2.21** The gaussian wave packet. A free particle has the initial wave function

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

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

- (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:*

$$\Psi(x, t) = \left(\frac{2a}{\pi}\right)^{1/4} \frac{1}{\gamma} e^{-ax^2/\gamma^2}, \quad \text{where} \quad \gamma \equiv \sqrt{1 + (2i\hbar at/m)}. \quad (2.111)$$

- (c) Find $|\Psi(x, t)|^2$. Express your answer in terms of the quantity

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

Sketch $|\Psi|^2$ (as a function of x) at $t = 0$, and again for some very large t . Qualitatively, what happens to $|\Psi|^2$, as time goes on?

- (d) Find $\langle x \rangle$, $\langle p \rangle$, $\langle x^2 \rangle$, $\langle p^2 \rangle$, σ_x , and σ_p . *Partial answer:* $\langle p^2 \rangle = a\hbar^2$, but it may take some algebra to reduce it to this simple form.
 (e) Does the uncertainty principle hold? At what time t does the system come closest to the uncertainty limit?

2.5 The Delta-Function Potential

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 2.11(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 2.11(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.

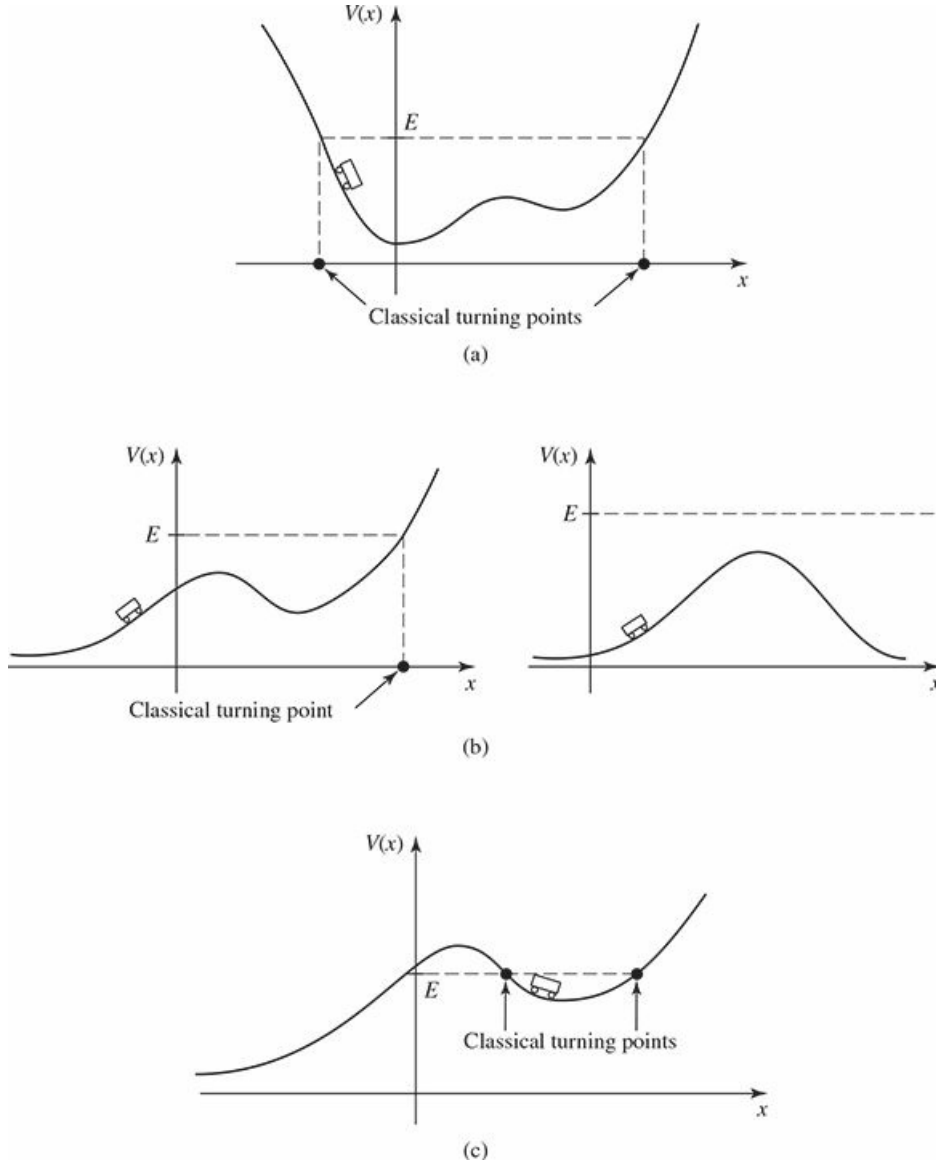


Figure 2.11: (a) A bound state. (b) Scattering states. (c) A *classical* bound state, but a quantum scattering state.

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 2.11(c)):

$$\begin{cases} E < V(-\infty) \text{ and } V(+\infty) \Rightarrow & \text{bound state,} \\ E > V(-\infty) \text{ or } V(+\infty) \Rightarrow & \text{scattering state.} \end{cases} \quad (2.112)$$

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

$$\begin{cases} E < 0 \Rightarrow & \text{bound state,} \\ E > 0 \Rightarrow & \text{scattering state.} \end{cases} \quad (2.113)$$

Because the infinite square well and harmonic oscillator potentials go to infinity as $x \rightarrow \pm\infty$, they admit bound states only; because the free particle potential is zero everywhere, it only allows scattering states.⁴³ In

this section (and the following one) we shall explore potentials that support both kinds of states.

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 2.12):

$$\delta(x) \equiv \begin{cases} 0, & \text{if } x \neq 0 \\ \infty, & \text{if } x = 0 \end{cases}, \text{ with } \int_{-\infty}^{+\infty} \delta(x) dx = 1. \quad (2.114)$$

Technically, it isn't a function at all, since it is not finite at $x = 0$ (mathematicians call it a **generalized function**, or **distribution**).⁴⁴ 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 $f(a)$,

$$f(x) \delta(x - a) = f(a) \delta(x - a), \quad (2.115)$$

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

$$\int_{-\infty}^{+\infty} f(x) \delta(x - a) dx = f(a) \int_{-\infty}^{+\infty} \delta(x - a) dx = f(a). \quad (2.116)$$

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 $\epsilon > 0$.)

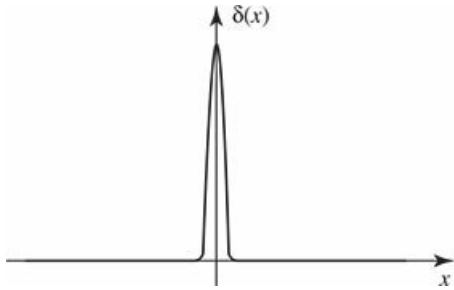


Figure 2.12: The Dirac delta function (Equation 2.114).

Let's consider a potential of the form

$$V(x) = -\alpha \delta(x), \quad (2.117)$$

where α is some positive constant.⁴⁵ 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

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} - \alpha \delta(x) \psi = E \psi; \quad (2.118)$$

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

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = \kappa^2\psi, \quad (2.119)$$

where

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}. \quad (2.120)$$

(E is negative, by assumption, so κ is real and positive.) The general solution to Equation 2.119 is

$$\psi(x) = Ae^{-\kappa x} + Be^{\kappa x}, \quad (2.121)$$

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

$$\psi(x) = Be^{\kappa x}, \quad (x < 0). \quad (2.122)$$

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 $x \rightarrow +\infty$), so

$$\psi(x) = Fe^{-\kappa x}, \quad (x > 0). \quad (2.123)$$

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 :

$$\begin{cases} 1. & \psi \text{ is always continuous;} \\ 2. & d\psi/dx \text{ is continuous except at points where the potential is infinite.} \end{cases}$$

(2.124)

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

$$\psi(x) = \begin{cases} Be^{\kappa x}, & (x \leq 0), \\ Be^{-\kappa x}, & (x \geq 0); \end{cases} \quad (2.125)$$

$\psi(x)$ is plotted in Figure 2.13. The second boundary condition tells us nothing; this is (like the walls of 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. It turns out that the delta function determines the *discontinuity in the derivative* of ψ , at $x = 0$. I'll show you now how this works, and as a byproduct we'll see why $d\psi/dx$ is ordinarily continuous.

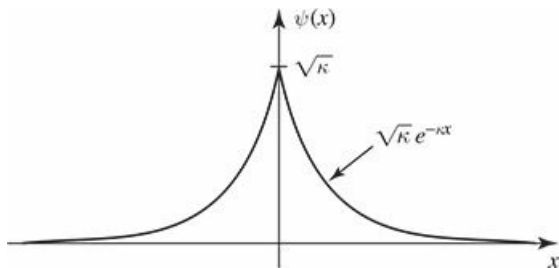


Figure 2.13: Bound state wave function for the delta-function potential (Equation 2.125).

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

$$-\frac{\hbar^2}{2m} \int_{-\epsilon}^{+\epsilon} \frac{d^2\psi}{dx^2} dx + \int_{-\epsilon}^{+\epsilon} V(x) \psi(x) dx = E \int_{-\epsilon}^{+\epsilon} \psi(x) dx \quad (2.126)$$

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

$$\Delta \left(\frac{d\psi}{dx} \right) \equiv \lim_{\epsilon \rightarrow 0} \left(\frac{\partial\psi}{\partial x} \Big|_{+\epsilon} - \frac{\partial\psi}{\partial x} \Big|_{-\epsilon} \right) = \frac{2m}{\hbar^2} \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{+\epsilon} V(x) \psi(x) dx. \quad (2.127)$$

Ordinarily, 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 2.116 yields

$$\Delta \left(\frac{d\psi}{dx} \right) = -\frac{2m\alpha}{\hbar^2} \psi(0). \quad (2.128)$$

For the case at hand (Equation 2.125),

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

and hence $\Delta(d\psi/dx) = -2B\kappa$. And $\psi(0) = B$. So Equation 2.128 says

$$\kappa = \frac{m\alpha}{\hbar^2}, \quad (2.129)$$

and the allowed energy (Equation 2.120) is

$$E = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{m\alpha^2}{2\hbar^2}. \quad (2.130)$$

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 the positive real root):

$$B = \sqrt{\kappa} = \frac{\sqrt{m\alpha}}{\hbar}. \quad (2.131)$$

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

$$\boxed{\psi(x) = \frac{\sqrt{m\alpha}}{\hbar} e^{-m\alpha|x|/\hbar^2}; \quad E = -\frac{m\alpha^2}{2\hbar^2}.} \quad (2.132)$$

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

$$k \equiv \frac{\sqrt{2mE}}{\hbar} \quad (2.133)$$

is real and positive. The general solution is

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad (2.134)$$

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

$$\psi(x) = Fe^{ikx} + Ge^{-ikx}. \quad (2.135)$$

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

$$F + G = A + B. \quad (2.136)$$

The derivatives are

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

and hence $\Delta(d\psi/dx) = ik(F - G - A + B)$. Meanwhile, $\psi(0) = (A + B)$, so the second boundary condition (Equation 2.128) says

$$ik(F - G - A + B) = -\frac{2m\alpha}{\hbar^2}(A + B), \quad (2.137)$$

or, more compactly,

$$F - G = A(1 + 2i\beta) - B(1 - 2i\beta), \quad \text{where } \beta \equiv \frac{m\alpha}{\hbar^2 k}. \quad (2.138)$$

Having imposed both boundary conditions, we are left with two equations (Equations 2.136 and 2.138) 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 wiggle 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 2.134) is the amplitude of a wave coming in from the left, B is the amplitude of a wave returning to the left; F (Equation 2.135) 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 2.14). 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*:

$$G = 0 \quad (\text{for scattering from the left}); \quad (2.139)$$

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 2.136 and 2.138 for B and F , we find

$$B = \frac{i\beta}{1 - i\beta}A, \quad F = \frac{1}{1 - i\beta}A. \quad (2.140)$$

(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.)

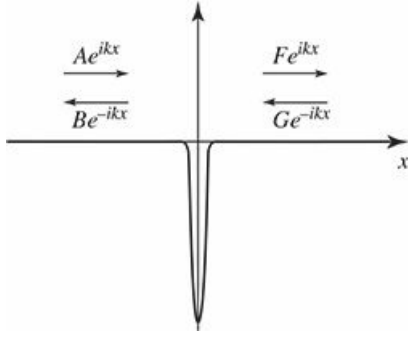


Figure 2.14: Scattering from a delta function well.

Now, the probability of finding the particle at a specified location is given by $|\Psi|^2$, so the *relative*⁴⁶ probability that an incident particle will be reflected back is

$$R \equiv \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2}. \quad (2.141)$$

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 that a particle will continue right on through is the **transmission coefficient**⁴⁷

$$T \equiv \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2}. \quad (2.142)$$

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

$$R + T = 1. \quad (2.143)$$

Notice that R and T are functions of β , and hence (Equations 2.133 and 2.138) of E :

$$R = \frac{1}{1 + (2\hbar^2 E / m\alpha^2)}, \quad T = \frac{1}{1 + (m\alpha^2 / 2\hbar^2 E)}. \quad (2.144)$$

The higher the energy, the greater the probability of transmission (which makes sense).

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. We know the resolution to this problem: 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.⁴⁸ 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 with energies 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, and flies off to infinity) using *stationary* states. After all, ψ (in Equations 2.134 and 2.135) 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 2.42).

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 2.15). 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).

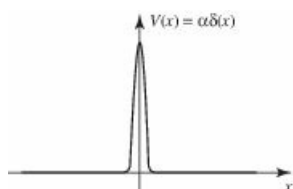


Figure 2.15: The delta-function barrier.

* **Problem 2.22** 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 2.23** 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

$$\delta(cx) = \frac{1}{|c|} \delta(x), \quad (2.145)$$

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

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

$$\theta(x) \equiv \begin{cases} 1, & x > 0, \\ 0, & x < 0. \end{cases} \quad (2.146)$$

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

**

Problem 2.24 Check the uncertainty principle for the wave function in Equation 2.132. *Hint:* Calculating $\langle p^2 \rangle$ can be tricky, because the derivative of ψ has a step discontinuity at $x = 0$. You may want to use the result in Problem 2.23(b). *Partial answer:* $\langle p^2 \rangle = (m\alpha/\hbar)^2$.

Problem 2.25 Check that the bound state of the delta-function well (Equation 2.132) is orthogonal to the scattering states (Equations 2.134 and 2.135).

*

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

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx} dk. \quad (2.147)$$

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 2.147 to mean the *average* value of the finite integral, as $L \rightarrow \infty$). The source of the problem is that the delta function doesn't meet the requirement (square-integrability) for Plancherel's theorem (see footnote 42). In spite of this, Equation 2.147 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.

- Sketch this potential.
- 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.
- What are the bound state energies in the limiting cases (i) $a \rightarrow 0$ and (ii) $a \rightarrow \infty$ (holding α fixed)? Explain why your answers are reasonable, by comparison with the single delta-function well.

**

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

$$V(x) = \begin{cases} -V_0, & -a \leq x \leq a, \\ 0, & |x| > a, \end{cases} \quad (2.148)$$

where V_0 is a (positive) constant (Figure 2.16). 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.

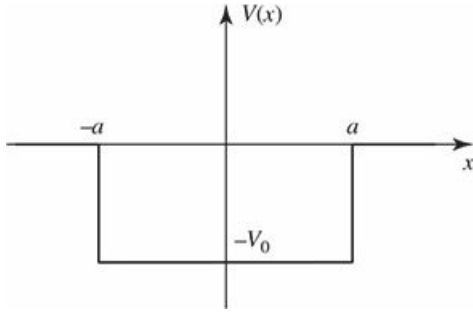


Figure 2.16: The finite square well (Equation 2.148).

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

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar} \quad (2.149)$$

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 $x \rightarrow -\infty$), so the physically admissible solution is

$$\psi(x) = B e^{\kappa x}, \quad (x < -a). \quad (2.150)$$

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

$$l \equiv \frac{\sqrt{2m(E + V_0)}}{\hbar}. \quad (2.151)$$

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 is⁴⁹

$$\psi(x) = C \sin(lx) + D \cos(lx), \quad (-a < x < a), \quad (2.152)$$

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 $x \rightarrow \infty$), so we are left with

$$\psi(x) = F e^{-\kappa x}, \quad (x > a). \quad (2.153)$$

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

$$\psi(x) = \begin{cases} F e^{-\kappa x}, & (x > a), \\ D \cos(lx), & (0 < x < a), \\ \psi(-x), & (x < 0). \end{cases} \quad (2.154)$$

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

$$F e^{-\kappa a} = D \cos(la), \quad (2.155)$$

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

$$-\kappa F e^{-\kappa a} = -l D \sin(la). \quad (2.156)$$

Dividing Equation 2.156 by Equation 2.155, we find that

$$\kappa = l \tan(la). \quad (2.157)$$

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

$$z \equiv la, \quad \text{and} \quad z_0 \equiv \frac{a}{\hbar} \sqrt{2m V_0}. \quad (2.158)$$

According to Equations 2.149 and 2.151, $(\kappa^2 + l^2) = 2m V_0/\hbar^2$, so $\kappa a = \sqrt{z_0^2 - z^2}$, and Equation 2.157 reads

$$\tan z = \sqrt{(z_0/z)^2 - 1}. \quad (2.159)$$

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 2.17). Two limiting cases are of special interest:

1. **Wide, deep well.** If z_0 is very large (pushing the curve $\sqrt{(z_0/z)^2 - 1}$ upward on the graph, and sliding the zero crossing, z_0 , to the right) the intersections occur just slightly below $z_n = n\pi/2$, with n odd; it follows (Equations 2.158 and 2.151) that

$$E_n + V_0 \approx \frac{n^2 \pi^2 \hbar^2}{2m(2a)^2} \quad (n = 1, 3, 5, \dots). \quad (2.160)$$

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 2.30)—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 $V_0 \rightarrow \infty$; 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 $z_0 < \pi/2$, only one remains. It is interesting to note, however, that there is always *one* bound state, no matter *how* “weak” the well becomes.

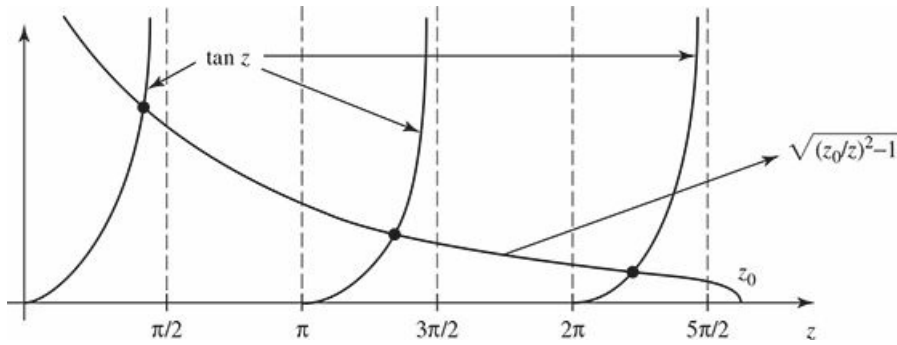


Figure 2.17: Graphical solution to Equation 2.159, for $z_0 = 8$ (even states).

You're welcome to normalize ψ (Equation 2.154), 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

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad \text{for } (x < -a), \quad (2.161)$$

where (as usual)

$$k \equiv \frac{\sqrt{2mE}}{\hbar}. \quad (2.162)$$

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

$$\psi(x) = C \sin(lx) + D \cos(lx), \quad \text{for } (-a < x < a), \quad (2.163)$$

where, as before,

$$l \equiv \frac{\sqrt{2m(E + V_0)}}{\hbar}. \quad (2.164)$$

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

$$\psi(x) = Fe^{ikx}. \quad (2.165)$$

Here A is the incident amplitude, B is the reflected amplitude, and F is the transmitted amplitude.⁵⁰

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

$$Ae^{-ika} + Be^{ika} = -C \sin(la) + D \cos(la), \quad (2.166)$$

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

$$ik \left[A e^{-ika} - B e^{ika} \right] = l [C \cos(la) + D \sin(la)] \quad (2.167)$$

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

$$C \sin(la) + D \cos(la) = F e^{ika}, \quad (2.168)$$

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

$$l [C \cos(la) - D \sin(la)] = ik F e^{ika}. \quad (2.169)$$

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

$$B = i \frac{\sin(2la)}{2kl} (l^2 - k^2) F, \quad (2.170)$$

$$F = \frac{e^{-2ika} A}{\cos(2la) - i \frac{(k^2 + l^2)}{2kl} \sin(2la)}. \quad (2.171)$$

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

$$T^{-1} = 1 + \frac{V_0^2}{4E(E + V_0)} \sin^2 \left(\frac{2a}{\hbar} \sqrt{2m(E + V_0)} \right). \quad (2.172)$$

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

$$\frac{2a}{\hbar} \sqrt{2m(E_n + V_0)} = n\pi, \quad (2.173)$$

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

$$E_n + V_0 = \frac{n^2 \pi^2 \hbar^2}{2m(2a)^2}, \quad (2.174)$$

which happen to be precisely the allowed energies for the *infinite* square well. T is plotted in Figure 2.18, as a function of energy.⁵¹

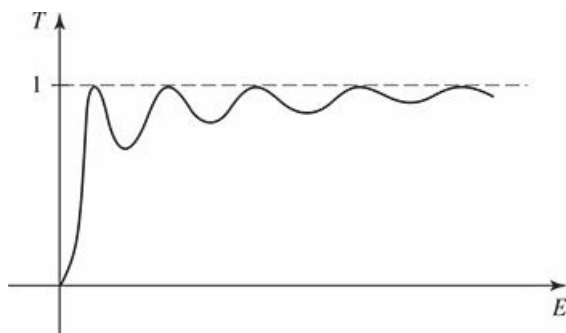


Figure 2.18: Transmission coefficient as a function of energy (Equation 2.172).

* **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?

Problem 2.30 Normalize $\psi(x)$ in Equation 2.154, 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 2.117) is a “weak” potential (even though it is infinitely deep), in the sense that $z_0 \rightarrow 0$. 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 2.132. Also show that Equation 2.172 reduces to Equation 2.144 in the appropriate limit.

Problem 2.32 Derive Equations 2.170 and 2.171. *Hint:* Use Equations 2.168 and 2.169 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 2.166 and 2.167. Obtain the transmission coefficient, and confirm Equation 2.172.

**** Problem 2.33** Determine the transmission coefficient for a rectangular *barrier* (same as Equation 2.148, 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 $E < V_0$,⁵²

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

*** Problem 2.34** Consider the “step” potential:⁵³

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

- Calculate the reflection coefficient, for the case $E < V_0$, and comment on the answer.
- Calculate the reflection coefficient for the case $E > V_0$.

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

$$T = \sqrt{\frac{E - V_0}{E}} \frac{|F|^2}{|A|^2}, \quad (2.175)$$

for $E > V_0$. *Hint:* You can figure it out using Equation 2.99, or—more elegantly, but less informatively—from the probability current (Problem 2.18). 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 2.19).⁵⁴

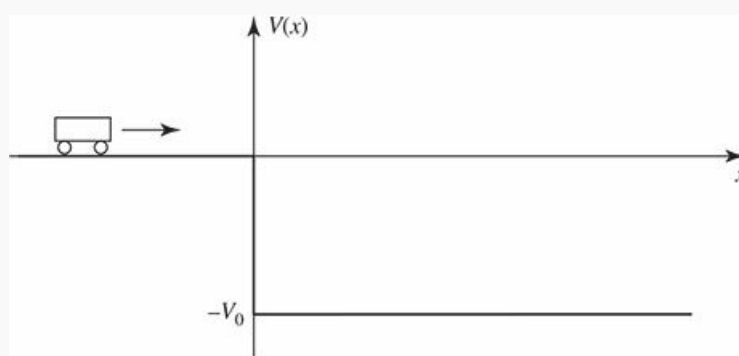


Figure 2.19: Scattering from a “cliff” (Problem 2.35).

- (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*