Chapter 7

The Schrödinger Equation in One Dimension
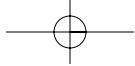
7.1   Introduction

In classical mechanics the state of motion of a particle is specified by giving the particle's position and velocity. In quantum mechanics the state of motion of a particle is specified by giving the wave function. In either case the fundamental question is to predict how the state of motion will evolve as time goes by, and in each case the answer is given by an *equation of motion*. The classical equation of motion is Newton's second law, $\mathbf{F} = m\mathbf{a}$; if we know the particle's position and velocity at time $t = 0$, Newton's second law determines the position and velocity at any other time. In quantum mechanics the equation of motion is the *time-dependent Schrödinger equation*. If we know a particle's wave function at $t = 0$, the time-dependent Schrödinger equation determines the wave function at any other time.

The time-dependent Schrödinger equation is a partial differential equation, a complete understanding of which requires more mathematical preparation than we are assuming here. Fortunately, the majority of interesting problems in quantum mechanics do not require use of the equation in its full generality. By far the most interesting states of any quantum system are those states in which the system has a definite total energy, and it turns out that for these states the wave function is a *standing wave*, analogous to the familiar standing waves on a string. When the time-dependent Schrödinger equation is applied to these standing waves, it reduces to a simpler equation called the *time-independent Schrödinger equation*. We will need only this

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time-independent equation, which will let us find the wave functions of the standing waves and the corresponding allowed energies. Because we will be using only the time-independent Schrödinger equation we will often refer to it as just "the Schrödinger equation." Nevertheless, you should know that there are really two Schrödinger equations (the time-dependent and the time-independent). Unfortunately, it is almost universal to refer to either as "the Schrödinger equation" and to let the context decide which is being discussed. In this book, however, "the Schrödinger equation" will always mean the simpler time-independent equation.

In Section 7.2 we review some properties of classical standing waves, using waves on a uniform, stretched string as our example. In Section 7.3 we discuss quantum standing waves. Then, in Section 7.4, we show how the familiar properties of classical standing waves let one find the allowed energies of one simple quantum system, namely a particle that moves freely inside a perfectly rigid box.

Using our experience with the wave functions of a particle in a rigid box we next write down the time-independent Schrödinger equation, with which one can, in principle, find the allowed energies and wave functions for any system. Then in Sections 7.6 to 7.9 we use the Schrödinger equation to find the allowed energies of various simple systems.
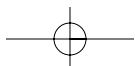
Sections 7.10 and 7.11 treat two further topics, quantum tunneling and the time-dependent Schrödinger equation. While both of these are very important, we will not be using these ideas until later (the former in Chapters 14 and 17, and the latter in Chapter 11), so you could skip these sections on your first reading.

Throughout this chapter we treat particles that move nonrelativistically in one dimension. All real systems are, of course, three-dimensional. Nevertheless, just as is the case in classical mechanics, it is a good idea to start with the simpler problem of a particle confined to move in just one dimension. In the classical case it is easy to find examples of systems that are at least approximately one-dimensional — a railroad car on a straight track, a bead threaded on a taut string. In quantum mechanics there are fewer examples of one-dimensional systems. However, we can for the moment imagine an electron moving along a very narrow wire.* The main importance of one-dimensional systems is that they provide a good introduction to three-dimensional systems, and that several one-dimensional solutions find direct application in three-dimensional problems.

7.2 Classical Standing Waves

We start with a review of some properties of classical standing waves in one dimension. We could discuss waves on a string, for which the wave function is the string's transverse displacement $y(x, t)$; or we might consider sound waves, for which the wave function is the pressure variation, $p(x, t)$. If we considered electromagnetic waves, the wave function would be the electric field strength, $\mathscr{E}(x, t)$. In this section we choose to discuss waves on a string, but since our considerations apply equally to all waves, we will use the general notation $\Psi(x, t)$ to represent the wave function.

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*More realistic examples include the motion of electrons along one axis in certain crystals and in some linear molecules.

Let us consider first two sinusoidal traveling waves, one moving to the right,

$$\Psi_1(x, t) = B \sin(kx - \omega t)$$

(this is the wave sketched in Fig. 6.8) and the other moving to the left with the same amplitude,

$$\Psi_2(x, t) = B \sin(kx + \omega t)$$

The superposition principle guarantees that the sum of these two waves is itself a possible wave motion*:

$$\Psi(x, t) = \Psi_1(x, t) + \Psi_2(x, t) = B[\sin(kx - \omega t) + \sin(kx + \omega t)] \quad (7.1)$$

If we recall the important trigonometric identity (Appendix B)

$$\sin a + \sin b = 2 \sin \frac{a + b}{2} \cos \frac{a - b}{2}$$

we can rewrite the wave (7.1) as

$$\Psi(x, t) = 2B \sin kx \cos \omega t$$

or if we set $2B = A$,

$$\Psi(x, t) = A \sin kx \cos \omega t \qquad (7.2)$$

A series of snapshots of the resultant wave (7.2) is sketched in Fig. 7.1. The important point to observe is that the resultant wave is not traveling to the right or left. At certain fixed points called **nodes,** where $\sin kx$ is zero, $\Psi(x, t)$ is always zero and the string is stationary. At any other point the string simply oscillates up and down in proportion to $\cos \omega t$, with amplitude $A \sin kx$. By superposing two traveling waves, we have formed a **standing wave.**

Because the string never moves at the nodes, we could clamp it at two nodes and remove the string outside the clamps, leaving a standing wave on a finite length of string as in Fig. 7.2. This is the kind of wave produced on a piano or guitar string when it sounds a pure musical tone.

If we now imagine a string clamped between two fixed points separated by a distance a, we can ask: What are the possible standing waves that can fit on the string? The answer is that a standing wave is possible, *provided* that it has nodes at the two fixed ends of the string. The distance between two adjacent nodes is $\lambda/2$, so the distance between any pair of nodes is an integer multiple of this, $n\lambda/2$. Therefore a standing wave fits on the string provided $n\lambda/2 = a$ for some integer n; that is, if

$$\lambda = \frac{2a}{n}, \qquad \text{where } n = 1, 2, 3, \ldots \qquad (7.3)$$
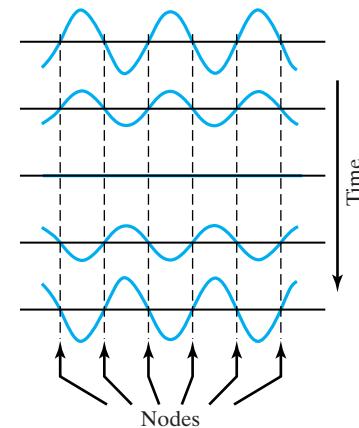

FIGURE 7.1

Five successive snapshots of the standing wave of Eq. (7.2). The nodes are points where the string remains stationary at all times. The distance between successive nodes is half a wavelength, $\lambda/2$.
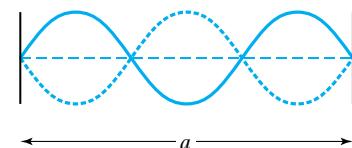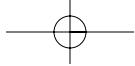

FIGURE 7.2

Three successive snapshots of a standing wave on a finite string, of length a, clamped at its two ends. The solid curve shows the string at maximum displacement; the dashed and dotted curves show it after successive quarter-cycle intervals.

*The superposition principle asserts that if Ψ_1 and Ψ_2 are possible waves, the same is true of $A\Psi_1 + B\Psi_2$ for any constants A and B. This important principle is true of any wave whose medium responds linearly to the disturbance. It applies to all the waves we will be considering.

$\lambda = 2a$

$\lambda = a$

$\lambda = 2a/3$
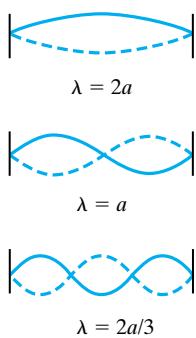
FIGURE 7.3

The first three possible standing waves on a string of length a, fixed at both ends. Each dashed curve is one half-cycle after the corresponding solid curve.

We see that the possible wavelengths of a standing wave on a string of length a are *quantized*, the allowed values being $2a$ divided by any positive integer. The first three of these allowed waves are sketched in Fig. 7.3.

It is important to recognize that the quantization of wavelengths arises from the requirement that the wave function must always be zero at the two fixed ends of the string. We refer to this kind of requirement as a **boundary condition,** since it relates to the boundaries of the system. We will find that for quantum waves, just as for classical waves, it is the boundary conditions that lead to quantization.

7.3 Standing Waves in Quantum Mechanics; Stationary States

Before we discuss quantum standing waves, we need to examine more closely the form of the classical standing wave (7.2):

$$\Psi(x, t) = A \sin kx \cos \omega t \qquad (7.4)$$

This function is a *product* of one function of x (namely, $A \sin kx$) and one function of t (namely, $\cos \omega t$). We can emphasize this by rewriting (7.4) as

$$\Psi(x, t) = \psi(x) \cos \omega t \qquad (7.5)$$

where we have used the capital letter Ψ for the full wave function $\Psi(x, t)$ and the lower case letter ψ for its **spatial part** $\psi(x)$. The spatial function $\psi(x)$ gives the full wave function $\Psi(x, t)$ at time $t = 0$ (since $\cos \omega t = 1$ when $t = 0$); more generally, at any time t the full wave function $\Psi(x, t)$ is $\psi(x)$ times the oscillatory factor $\cos \omega t$.

In our particular example (a wave on a uniform string) the spatial function $\psi(x)$ was a sine function
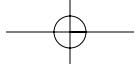
$$\psi(x) = A \sin kx \qquad (7.6)$$

but in more general problems, such as waves on a nonuniform string, $\psi(x)$ can be a more complicated function of x. On the other hand, even in these more complicated problems the time dependence is still sinusoidal; that is, it is given by a sine or cosine function of t. The difference between the sine and the cosine is just a difference in the choice of origin of time. Thus either function is possible, and the general sinusoidal standing wave is a combination of both:

$$\Psi(x, t) = \psi(x)(a \cos \omega t + b \sin \omega t) \qquad (7.7)$$

Different choices for the ratio of the coefficients a and b correspond to different choices of the origin of time. (See Problem 7.13.)

The standing waves of a quantum system have the same form (7.7), but with one important difference. For a classical wave, the function $\Psi(x, t)$ is, of course, a real number. (It would make no sense to say that the displacement of a string, or the pressure of a sound wave, had an imaginary part.) Therefore, the function $\psi(x)$ and the coefficients a and b in (7.7) are always real for any

classical wave.* In quantum mechanics, on the other hand, the wave function can be a complex number; and for quantum standing waves it usually is complex. Specifically, the time-dependent part of the wave function (7.7) always occurs in precisely the combination

$$\cos \omega t - i \sin \omega t \tag{7.8}$$

where i is the imaginary number $i = \sqrt{-1}$ (often denoted j by engineers). That is, the standing waves of a quantum particle have the form

$$\Psi(x, t) = \psi(x)(\cos \omega t - i \sin \omega t) \tag{7.9}$$

In Section 7.11 we will prove this from the time-dependent Schrödinger equation. For now, we simply assert that quantum standing waves have the sinusoidal time dependence of the particular combination of $\cos \omega t$ and $\sin \omega t$ in (7.9).

The form (7.9) can be simplified if we use Euler's formula from the theory of complex numbers (Problem 7.14),

$$\cos \theta + i \sin \theta = e^{i\theta} \tag{7.10}$$

This identity can be illustrated in the complex plane, as in Fig. 7.4, where the complex number $z = x + iy$ is represented by a point with coordinates x and y in the complex plane. Since the number $e^{i\theta}$ (with θ any real number) has coordinates $\cos \theta$ and $\sin \theta$, we see from Pythagoras' theorem that its absolute value is 1:
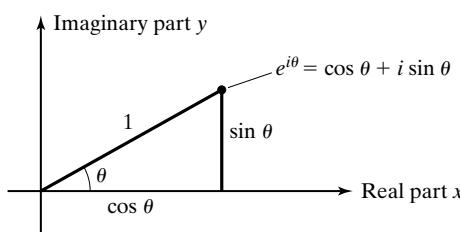
$$\left| e^{i\theta} \right| = \sqrt{(\cos \theta)^2 + (\sin \theta)^2} = 1$$

Thus the complex number $e^{i\theta}$ lies on a circle of radius 1, with polar angle θ as shown. Notice that since $\cos(-\theta) = \cos \theta$ and $\sin(-\theta) = -\sin \theta$,

$$\cos \theta - i \sin \theta = e^{-i\theta}$$
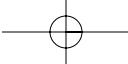
Returning to (7.9) and using the identity (7.10), we can write for the general standing wave of a quantum system

$$\Psi(x, t) = \psi(x)e^{-i\omega t} \tag{7.11}$$

FIGURE 7.4

The complex number $e^{i\theta} = \cos \theta + i \sin \theta$ is represented by a point with coordinates $(\cos \theta, \sin \theta)$ in the complex plane. The absolute value of any complex number $z = x + iy$ is defined as $|z| = \sqrt{x^2 + y^2}$. Since $\cos^2 \theta + \sin^2 \theta = 1$, it follows that $\left| e^{i\theta} \right| = 1$.

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*As you may know, it is sometimes a mathematical convenience to introduce a certain complex wave function. Nonetheless, in classical physics the actual wave function is always the real part of this complex function.

Since this function has a definite angular frequency, ω, any quantum system with this wave function has a definite energy given by the de Broglie relation $E = \hbar\omega$ (6.23). Conversely, any quantum system that has a definite energy has a wave function of the form (7.11) — a statement we will prove in Section 7.11.

We saw in Chapter 6 that the probability density associated with a quantum wave function $\Psi(x, t)$ is the absolute value squared, $|\Psi(x, t)|^2$. For the complex standing wave (7.11) this has a remarkable property:

$$|\Psi(x, t)|^2 = |\psi(x)|^2 |e^{-i\omega t}|^2$$

or, since $|e^{-i\omega t}| = 1$,

$$|\Psi(x, t)|^2 = |\psi(x)|^2 \qquad \text{(for quantum standing waves)} \qquad (7.12)$$

That is, for a quantum standing wave, the probability density is *independent of time*. This is possible because the time-dependent part of the wave function,

$$e^{-i\omega t} = \cos \omega t - i \sin \omega t$$

is complex, with two parts that oscillate 90° out of phase; when one is growing, the other is shrinking in such a way that the sum of their squares is constant. Thus for a quantum standing wave, the distribution of matter (of electrons in an atom, or nucleons in a nucleus, for example) is time independent or *stationary*. For this reason a quantum standing wave is often called a **stationary state.** The stationary states are the modern counterpart of Bohr's stationary orbits and are precisely the states of definite energy. Because their charge distribution is static, atoms in stationary states do not radiate.*

An important practical consequence of (7.12) is that in most problems the only interesting part of the wave function $\Psi(x, t)$ is its spatial part $\psi(x)$. We will see that a large part of quantum mechanics is devoted to finding the possible spatial functions $\psi(x)$ and their corresponding energies. Our principal tool in finding these will be the time-independent Schrödinger equation.

7.4   The Particle in a Rigid Box

Before we write down the Schrödinger equation, we consider a simple example that we can solve using just our experience with standing waves on a string. We consider a particle that is confined to some finite interval on the x-axis, and moves freely inside that interval — a situation we describe as a **one-dimensional rigid box** and (for reasons we explain later) is often called the infinite square well. For example, in classical mechanics we could consider a bead on a frictionless straight thread between two rigid knots; the bead can move freely between the knots, but cannot escape outside them. In quantum mechanics we can imagine an electron inside a length of very thin conducting wire; to a fair approximation, the electron would move freely back and forth inside the wire, but could not escape from it.

Let us consider, then, a quantum particle of mass m moving nonrelativistically in a one-dimensional rigid box of length a, with no forces acting on it between $x = 0$ and $x = a$. The absence of forces means that the potential

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*Of course, atoms do radiate from excited states, but as we discuss in Chapter 11, this is always because some external influence disturbs the stationary state.

energy is constant inside the box, and we are free to choose that constant to be zero. Therefore, its total energy is just its kinetic energy. In quantum mechanics it is almost always more convenient to think of the kinetic energy as $p^2/2m$, rather than $\frac{1}{2}mv^2$, because of the de Broglie relation, $\lambda = h/p$ (6.1), between the momentum and wavelength. Therefore, we write the energy as

$$E = K = \frac{p^2}{2m} \tag{7.13}$$

As we have said, the states of definite energy are the standing waves. Therefore, to find the allowed energies, we must find the possible standing waves for the particle's wave function $\Psi(x, t)$. We have asserted that the standing waves have the form

$$\Psi(x, t) = \psi(x)e^{-i\omega t} \tag{7.14}$$

By analogy, with waves on a string, one might guess that the spatial function $\psi(x)$ will be a sinusoidal function inside the box; that is, $\psi(x)$ should have the form $\sin kx$ or $\cos kx$ or a combination of both:

$$\psi(x) = A \sin kx + B \cos kx \tag{7.15}$$

for $0 \le x \le a$. (We make no claim to have proved this; but it is certainly a reasonable guess, and we will prove it in Section 7.6.)

Since it is impossible for the particle to escape from the box, the wave function must be zero outside; that is, $\psi(x) = 0$ when $x < 0$ and when $x > a$. If we make the plausible (and, again, correct) assumption that $\psi(x)$ is continuous, then it must also vanish at $x = 0$ and $x = a$:

$$\psi(0) = \psi(a) = 0 \tag{7.16}$$

These are the boundary conditions that the wave function (7.15) must satisfy. Notice that these boundary conditions are identical to those for a classical wave on a string clamped at $x = 0$ and $x = a$.

From (7.15) we see that $\psi(0) = B$. Thus the wave function (7.15) can satisfy the boundary condition (7.16) only if the coefficient B is zero; that is, the condition $\psi(0) = 0$ restricts $\psi(x)$ to have the form

$$\psi(x) = A \sin kx \tag{7.17}$$
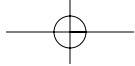
Next, the boundary condition that $\psi(a) = 0$ requires that

$$A \sin ka = 0 \tag{7.18}$$

which implies that*

$$ka = \pi, \quad \text{or } 2\pi, \quad \text{or } 3\pi, \ldots \tag{7.19}$$

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*Strictly speaking, (7.18) implies *either* that k satisfies (7.19) *or* that $A = 0$; but if $A = 0$, then $\psi = 0$ for all x, and we get no wave at all. Thus, only the solution (7.19) corresponds to a particle in a box. Notice also that there is no reason to include negative integer values of n in (7.20) since $\sin(-kx)$ is just a multiple of $\sin(kx)$.

or

$$k = \frac{n\pi}{a}, \qquad n = 1, 2, 3, \ldots \tag{7.20}$$

We conclude that the only standing waves that satisfy the boundary conditions (7.16) have the form $\psi(x) = A \sin kx$ with k given by (7.20). In terms of wavelength, this condition implies that

$$\lambda = \frac{2\pi}{k} = \frac{2a}{n} \qquad n = 1, 2, 3, \ldots \tag{7.21}$$

which is precisely the condition (7.3) for standing waves on a string. This is, of course, not an accident. In both cases, the quantization of wavelengths arose from the boundary condition that the wave function must be zero at $x = 0$ and $x = a$.

For our present discussion, the important point is that quantization of wavelength λ implies quantization of momentum, and hence also of energy. Specifically, substituting (7.21) into the de Broglie relation $p = h/\lambda$, we find that

$$p = \frac{nh}{2a} = \frac{n\pi\hbar}{a} \qquad n = 1, 2, 3, \ldots \tag{7.22}$$

Since $E = K + U$ and $U = 0$ in this case, we have $E = p^2/2m$. Therefore, (7.22) means that the allowed energies for a particle in a one-dimensional rigid box are

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2ma^2} \qquad n = 1, 2, 3, \ldots \tag{7.23}$$

The lowest energy for our particle, termed the **ground-state energy,** is obtained when $n = 1$ and is

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2} \tag{7.24}$$

This is consistent with the lower bound derived from the Heisenberg uncertainty principle in Chapter 6, where we argued — see (6.39) — that for a particle confined in a region of length a,
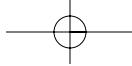
$$E \geq \frac{\hbar^2}{2ma^2} \tag{7.25}$$

For our particle in a rigid box, the actual minimum energy (7.24) is larger than the lower bound (7.25) by a factor of $\pi^2 \approx 10$.

In terms of the ground-state energy E_1, the energy of the nth level (7.23) is

$$E_n = n^2 E_1 \qquad n = 1, 2, 3, \ldots \tag{7.26}$$

These energy levels are sketched in Fig. 7.5. Notice that (quite unlike those of the hydrogen atom) the energy levels are farther and farther apart as n increases and that E_n increases without limit as $n \to \infty$. The corresponding wave functions $\psi(x)$ (which look exactly like the standing waves on a string)

FIGURE 7.5

A composite picture showing the first four energy levels and wave functions for a particle in a rigid box. Each horizontal line indicates an energy level and is also used as the axis for a plot of the corresponding wave function.

have been superimposed on the same picture, the wave function for each level being plotted on the line that represents its energy. Notice how the number of nodes of the wave functions increases steadily with energy; this is what one should expect since more nodes mean shorter wavelength (larger curvature of ψ) and hence larger momentum and kinetic energy.

The complete wave function $\Psi(x, t)$ for any of our standing waves has the form

$$\Psi(x, t) = \psi(x)e^{-i\omega t} = A\sin(kx)e^{-i\omega t}$$

We can rewrite this, using the identity (Problem 7.16)

$$\sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2i} \tag{7.27}$$

to give

$$\Psi(x, t) = \frac{A}{2i}\left(e^{i(kx-\omega t)} - e^{-i(kx+\omega t)}\right) \tag{7.28}$$
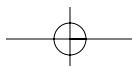
We see that our quantum standing wave (just like the classical standing wave of Section 7.2) can be expressed as the sum of two traveling waves, one moving to the right and one moving to the left. The wave moving to the right represents a particle with momentum $\hbar k$ *directed to the right*, and that moving to the left, a particle with momentum of the same magnitude $\hbar k$ but *directed to the left*. Thus a particle in one of our stationary states has a definite magnitude, $\hbar k$, for its momentum but is an equal superposition of momenta in either direction. This corresponds to the result that *on average* a classical particle is equally likely to be moving in either direction as it bounces back and forth inside a rigid box.
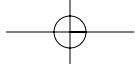
7.5   The Time-Independent Schrödinger Equation

Our discussion of the particle in a rigid box depended on some guessing as to the form of the spatial wave function $\psi(x)$. There are very few problems where this kind of guesswork is possible, and no problems where it is entirely satisfying. What we need is the equation that determines $\psi(x)$ in *any* problem, and this equation is the time-independent Schrödinger equation. Like all basic laws of physics, the Schrödinger equation cannot be *derived*. It is simply a relation, like Newton's second law, that experience has shown to be true. Thus a legitimate procedure would be simply to state the equation and to start using it. Nevertheless, it may be helpful to offer some arguments that *suggest* the equation, and this is what we will try to do.

Almost all laws of physics can be expressed as *differential equations*, that is, as equations that involve the variable of interest and some of its derivatives. The most familiar example is Newton's second law for a single particle, which we can write as

$$m\frac{d^2x}{dt^2} = \sum F \tag{7.29}$$

If, for example, the particle in question were immersed in a viscous fluid that exerted a drag force $-bv$, and attached to a spring that exerted a restoring force $-kx$, then (7.29) would read

$$m\frac{d^2x}{dt^2} = -b\frac{dx}{dt} - kx \tag{7.30}$$

This is a differential equation for the particle's position x as a function of time t, and since the highest derivative involved is the second derivative, the equation is called a *second-order differential equation*.

The equation of motion for classical waves (which is often not discussed in an introductory physics course) is a differential equation. It is therefore natural to expect the equation that determines the possible standing waves of a quantum system to be a differential equation. Since we already know the form of the wave functions for a particle in a rigid box, what we will do is examine these wave functions and try to spot a simple differential equation that they satisfy and that we can generalize to more complicated systems.

We saw in Section 7.4 that the spatial wave functions for a particle in a rigid box have the form

$$\psi(x) = A \sin kx \tag{7.31}$$

To find a differential equation that this function satisfies, we naturally differentiate it, to give

$$\frac{d\psi}{dx} = kA \cos kx \tag{7.32}$$

There are several ways in which we could relate $\cos kx$ in (7.32) to $\sin kx$ in (7.31) and hence obtain an equation connecting $d\psi/dx$ with ψ. However, a simpler course is to differentiate a second time to give

$$\frac{d^2\psi}{dx^2} = -k^2 A \sin kx \tag{7.33}$$

Comparing (7.33) and (7.31), we see at once that $d^2\psi/dx^2$ is proportional to ψ; specifically,
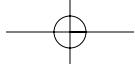
$$\frac{d^2\psi}{dx^2} = -k^2\psi \tag{7.34}$$

We can rewrite k^2 in (7.34) in terms of the particle's kinetic energy, K. We know that $p = \hbar k$. Therefore,

$$K = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \tag{7.35}$$

hence

$$k^2 = \frac{2mK}{\hbar^2} \tag{7.36}$$

Thus, we can write (7.34) as

$$\frac{d^2\psi}{dx^2} = -\frac{2mK}{\hbar^2}\psi \tag{7.37}$$

which gives us a second-order differential equation satisfied by the wave function $\psi(x)$ of a particle in a rigid box.

The particle in a rigid box is an especially simple system, with potential energy equal to zero throughout the region where the particle moves. It is not at all obvious how the equation (7.37) should be generalized to include the possibility of a nonzero potential energy, $U(x)$, which may vary from point to point. However, since the kinetic energy K is the difference between the total energy E and the potential energy $U(x)$, it is perhaps natural to replace K in (7.37) by

$$K = E - U(x) \tag{7.38}$$

This gives us the differential equation*

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}[U(x) - E]\psi \tag{7.39}$$

This differential equation is called the **Schrödinger equation** (**time-independent Schrödinger equation,** in full), to honor the Austrian physicist, Erwin Schrödinger, who first published it in 1926. Like us, Schrödinger had no way to *prove* that his equation was correct. All he could do was argue that the equation seemed reasonable and that its predictions should be tested against experiment. In the 80 years or so since then, it has passed this test repeatedly. In particular, Schrödinger himself showed that it predicts correctly the energy levels of the hydrogen atom, as we describe in Chapter 8. Today, it is generally accepted that the Schrödinger equation is the correct basis of nonrelativistic quantum mechanics, in just the same way that Newton's second law is accepted as the basis of nonrelativistic classical mechanics.

The Schrödinger equation as written in (7.39) applies to one particle moving in one dimension. We will need to generalize it later to cover systems of several particles, in two or three dimensions. Nevertheless, the general procedure for using the equation is the same in all cases. Given a system whose stationary states and energies we want to know, we must first find the potential energy function $U(x)$. For example, a particle held in equilibrium at $x = 0$ by a force obeying Hooke's law $(F = -kx)$ has potential energy

$$U(x) = \tfrac{1}{2}kx^2 \tag{7.40}$$

Erwin Schrödinger
(1887–1961, Austrian)

?
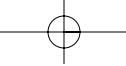
After learning of de Broglie's matter waves, Schrödinger proposed the equation — the Schrödinger equation — that governs the waves' behavior and earned him the 1933 Nobel Prize in physics. He left Austria after Hitler's invasion and became a professor in Dublin, Ireland. A person with remarkably broad interests, he was an ardent student of Italian painting and botany, as well as chemistry and physics. Late in his career, he became a pioneer in the new field of biophysics and wrote a popular book entitled *What is Life?*.

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*In more advanced texts this equation is usually written in the form

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi = E\psi$$

Because the differential operator $-(\hbar^2/2m)d^2/dx^2$ is intimately connected with the kinetic energy, this way of writing the **Schrödinger** equation is perhaps easier to remember because it looks like $K + U = E$. Nevertheless, for the applications in this book, the form (7.39) is the most convenient, and we will almost always write it this way.

An electron in a hydrogen atom has

$$U(r) = -\frac{ke^2}{r} \tag{7.41}$$

(We will return to this three-dimensional example in Chapter 8.) Once we have identified $U(x)$, the Schrödinger equation (7.39) becomes a well-defined equation that we can try to solve.* In most cases, it turns out that for many values of the energy E the Schrödinger equation *has no solutions* (no acceptable solutions, satisfying the particular conditions of the problem, that is). This is exactly what leads to the quantization of energies. Those values of E for which the Schrödinger equation has no solution are not allowed energies of the system. Conversely, those values of E for which there is a solution *are* allowed energies, and the corresponding solutions $\psi(x)$ give the spatial wave functions of these stationary states.

As we hinted in the last paragraph, there are usually certain conditions that the wave function $\psi(x)$ must satisfy to be an acceptable solution of the Schrödinger equation. First, there may be boundary conditions on $\psi(x)$, for example, the condition that $\psi(x)$ must vanish at the walls of a perfectly rigid box. In addition, there are certain general restrictions on $\psi(x)$; for example, as we anticipated in Section 7.4, $\psi(x)$ must always be *continuous*, and in most problems its first derivative must also be continuous. When we speak of an acceptable solution of the Schrödinger equation, we mean a solution that satisfies all the conditions appropriate to the problem at hand.

In this section you may have noticed that in quantum mechanics it is the potential energy $U(x)$ that appears in the basic equation, whereas in classical mechanics it is the *force F*. Of course, U and F are closely related: F being the derivative of U, U being the integral of F. Nevertheless, it is an important difference of emphasis that quantum mechanics focuses primarily on potential energies, whereas Newtonian mechanics focuses on forces.

7.6   The Rigid Box Again

As a first application of the Schrödinger equation, we use it to rederive the allowed energies of a particle in a rigid box and check that we get the same answers as before.† The first step in applying the Schrödinger equation to any system is to identify the potential-energy function $U(x)$. Inside the box we can choose the potential energy to be zero, and outside the box it is infinite. This is the mathematical expression of our idealized *perfectly* rigid box — no finite amount of energy can remove the particle from it. Thus

$$U(x) = \begin{cases} 0 & \text{for } 0 \leq x \leq a \\ \infty & \text{for } x < 0 \text{ and } x > a \end{cases} \tag{7.42}$$

---

*The necessity of identifying U before one can solve the Schrödinger equation corresponds to the necessity of identifying the total force F on a classical particle before one can solve Newton's second law, $F = ma$. The two are, of course, closely related since $F = -dU/dx$.

† You may reasonably object that it is circular to apply the Schrödinger equation to a particle in a box, when we used the latter to derive the former. Nevertheless, it is a legitimate consistency check, as well as an instructive exercise, to see how the Schrödinger equation gives back the known energies and wave functions.

That $U(x) = \infty$ outside the box implies that the particle can never be found there and hence that the wave function $\psi(x)$ must be zero when $x < 0$ and when $x > a$. The potential-energy function is described as an infinitely deep potential well or an infinite square well because of the square ($90°$) angles at the bottom of the well. The continuity of $\psi(x)$ then requires that

$$\psi(0) = \psi(a) = 0 \qquad\qquad (7.43)$$

(all of which we had argued in Section 7.4). Inside the box, where $U(x) = 0$, the Schrödinger equation (7.39) reduces to

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi \qquad \text{for } 0 \le x \le a \qquad (7.44)$$

This is the differential equation whose solutions we must investigate. In particular, we want to find those values of E for which it has a solution satisfying the boundary conditions (7.43).

Before solving (7.44), we remark that it is a nuisance, both for the printer of a book and for the student taking notes, to keep writing the symbols $d\psi/dx$ and $d^2\psi/dx^2$. For this reason, we introduce the shorthand

$$\psi' \equiv \frac{d\psi}{dx} \quad \text{and} \quad \psi'' \equiv \frac{d^2\psi}{dx^2}$$

From now on we will use this notation whenever convenient. In particular, we rewrite (7.44) as

$$\psi''(x) = -\frac{2mE}{\hbar^2}\psi(x) \qquad\qquad (7.45)$$

We now consider whether there is an acceptable solution of (7.45) for any particular value of E, starting with the case that E is negative. (We do not expect any states with $E < 0$, since then E would be less than the minimum potential energy. But we have already encountered several unexpected consequences of quantum mechanics, and we should check this possibility.) If E were negative, the coefficient $-2mE/\hbar^2$ on the right of (7.45) would be *positive* and we could call it α^2, where

$$\alpha = \frac{\sqrt{-2mE}}{\hbar} \qquad\qquad (7.46)$$

With this notation, (7.45) becomes
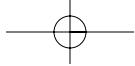
$$\psi''(x) = \alpha^2\psi(x) \qquad\qquad (7.47)$$

The simplification of rewriting (7.45) in the form (7.47) has the disadvantage of requiring a new symbol (namely α); but it has the important advantage of letting us focus on the mathematical structure of the equation.

Equation (7.47) is a second-order differential equation, which has the solutions (Problem 7.22) $e^{\alpha x}$ and $e^{-\alpha x}$ or any combination of these,

$$\psi(x) = Ae^{\alpha x} + Be^{-\alpha x} \qquad\qquad (7.48)$$

where A and B are any constants, real or complex.

It is important in what follows that (7.48) is the most general solution of (7.47), that is, that *every* solution of (7.47) has the form (7.48). This follows from a theorem about second-order differential equations of the same type as the one-dimensional Schrödinger equation.* This theorem states three facts: First, these equations always have two independent solutions. For example, $e^{\alpha x}$ and $e^{-\alpha x}$ are two independent solutions of (7.47).† Second, if $\psi_1(x)$ and $\psi_2(x)$ denote two such independent solutions, then the linear combination

$$A\psi_1(x) + B\psi_2(x) \qquad (7.49)$$

is also a solution, for any constants A and B. (This is the superposition principle.) Third, given two independent solutions $\psi_1(x)$ and $\psi_2(x)$, *every* solution can be expressed as a linear combination of the form (7.49). These three properties are illustrated in Problems 7.22 to 7.28.

That the general solution of a second-order differential equation contains two arbitrary constants is easy to understand: A second-order differential equation amounts to a statement about the second derivative ψ''; to find ψ, one must somehow accomplish two integrations, which should introduce two constants of integration; and this is what the two arbitrary constants A and B in (7.49) are. The theorem above is very useful in seeking solutions of such differential equations. If, by any means, we can spot two independent solutions, we are assured that *every* solution is a combination of these two. Since $e^{\alpha x}$ and $e^{-\alpha x}$ are independent solutions of (7.47), it follows from the theorem that the most general solution is (7.48).

Equation (7.48) gives all solutions of the Schrödinger equation for negative values of E. The important question now is whether any of these solutions could satisfy the required boundary conditions (7.43), and the answer is "no." With $\psi(x)$ given by (7.48), the condition that $\psi(0) = 0$ implies that

$$A + B = 0$$

while the requirement that $\psi(a) = 0$ implies that

$$Ae^{\alpha a} + Be^{-\alpha a} = 0$$

One can verify (Problem 7.23) that the only values of A and B that satisfy these two simultaneous equations are $A = B = 0$. That is, if $E < 0$, the only solution of the Schrödinger equation that satisfies the boundary conditions is the zero function. In other words, with $E < 0$, there can be no standing waves, so negative values of E are not allowed. A similar argument gives the same conclusion for $E = 0$.

Let us next see if the Schrödinger equation (7.45) has any acceptable solutions for positive energies (as we expect it does). With $E > 0$, the coefficient $-2mE/\hbar^2$ on the right of (7.45) is negative and can conveniently be called $-k^2$ where

$$k = \frac{\sqrt{2mE}}{\hbar} \qquad (7.50)$$

---

*To be precise, ordinary second-order differential equations that are linear and homogeneous.

† When we say that two functions are *independent*, we mean that neither function is just a constant multiple of the other. For example, $e^{\alpha x}$ and $e^{-\alpha x}$ are independent, but $e^{\alpha x}$ and $2e^{\alpha x}$ are not; similarly $\sin x$ and $\cos x$ are independent, but $5\cos x$ and $\cos x$ are not.

With this notation, the Schrödinger equation reads

$$\psi''(x) = -k^2 \psi(x) \tag{7.51}$$

This differential equation has the solutions $\sin kx$ and $\cos kx$, or any combination of both:

$$\psi(x) = A \sin kx + B \cos kx \tag{7.52}$$

(see Example 7.1 below). This is exactly the form of the wave function that we assumed at the beginning of Section 7.4. The important difference is that in Section 7.4 we could only guess the form (7.52), whereas we have now *derived* it from the Schrödinger equation. From here on, the argument follows precisely the argument given before. As we saw, the boundary condition $\psi(0) = 0$ requires that the coefficient B in (7.52) be zero, whereas the condition that $\psi(a) = 0$ can be satisfied without A being zero, provided that ka is an integer multiple of π (so that $\sin ka = 0$); that is,

$$k = \frac{n\pi}{a}$$

or, from (7.50),

$$E = \frac{\hbar^2 k^2}{2m} = n^2 \frac{\pi^2 \hbar^2}{2ma^2}$$

exactly as before.

Example 7.1

Verify explicitly that the function (7.52) is a solution of the Schrödinger equation (7.51) for any values of the constants A and B. [This illustrates part of the theorem stated in connection with (7.49).]
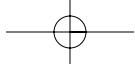
To verify that a given function satisfies an equation, one must substitute the function into one side of the equation and then manipulate it until one arrives at the other side. Thus, for the proposed solution (7.52),

$$\begin{aligned}
\psi''(x) &= \frac{d^2}{dx^2}(A \sin kx + B \cos kx) \\
&= \frac{d}{dx}(kA \cos kx - kB \sin kx) \\
&= -k^2 A \sin kx - k^2 B \cos kx \\
&= -k^2(A \sin kx + B \cos kx) \\
&= -k^2 \psi(x)
\end{aligned}$$

and we conclude that the proposed solution does satisfy the desired equation.

There is one loose end in our discussion of the particle in a rigid box that we can now dispose of. We have seen that the stationary states have wave functions

$$\psi(x) = A \sin \frac{n\pi x}{a} \tag{7.53}$$

but we have not yet found the constant A. Whatever the value of A, the function (7.53) satisfies the Schrödinger equation and the boundary conditions. Clearly, therefore, neither the Schrödinger equation nor the boundary conditions fix the value of A.

To see what does fix A, recall that $|\psi(x)|^2$ is the probability density for finding the particle at x. This means, in the case of a one-dimensional system, that $|\psi(x)|^2\,dx$ is the probability P of finding the particle between x and $x + dx$.

$$P(\text{between } x \text{ and } x + dx) = |\psi(x)|^2\,dx \tag{7.54}$$

Since the total probability of finding the particle *anywhere* must be 1, it follows that

$$\int_{-\infty}^{\infty} |\psi(x)|^2\,dx = 1 \tag{7.55}$$

This relation is called the **normalization condition** and a wave function that satisfies it is said to be **normalized.** It is the condition (7.55) that fixes the value of the constant A, which is therefore called the **normalization constant.**

In the case of the rigid box, $\psi(x)$ is zero outside the box; therefore, (7.55) can be rewritten as

$$\int_{0}^{a} |\psi(x)|^2\,dx = 1 \tag{7.56}$$

or, with the explicit form (7.53) for $\psi(x)$,

$$A^2 \int_{0}^{a} \sin^2\!\left(\frac{n\pi x}{a}\right) dx = 1 \tag{7.57}$$

The integral here turns out to be $a/2$ (Problem 7.29). Therefore, (7.57) implies that

$$\frac{A^2 a}{2} = 1 \tag{7.58}$$
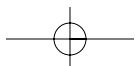
and hence that*

$$A = \sqrt{\frac{2}{a}} \tag{7.59}$$

We conclude that the normalized wave functions for the particle in a rigid box are given by

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a} \tag{7.60}$$

---

*You may have noticed that, strictly speaking, the argument leading from (7.55) to (7.59) implies only that the *absolute value* of A is $\sqrt{2/a}$. However, since the probability density depends only on the absolute value of ψ, we are free to choose any value of A satisfying $|A| = \sqrt{2/a}$ (for example, $A = -\sqrt{2/a}$ or $i\sqrt{2/a}$); the choice (7.59) is convenient and customary.

Example 7.2

Consider a particle in the ground state of a rigid box of length a. **(a)** Find the probability density $|\psi|^2$. **(b)** Where is the particle most likely to be found? **(c)** What is the probability of finding the particle in the interval between $x = 0.50a$ and $x = 0.51a$? **(d)** What is it for the interval $[0.75a, 0.76a]$? **(e)** What would be the average result if the position of a particle in the ground state were measured many times?

(a) The probability density is just $|\psi(x)|^2$, where $\psi(x)$ is given by (7.60) with $n = 1$. Therefore, it is

$$|\psi(x)|^2 = \frac{2}{a}\sin^2\left(\frac{\pi x}{a}\right) \tag{7.61}$$

which is sketched in Fig. 7.6.

(b) The most probable value x, is the value of x for which $|\psi(x)|^2$ is maximum. From Fig. 7.6 this is clearly seen to be

$$x_{mp} = a/2 \tag{7.62}$$

(c) The probability of finding the particle in any small interval from x to $x + \Delta x$ is given by (7.54) as

$$P(\text{between } x \text{ and } x + \Delta x) \approx |\psi(x)|^2\,\Delta x \tag{7.63}$$

(This is exact in the limit $\Delta x \rightarrow 0$ and is therefore a good approximation for any small interval Δx.) Thus, the two probabilities are

$$P(0.50a \leq x \leq 0.51a) \approx |\psi(0.50a)|^2\,\Delta x = \frac{2}{a}\sin^2\left(\frac{\pi}{2}\right) \times 0.01a$$

$$= 0.02 = 2\%$$

(d) and, similarly,
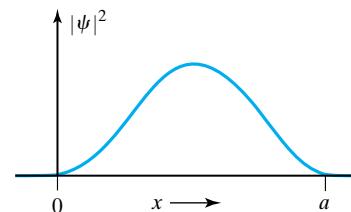
$$P(0.75a \leq x \leq 0.76a) \approx \frac{2}{a}\sin^2\left(\frac{3\pi}{4}\right) \times 0.01a = 0.01 = 1\%$$

(e) The average result if we measure the position many times (always with the particle in the same state) is the integral, over all possible positions, of x times the probability of finding the particle at x:
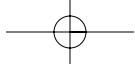
$$\langle x \rangle = \int_0^a x|\psi(x)|^2\,dx \tag{7.64}$$

(If you are not familiar with this argument, see the following paragraphs.) This average value $\langle x \rangle$ (also denoted $\bar{x}$ or x_{av}) is often called the **expectation value** of x. (But note that it is not the value we expect in any one measurement; it is rather the average value expected after many measurements.) In the present case

$$\langle x \rangle = \frac{2}{a}\int_0^a x\sin^2\left(\frac{\pi x}{a}\right)dx \tag{7.65}$$


FIGURE 7.6

The probability density $|\psi(x)|^2$ for a particle in the ground state of a rigid box. Inside the box, $|\psi|^2$ is given by (7.61); outside, it is zero.

This integral can be evaluated to give (Problem 7.33)

$$\langle x \rangle = \frac{a}{2} \tag{7.66}$$

an answer that is easily understood from Fig. 7.6: Since $|\psi(x)|^2$ is symmetric about the middle position $x = a/2$, the average value must be $a/2$. We see from (7.62) and (7.66) that for the ground state of a rigid box, the most probable position x_{mp} and the mean position $\langle x \rangle$ are the same. We will see in the next example that x_{mp} and $\langle x \rangle$ are not always equal.

Expectation Values

In Example 7.2 we introduced the notion of the expectation value $\langle x \rangle$ of x. This is *not* the value of x expected in any one measurement; rather it is the average value expected if we repeat the measurement many times (always with the system in the same state). This kind of average comes up in many other branches of physics, especially in statistical mechanics, and is worth discussing in a little more detail. In particular, we want to justify the expression (7.64).

Suppose that we are interested in a quantity x that can take on various values with definite probabilities. The quantity x could be a continuous variable, such as the position of a quantum particle, or a discrete variable, such as the number of offspring of a female fruit fly chosen at random in a large colony of fruit flies. Let us consider first the discrete case: Suppose that the possible results of the measurement are $x_1, x_2, \ldots, x_i, \ldots$ and that these results occur with probabilities $P_1, P_2, \ldots, P_i, \ldots$. This statement means that if a large number N of statistically independent measurements are made, the number of measurements resulting in value x_i will be $n_i = P_i \cdot N$; in other words, $P_i = n_i/N$ is the fraction of the measurements that yield the value x_i. The average value of x is the sum of all the results of all the measurements divided by the total number N. Since n_i of the measurements produce the value x_i, this sum of all the measurement results is $\sum_i n_i x_i$, and the average value is

$$\langle x \rangle = \frac{1}{N} \sum_i n_i x_i$$

This expression can be rewritten in terms of the probabilities P_i as

$$\langle x \rangle = \frac{1}{N} \sum_i n_i x_i = \sum_i \frac{n_i}{N} x_i = \sum_i P_i x_i \tag{7.67}$$

If x is a continuous variable, the probability P_i is replaced with a probability increment $p(x)\,dx$, where $p(x)$ is the probability density. [For example, in the case of interest to us now, x is the position of a quantum particle and the probability density is $p(x) = |\psi(x)|^2$.] The sum (7.67) becomes an integral,

$$\langle x \rangle = \sum_i x_i P_i \rightarrow \langle x \rangle = \int x p(x)\,dx. \tag{7.68}$$

In particular, for a quantum particle $p(x) = |\psi(x)|^2$, and we have the expression (7.64) for the expectation value of the position. More generally, if we

measure x^2 or x^3 or any function $f(x)$, we can repeat the same argument, simply replacing x with $f(x)$, and conclude that

$$\langle f(x) \rangle = \int f(x) p(x)\, dx \tag{7.69}$$

Example 7.3

Answer the same questions as in Example 7.2 but for the first excited state of the rigid box.

The wave function is given by (7.60) with $n = 2$, so

$$|\psi(x)|^2 = \frac{2}{a} \sin^2\!\left(\frac{2\pi x}{a}\right)$$

This is plotted in Fig. 7.7, where it is clear that $|\psi(x)|^2$ has two equal maxima at

$$x_{mp} = \frac{a}{4} \quad \text{and} \quad \frac{3a}{4}$$

The expectation value $\langle x \rangle$ is easily found without actually doing any integration. Since $|\psi(x)|^2$ is symmetric about $x = a/2$, contributions to the integral (7.64) from either side of $x = a/2$ exactly balance one another, and we find the same answer as for the ground state

$$\langle x \rangle = \frac{a}{2}$$

The probabilities of finding the particle in any small intervals are given by (7.63) as

$$P(0.50a \le x \le 0.51a) \approx |\psi(0.50a)|^2\, \Delta x = 0 \tag{7.70}$$

since* $\psi(0.50a) = 0$; and

$$P(0.75a \le x \le 0.76a) \approx |\psi(0.75a)|^2\, \Delta x = \frac{2}{a} \sin^2\!\left(\frac{3\pi}{2}\right) \times 0.01a = 0.02$$

In particular, notice that although $x = a/2$ is the average value of x, the probability of finding the particle in the immediate neighborhood of $x = a/2$ is zero. This result, although a little surprising at first, is easily understood by reference to Fig. 7.7.
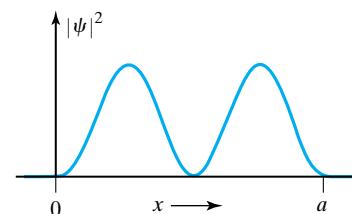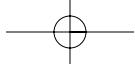

FIGURE 7.7
The probability density $|\psi(x)|^2$ for a particle in the first excited state ($n = 2$) of a rigid box.

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*Note that the probability for the interval $[0.50a, 0.51a]$ is not exactly zero since the probability density $|\psi(x)|^2$ is zero only at the one point $0.50a$. The significance of (7.70) is really that the probability for this interval is *very small* compared to the probability for intervals of the same width elsewhere.

7.7 The Free Particle

As a second application of the Schrödinger equation, we investigate the possible energies of a free particle; that is, a particle subject to no forces and completely unconfined (still in one dimension, of course). The potential energy of a free particle is constant and can be chosen to be zero. With this choice, we will show that the energy of the particle can have any positive value, $E \geq 0$. That is, the energy of a free particle is not quantized, and its allowed values are the same as those of a classical free particle.

To prove these assertions, we must write down the Schrödinger equation and find those E for which it has acceptable solutions. With $U(x) = 0$, the Schrödinger equation is

$$\psi''(x) = -\left(\frac{2mE}{\hbar^2}\right)\psi(x) \tag{7.71}$$

This is the same equation that we solved for a particle in a rigid box. However, there is an important difference since the free particle can be anywhere in the range

$$-\infty < x < \infty$$

Thus we must look for solutions of (7.71) for all x rather than just those x between 0 and a.

If we consider first the possibility of states with $E < 0$, the coefficient $-2mE/\hbar^2$ in front of ψ in (7.71) is positive and we can write (7.71) as

$$\psi''(x) = \alpha^2\psi(x)$$

where $\alpha = \sqrt{-2mE}/\hbar$. Just as with the rigid box, this equation has the solutions $e^{\alpha x}$ and $e^{-\alpha x}$ or any combination of both:

$$\psi(x) = Ae^{\alpha x} + Be^{-\alpha x} \tag{7.72}$$

But in the present case we can immediately see that none of these solutions can possibly be physically acceptable. The point is that (7.72) is the solution in the whole range $-\infty < x < \infty$. Now, as $x \to \infty$, the exponential $e^{\alpha x}$ grows without limit or "blows up," and it is not physically reasonable to have a wave function $\psi(x)$ that grows without limit as we move farther from the origin. Such a $\psi(x)$ cannot be normalized. The only way out of this difficulty is to have the coefficient A of $e^{\alpha x}$ in (7.72) equal to zero. Similarly, as $x \to -\infty$, the exponential $e^{-\alpha x}$ blows up; thus by the same argument the coefficient B must also be zero, and we are left with just the zero solution $\psi(x) \equiv 0$. That is, there are no acceptable states with $E < 0$, just as we expected.

The argument just given crops up surprisingly often in solving the Schrödinger equation. If a solution of the equation blows up as $x \to \infty$ or as $x \to -\infty$, that solution is obviously not acceptable. Thus we can add to our list of conditions that must be satisfied by an acceptable wave function $\psi(x)$ the requirement that $\psi(x)$ must not blow up as $x \to \pm\infty$. We speak of a function that satisfies this requirement as being "well behaved" as $x \to \pm\infty$. This requirement is actually another example of a boundary condition, since the "points" $x = \pm\infty$ are the boundaries of our system.

Let us next examine the possibility of states of our free particle with $E \geq 0$. In this case the Schrödinger equation can be written as

$$\psi''(x) = -\left(\frac{2mE}{\hbar^2}\right)\psi(x) = -k^2\psi(x) \qquad (7.73)$$

where

$$k = \frac{\sqrt{2mE}}{\hbar} \qquad (7.74)$$

As before, the general solution of this equation is

$$\psi(x) = A \sin kx + B \cos kx \qquad (7.75)$$

The important point about this solution is that neither $\sin kx$ nor $\cos kx$ blows up as $x \rightarrow \pm\infty$. Thus neither function suffers the difficulty that we encountered with negative energies,* and, for any value of k, the function (7.75) is an acceptable solution, for any constants A and B. According to (7.74), this means that all energies in the continuous range $0 \leq E < \infty$ are allowed. In particular, the energy of a free particle is not quantized. Evidently, it is only when a particle is confined in some way, that its energy is quantized.

To understand what the positive-energy wave functions (7.75) represent, it is helpful to recall the identities (Problem 7.16)

$$\sin kx = \frac{e^{ikx} - e^{-ikx}}{2i} \quad \text{and} \quad \cos kx = \frac{e^{ikx} + e^{-ikx}}{2} \qquad (7.76)$$

Substituting these expansions into the wave function (7.75), we can write

$$\psi(x) = Ce^{ikx} + De^{-ikx} \qquad (7.77)$$
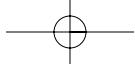
where you can easily find C and D in terms of the original coefficients A and B. It is important to note that since A and B were arbitrary, the same is true of C and D; that is, (7.77) is an acceptable solution for any values of C and D.

The full, time-dependent wave function $\Psi(x, t)$ for the spatial function (7.77) is

$$\Psi(x, t) = \psi(x)e^{-i\omega t} = Ce^{i(kx-\omega t)} + De^{-i(kx+\omega t)} \qquad (7.78)$$

This is a superposition of two traveling waves, one moving to the right (with coefficient C) and the other moving to the left (with coefficient D). If we choose the coefficient $D = 0$, then (7.78) represents a particle with definite momentum $\hbar k$ to the right; if we choose $C = 0$, then (7.78) represents a particle with momentum of the same magnitude $\hbar k$ but directed to the left. If both C and D are nonzero, then (7.78) represents a superposition of both momenta.

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*Although the function (7.75) doesn't blow up as $x \rightarrow \pm\infty$, it does still suffer a lesser difficulty, that it cannot be normalized since $\int_{-\infty}^{\infty}|\psi(x)|^2\,dx$ is infinite. However, this difficulty can be circumvented since we can build normalizable functions out of (7.75) using the Fourier integral.

7.8 The Nonrigid Box

So far, our only example of a particle that is confined, or bound, is the rather unrealistic case of a particle in a perfectly rigid box, the infinite square well. In this section we apply the Schrödinger equation to a particle in the more realistic nonrigid box, a potential well of finite depth. This is a rather long section, but the ideas it contains are all fairly simple and are central to an understanding of many quantum systems.

The first step in applying the Schrödinger equation to any system is to determine the potential-energy function. Therefore, we must first decide what is the potential energy, $U(x)$, of a particle in a nonrigid box. For a *rigid* box we know that

$$U(x) = \begin{cases} 0 & 0 \le x \le a \\ \infty & x < 0 \quad \text{and} \quad x > a \end{cases} \tag{7.79}$$

No finite amount of energy can remove the particle from a perfectly rigid box.* For most systems, a more realistic assumption would be that there is *a finite* minimum energy needed to remove a stationary particle from the box. If we call this minimum energy U_0, the potential-energy function would be

$$U(x) = \begin{cases} 0 & 0 \le x \le a \\ U_0 & x < 0 \quad \text{and} \quad x > a \end{cases} \tag{7.80}$$
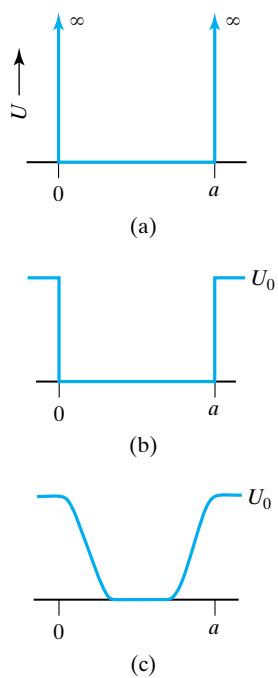

FIGURE 7.8

Three potential wells: **(a)** the infinite well (7.79); **(b)** the finite square well (7.80); **(c)** a finite rounded well.
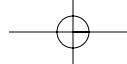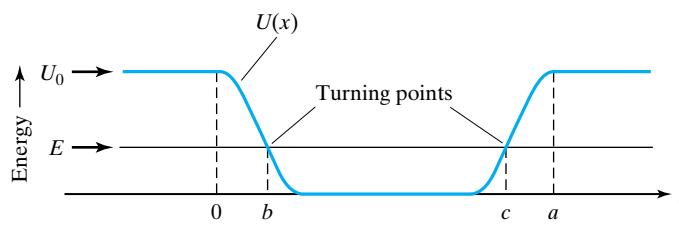
This potential, which we call the nonrigid box, is often called a finite square well. In Fig. 7.8(a) and (b) we plot the potential-energy functions (7.79) and (7.80).

Even the finite square well of Fig. 7.8(b) is somewhat unrealistic in that the potential energy jumps abruptly from 0 to U_0 at $x = 0$ and $x = a$. For a real particle in a box (for example, an electron in a conductor) the potential energy changes continuously near the walls, more like the well shown in Fig. 7.8(c). This well is sometimes called a *rounded well*. To simplify our discussion, we will suppose that the rounded well has $U(x)$ exactly constant, $U(x) = U_0$, for $x < 0$ and $x > a$, as shown in Fig. 7.8(c).

In this section we want to investigate the energy levels of a particle confined in a nonrigid box such as either Fig. 7.8(b) or (c). As one might expect, the properties of both wells are qualitatively similar.

Like the infinite well, the finite wells allow no states with $E < 0$ if we define the zero of U at the bottom of the well. (See Problem 7.38.) An important difference between the infinite and finite wells is that in the finite well the particle can escape from the well if $E > U_0$. This means that the wave functions for $E > U_0$ are quite similar to those of a free particle. In particular, the possible energies for $E > U_0$ are not quantized, but we will not pursue this point here since our main interest is in the bound states, whose energies lie in the interval $0 < E < U_0$.

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*Until about 30 years ago, one would have said that in this respect the perfectly rigid box is totally unrealistic — a real bound system might require a *large* energy to pull it apart, but surely not an infinite amount. As we discuss in Chapter 18, we now know that subatomic particles like neutrons and protons are made up of sub-subatomic particles called quarks, and that an infinite energy is needed to pull them apart (that is, they cannot be pulled apart). Thus a potential energy function like (7.79) may be more realistic than we had formerly appreciated.

FIGURE 7.9

The classical turning points. A classical particle of energy E trapped in the potential well oscillates back and forth, turning around at the points $x = b$ and $x = c$, where the kinetic energy is zero and hence $E = U(x)$.
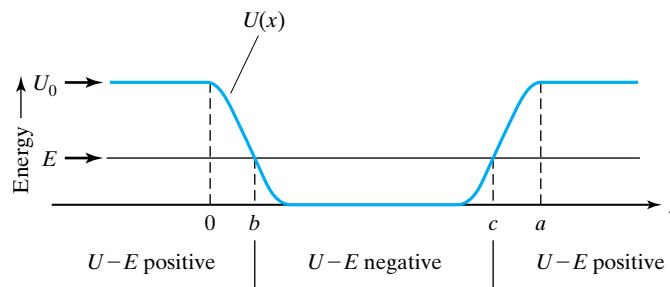
A classical particle moving in a finite well with energy in the interval $0 < E < U_0$ would simply bounce back and forth indefinitely. In the square well of Fig. 7.8(b) it would bounce between the points $x = 0$ and $x = a$. For the rounded well, the points at which the particle turns around are determined by the condition $E = U(x)$ (since the kinetic energy must be zero at the turning point where the particle comes instantaneously to rest). These points can be found graphically as in Fig. 7.9 by drawing a horizontal line at the height representing the energy E. The points $x = b$ and $x = c$, at which this line meets the potential-energy curve, are the two classical turning points, and a classical particle with energy E simply bounces back and forth between these points.

We now consider the Schrödinger equation,
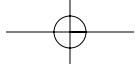
$$\psi''(x) = \frac{2m}{\hbar^2}[U(x) - E]\psi$$

for a quantum particle in a finite potential well. We seek values of E in the range $0 < E < U_0$, which possess physically acceptable solutions. To understand when we should expect to find allowed energies, it is useful to examine the general behavior of solutions of the Schrödinger equation.

Focusing attention on a particular value of E (with $0 < E < U_0$), we can distinguish two important ranges of x: those x where the factor $[U(x) - E]$ is positive and those x where it is negative. The dividing points between these regions are the classical turning points $x = b$ and $x = c$, where $U(x) = E$. (These were defined in Fig. 7.9 and are shown again in Fig. 7.10.) The regions where $[U(x) - E]$ is positive are outside these turning points ($x < b$ and $x > c$) and are often called the *classically forbidden regions* since a classical particle with energy E cannot penetrate there. The region where $[U(x) - E]$ is negative is the interval $b < x < c$ and is called the classically allowed region. The behavior of the wave function $\psi(x)$ is quite different in these two regions.

FIGURE 7.10

The factor $[U(x) - E]$, which appears on the right side of the Schrödinger equation, is positive for $x < b$ and $x > c$ and is negative for $b < x < c$.
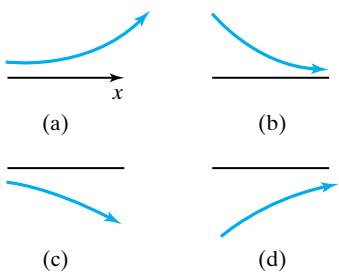
FIGURE 7.11

If $\psi(x)$ satisfies an equation of the form (7.81), it is concave away from the axis.

Wave Functions Outside the Well

In the region where $[U(x) - E]$ is positive, the Schrödinger equation has the form

$$\psi''(x) = (\text{positive function}) \times \psi(x) \qquad (7.81)$$

where the "positive function" is $(2m/\hbar^2)[U(x) - E]$. In an interval where $\psi(x)$ is positive, this implies that $\psi''(x)$ is also positive and hence that $\psi'(x)$ is increasing and $\psi(x)$ is concave *upward*, as in Fig. 7.11(a) and (b). If $\psi(x)$ is negative, then (7.81) implies that $\psi''(x)$ is negative and hence that $\psi(x)$ is concave *downward*, as in Fig. 7.11(c) and (d). In either case we see that $\psi(x)$ is concave *away from the x-axis*.

The behavior shown in Fig. 7.11 can be seen explicitly if we look in either of the regions $x < 0$ or $x > a$, where $U(x) = U_0 = \text{constant}$. The explicit form of $\psi(x)$ is readily found by solving the Schrödinger equation. Since $(U_0 - E) > 0$, we can define a number α by the equation

$$\frac{2m}{\hbar^2}[U_0 - E] = +\alpha^2 \qquad (7.82)$$

and the Schrödinger equation becomes

$$\psi''(x) = +\alpha^2 \psi(x) \qquad (7.83)$$

As we have seen before, the general solution of this differential equation has the form

$$\psi(x) = Ae^{\alpha x} + Be^{-\alpha x} \qquad (7.84)$$

with A and B arbitrary. As you can easily check, any function of this form is concave away from the x-axis as in Fig. 7.11.

If we look on the left of the well $(x < 0)$, then, as $x \rightarrow -\infty$, the exponential $e^{-\alpha x}$ blows up and is physically unacceptable. Thus, in the region $x < 0$, the solution (7.84) is physically acceptable only if $B = 0$.

Similarly, in the region $x > a$, the general solution has the same form

$$\psi(x) = Ce^{\alpha x} + De^{-\alpha x} \qquad x > a \qquad (7.85)$$
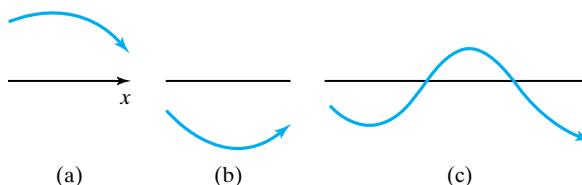
and this is acceptable only if $C = 0$. Thus, in these classically forbidden regions the physically acceptable wave functions die away exponentially as x goes to $\pm\infty$.

Wave Functions within the Well

In the region $b < x < c$, where $U(x) < E$, the Schrödinger equation has the form

$$\psi''(x) = (\text{negative function}) \times \psi(x) \qquad (7.86)$$

we can argue that $\psi(x)$ is concave *toward* the axis and tends to oscillate, as follows: If $\psi(x)$ is positive, then $\psi''(x)$ is negative and $\psi(x)$ curves *downward*, as in Fig. 7.12(a); if $\psi(x)$ is negative, the argument reverses and $\psi(x)$ bends

upward, as in Fig. 7.12(b). In either case, $\psi(x)$ curves toward the axis. If the interval $b < x < c$ is sufficiently wide, a function bending toward the axis will cross the axis and immediately start bending the other way, as in Fig. 7.12(c). Thus we can say that in the region $b < x < c$ the wave function tends to oscillate about the axis.

If the negative function in (7.86) has a large magnitude, then $\psi''(x)$ tends to be large and $\psi(x)$ curves and oscillates rapidly. Conversely, when the negative function is small, $\psi(x)$ bends gradually and oscillates slowly. This is all physically reasonable: The negative function in (7.86) is proportional to $[U(x) - E]$, which is just the negative of the kinetic energy; according to de Broglie, large kinetic energy means short wavelength and hence rapid oscillation, and vice versa.

For the case of a finite square well, where $U_0 = \text{constant} = 0$ within the well, the negative function of (7.86) is $-2mE/\hbar^2$. We can define a constant k by the equation

$$-\frac{2m}{\hbar^2}E = -k^2 \tag{7.87}$$

and the Schrödinger equation becomes

$$\psi''(x) = -k^2\psi \tag{7.88}$$

The most general solution of this equation is

$$\psi(x) = F \sin kx + G \cos kx \tag{7.89}$$
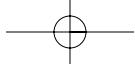
where F and G are arbitrary constants.

Solving for the allowed energies of a particle in a finite square well is rather messy. It involves starting with the general forms (7.84), (7.85), and (7.89), and then using the conditions that $\psi(x)$ and $\psi'(x)$ must be continuous at the edges of the well to solve for the coefficients A, D, F, and G (B and C are already known to be zero). It turns out there is no simple analytic solution to this problem and a numerical solution is needed, as explored in Problem 7.67. However, as we show in the next subsection, one can determine the detailed qualitative behavior of the solutions without doing any calculations at all.

### *Searching for Allowed Energies*

Now that we understand the qualitative behavior of solutions of the Schrödinger equation, let us return to our hunt for acceptable solutions. We consider the most general case of a rounded well of finite depth, and we start in the region $x < 0$, where $U(x)$ is constant (Fig. 7.10). There, the known, acceptable form is

$$\psi(x) = Ae^{\alpha x} \qquad (x < 0)$$

FIGURE 7.13

The wave function oscillates between the two turning points $x = b$ and $x = c$ and curves away from the axis outside them. The example shown is well behaved as $x \to -\infty$, but blows up as $x \to +\infty$.
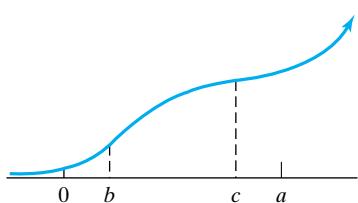
When we move to the right, our solution will cease to have this explicit form once $U(x)$ starts to vary, but it will continue to bend away from the axis until x reaches the point b. At $x = b$, it will start oscillating and continue to do so until $x = c$, where it will start curving away from the axis again. Thus, the general appearance of $\psi(x)$ will be as shown in Fig. 7.13, with two regions where $\psi(x)$ bends away from the axis, separated by one region where $\psi(x)$ oscillates. Figure 7.13 shows a solution that blows up on the right. We must now find out if there are any values of E for which the solution is well behaved both on the left and right.
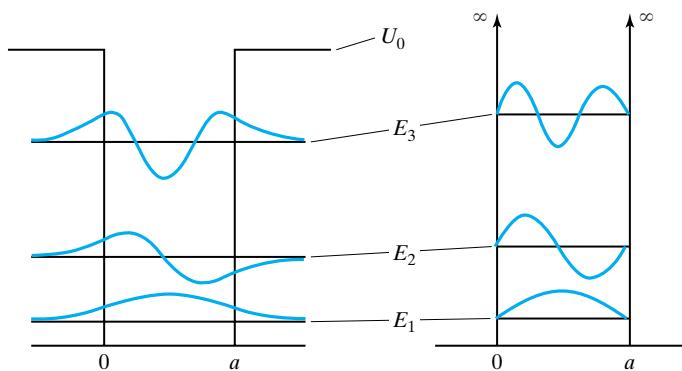
Let us begin a systematic search for allowed energies, starting with E close to zero. We will show first that with E sufficiently close to zero, an acceptable wave function is impossible. We start with the acceptable wave function $Ae^{\alpha x}$ in the region $x < 0$, and follow $\psi(x)$ to the right. When we reach the classical turning point $x = b$, $\psi(x)$ has a positive slope and starts to bend toward the axis. But with E very small, $\psi(x)$ bends very slowly. Thus, when we reach the second turning point $x = c$, the slope is still positive. With ψ and ψ' both positive, $\psi(x)$ continues to increase without limit, as shown in Fig. 7.14. Therefore, the wave function which is well behaved as $x \to -\infty$ blows up as $x \to +\infty$, and we conclude that there can be no acceptable wave function with E too close to zero.

FIGURE 7.14

When E is very small, the wave function bends too slowly inside the well. The function that has the form $Ae^{\alpha x}$ when $x < 0$ blows up as $x \to +\infty$.

Suppose now that we slowly increase E, continuing to hunt for an allowed energy. For larger values of E, the kinetic energy is larger and, as we have seen, $\psi(x)$ bends more rapidly inside the well. Thus it can bend enough that its slope becomes negative, as shown in Fig. 7.15, curve 2. Eventually, its value and slope at the right of the well will be just right to join onto the solution that is well behaved as $x \to \infty$, and we have an acceptable wave function (curve 3 in Fig. 7.15). If we increase E any further, $\psi(x)$ will bend over too far inside the well and will now approach $-\infty$ as $x \to \infty$, like curve 4 in Fig. 7.15. Evidently, there is exactly one allowed energy in the range explored so far.


FIGURE 7.15

Solutions of the Schrödinger equation for four successively larger energies. All four solutions have the well-behaved form $Ae^{\alpha x}$ for $x < 0$, but only number 3 is also well behaved as $x \to +\infty$.

If E is increased still further, the wave function may bend over *and back* just enough to fit onto the function that is well behaved as $x \to \infty$ as in Fig. 7.16(a). If this happens, we have a second allowed energy. Beyond this, we may find a third acceptable wave function, like that in Fig. 7.16(b), and so on.

Figure 7.17 shows the first three wave functions for a finite square well, beside the corresponding wave functions for an infinitely deep square well of

FIGURE 7.16

Wave functions for the second and third energy levels of a nonrigid box.

(a)   (b)

FIGURE 7.17
The lowest three energy levels and wave functions for a finite square well and for an infinite square well of the same width. The horizontal lines that represent each energy level have been used as the axes for drawing the corresponding wave functions.

the same width a. Notice the marked similarity of corresponding functions: The first wave function of the infinite well fits exactly half an oscillation into the well, while that of the finite well fits somewhat less than half an oscillation into the well since it doesn't actually vanish until $x = \pm\infty$. Similarly, the second function of the infinite well makes one complete oscillation, whereas that of the finite well makes just less than one oscillation. For this reason, the energy of each level in the finite well is slightly lower than that of the corresponding level in the infinite well.
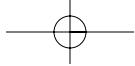
It is useful to note that the ground-state wave function for any finite well has no nodes, while that for the second level has one node, and that for the nth level has $n - 1$ nodes. This general trend (more nodes for higher energies) could have been anticipated since higher energy corresponds to a wave function that oscillates more quickly and hence has more nodes.

The wave functions in Fig. 7.17 illustrate two more important points. First, the wave functions of the finite well are nonzero outside the well, in the classically forbidden region. (Remember that a classical particle with energy $0 < E < U_0$ cannot escape outside the turning points.) However, since the wave function is largest inside the well, the particle is most likely to be found inside the well; and since $\psi(x)$ approaches zero rapidly as one moves away from the well, we can say that our particle is bound inside, *or close to*, the potential well. Nevertheless, there is a definite nonzero probability of finding the particle in the classically forbidden regions. This difference between classical and quantum mechanics is due to the wave nature of quantum particles. The ability of the quantum wave function to penetrate classically forbidden regions has important consequences, as we discuss in Section 7.10

A second important point concerns the number of bound states of the finite well. With the infinite well, one can increase E indefinitely and always encounter more bound states. With the finite well, however, the particle is no longer confined when E reaches U_0, and there are no more bound states. The number of bound states depends on the well depth U_0 and width a, but it is always finite. The number of bounds states can be approximately computed using a simple method described in Problem 7.45.

7.9 The Simple Harmonic Oscillator ★

★The simple harmonic oscillator plays an amazingly important role in many areas of quantum physics. Nevertheless, we won't be using the results of this section again until Chapter 12 on molecules. Thus you could, if you wish, omit it on a first reading.

As another example of a one-dimensional bound particle, we consider the simple harmonic oscillator. The name **simple harmonic oscillator (or SHO)** is used in classical and quantum mechanics for a system that oscillates about a stable equilibrium point to which it is bound by a force obeying Hooke's law, $F = -kx$.

Familiar classical examples of harmonic oscillators are a mass suspended from an ideal spring and a pendulum oscillating with small amplitude. Before we give any quantum examples, it may be worth recalling why the harmonic oscillator is such an important system. If a particle is in equilibrium at a point x_0, the total force F on the particle is zero at x_0; that is, $F(x_0) = 0$. If the particle is displaced slightly to a neighboring point x, the total force will be approximately

$$F(x) = F(x_0) + F'(x_0)(x - x_0) \tag{7.90}$$

with $F(x_0) = 0$ in this case. If x_0 is a point of stable equilibrium, the force is a restoring force; that is, $F(x)$ is negative when $x - x_0$ is positive, and vice versa. Therefore, $F'(x_0)$ must be negative and we denote it by $-k$, where k is called the *force constant*. With $F'(x_0) = -k$ and $F(x_0) = 0$, Eq. (7.90) becomes

$$F(x) = -k(x - x_0) \tag{7.91}$$

which is Hooke's law. Thus, any particle oscillating about a stable equilibrium point will oscillate harmonically* for sufficiently small displacements $(x - x_0)$.

An important example of a quantum harmonic oscillator is the motion of any one atom inside a solid crystal; each atom has a stable equilibrium position relative to its neighboring atoms and can oscillate harmonically about that position. Another important example is a diatomic molecule, such as HCl, whose two atoms can vibrate harmonically, in and out from one another.

In quantum mechanics we work, not with the force F, but with the potential energy U. This is easily found by integrating (7.91) to give

$$U(x) = -\int_{x_0}^{x} F(x)\, dx = \tfrac{1}{2}k(x - x_0)^2 \tag{7.92}$$

if we take U to be zero at x_0. Thus, in quantum mechanics the SHO can be characterized as a system whose potential energy has the form (7.92). This function is a parabola, with its minimum at $x = x_0$, as shown in Fig. 7.18(a).

It is important to remember that (7.91) and (7.92) are approximations that are usually valid only for small displacements from x_0. This point is illustrated in Fig. 7.18(b), which shows the potential energy of a typical diatomic molecule, as a function of the distance r between the two atoms. The molecule is in equilibrium at the separation r_0. For r close to r_0, the potential energy is well approximated by a parabola of the form $U(r) = \tfrac{1}{2}k(r - r_0)^2$, but when r is far from r_0, $U(r)$ is quite different. Thus for small displacements the molecule will behave like an SHO, but for large displacements it will not. This same statement can be made about almost any oscillating system. (For example, the
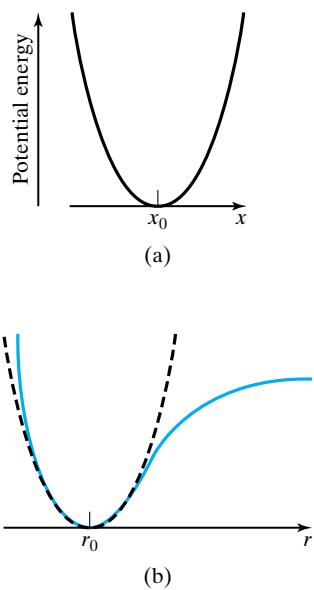
FIGURE 7.18

(a) The potential energy of an ideal simple harmonic oscillator is a parabola. **(b)** The potential energy of a typical diatomic molecule (solid curve) is well approximated by that of an SHO (dashed curve) when r is close to its equilibrium value r_0.

*Unless, of course, the first derivative happens to vanish at the equilibrium point, $F'(x_0) = 0$. This occurs for the quartic potential $U(x) \propto x^4$, with $F(x) \propto -x^3$, but we will not consider this special case here.

simple pendulum is well known to oscillate harmonically for small amplitudes, but not when the amplitude is large.) It is because small displacements from equilibrium are very common that the harmonic oscillator is so important.

There is a close connection between the classical and quantum harmonic oscillators, and we start with a quick review of the former. If we choose our origin at the equilibrium position, then $x_0 = 0$ and the force is $F = -kx$. If the particle has mass m, Newton's second law reads

$$ma = -kx$$

If we define the classical angular frequency

$$\omega_c = \sqrt{\frac{k}{m}} \tag{7.93}$$

this becomes

$$\frac{d^2x}{dt^2} = -\omega_c^2 x$$

which has the general solution

$$x = a \sin \omega_c t + b \cos \omega_c t \tag{7.94}$$

Thus, the position of the classical SHO varies sinusoidally in time with angular frequency ω_c. If we choose our origin of time, $t = 0$, at the moment when the particle is at $x = 0$ and moving to the right, then (7.94) takes the form

$$x = a \sin \omega_c t \tag{7.95}$$

The positive number a is the amplitude of the oscillations, and the particle oscillates between $x = a$ and $x = -a$. In other words, the points $x = \pm a$ are the classical turning points. When the particle is at $x = a$, all of its energy is potential energy; thus, $E = \frac{1}{2}ka^2$ and hence
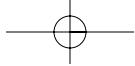
$$a = \sqrt{\frac{2E}{k}} \tag{7.96}$$

As one would expect, the classical amplitude a increases with increasing energy.

To find the allowed energies of a *quantum* harmonic oscillator, we must solve the Schrödinger equation with $U(x)$ given by

$$U(x) = \frac{1}{2}kx^2 \tag{7.97}$$

where we have again chosen $x_0 = 0$. Qualitatively, the analysis is very similar to that for the finite well discussed in the preceding section. For any choice of E, the solutions will bend away from the axis outside the classical turning points $x = a$ and $x = -a$ and will oscillate between these points. As before, most values of E do not produce an acceptable solution; only special values of E produce a solution that satisfies the boundary conditions, that is, decays exponentially as $x \to -\infty$ and $x \to \infty$. Thus, the allowed energies are quantized. The potential energy (7.97) increases indefinitely as x moves away from the

origin [see Fig. 7.18(a)], and the particle is therefore confined for all energies. In this respect, the SHO resembles the infinitely deep potential well, and we would expect to find infinitely many allowed energies, all of them quantized.

An important difference between the SHO and most other potential wells is that the Schrödinger equation for the SHO can be solved analytically. The solution is quite complicated and will not be given here. However, the answer for the energy levels is remarkably simple: The allowed energies turn out to be

$$E = \frac{1}{2}\hbar\sqrt{\frac{k}{m}}, \quad \frac{3}{2}\hbar\sqrt{\frac{k}{m}}, \quad \frac{5}{2}\hbar\sqrt{\frac{k}{m}}, \dots$$

The quantity $\sqrt{k/m}$ is the frequency ω_c, defined in (7.93), of a classical oscillator with the same force constant and mass. It is traditional to rewrite the allowed energies in terms of ω_c, as

$$E_n = \left(n + \tfrac{1}{2}\right)\hbar\omega_c \qquad n = 0, 1, 2, \dots \tag{7.98}$$

As anticipated, the allowed energies are all quantized, and there are levels with arbitrarily large energies. A remarkable feature of (7.98) is that the energy levels of the harmonic oscillator are all equally spaced. This is a property that we could not have anticipated in our qualitative discussion, but which emerges from the exact solution.

The allowed energies of the harmonic oscillator are shown in Fig. 7.19, which also shows the corresponding wave functions (each drawn on the line representing its energy). Notice the similarity of these wave functions to those of the finite well shown in Fig. 7.17. In particular, just as with the finite well, the lowest wave function has no nodes, the next has one node, and so on. Notice also that the wave functions with higher energy spread out farther from $x = 0$, just as the classical turning points $x = \pm a$ move farther out when E increases. Finally, note that the ground state ($n = 0$) has a zero-point energy (equal to $\frac{1}{2}\hbar\omega_c$) as required by the uncertainty principle, as discussed in connection with Eq. (6.39).

The wave functions shown in Fig. 7.19 were plotted using the known analytic solutions, which we list in Table 7.1, where, for convenience, we have introduced the parameter

$$b = \sqrt{\frac{\hbar}{m\omega_c}} \tag{7.99}$$
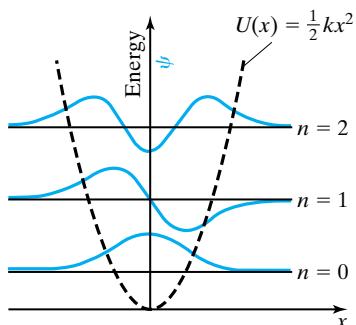
FIGURE 7.19

The first three energy levels and wave functions of the simple harmonic oscillator.

TABLE 7.1

The energies and wave functions of the first three levels of a quantum harmonic oscillator. The length b is defined as $\sqrt{\hbar/m\omega_c}$.

n	E_n	$\psi(x)$
0	$\frac{1}{2}\hbar\omega_c$	$A_0 e^{-x^2/2b^2}$
1	$\frac{3}{2}\hbar\omega_c$	$A_1 \dfrac{x}{b} e^{-x^2/2b^2}$
2	$\frac{5}{2}\hbar\omega_c$	$A_2\left(1 - 2\dfrac{x^2}{b^2}\right)e^{-x^2/2b^2}$

(This parameter has the dimensions of a length and is, in fact, the half-width of the SHO well at the ground-state energy — see Problem 7.48.) The factors A_0, A_1, and A_2 in the table are normalization constants*

Example 7.4

Verify that the $n = 1$ wave function given in Table 7.1 is a solution of the Schrödinger equation with $E = \frac{3}{2}\hbar\omega_c$. (For the cases $n = 0$ and $n = 2$, see Problems 7.49 and 7.52.)

The potential energy is $U = \frac{1}{2}kx^2$, and the Schrödinger equation is therefore

$$\psi'' = \frac{2m}{\hbar^2}\left(\tfrac{1}{2}kx^2 - E\right)\psi \qquad (7.100)$$

Differentiating the wave function ψ_1, of Table 7.1, we find that

$$\psi_1' = A_1\left(\frac{1}{b} - \frac{x^2}{b^3}\right)e^{-x^2/2b^2}$$

and

$$\psi_1'' = A_1\left(-\frac{3x}{b^3} + \frac{x^3}{b^5}\right)e^{-x^2/2b^2} = \left(\frac{x^2}{b^4} - \frac{3}{b^2}\right)A_1\frac{x}{b}e^{-x^2/2b^2}$$

where the last three factors together are just ψ_1. Using (7.99) to replace b, we find

$$\psi_1'' = \left(\frac{m^2\omega_c^2 x^2}{\hbar^2} - \frac{3m\omega_c}{\hbar}\right)\psi_1$$
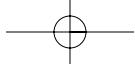
Replacing ω_c^2 by k/m in the first term, we get

$$\psi_1'' = \frac{2m}{\hbar^2}\left(\frac{1}{2}kx^2 - \frac{3}{2}\hbar\omega_c\right)\psi_1$$

which is precisely the Schrödinger equation (7.100), with $E = \frac{3}{2}\hbar\omega_c$ as claimed.

The properties of the quantum SHO are nicely illustrated by the example of a diatomic molecule, such as HCl. A diatomic molecule is, of course, a complicated, three-dimensional system. However, the energy of the molecule can be expressed as the sum of three terms: an electronic term, corresponding to the motions of the individual electrons; a rotational term, corresponding to rotation of the whole molecule; and a vibrational term, corresponding to the in-and-out, radial vibrations of the two atoms. Careful analysis of molecular spectra lets one disentangle the possible values of these three terms. In

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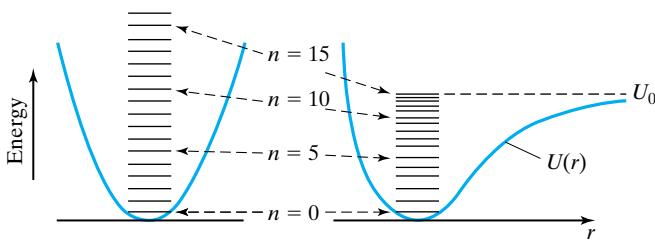
*The three functions in Table 7.1 illustrate what is true for all n, that the wave function of the nth level has the form $P_n(x)\exp(-x^2/2b^2)$, where $P_n(x)$ is a certain polynomial of degree n, called a Hermite polynomial.

FIGURE 7.20

Vibrational levels of a typical diatomic molecule (right) and the SHO that approximates the molecule for small displacements (left). The first five or so levels correspond very closely; the higher levels of the molecule are somewhat closer together, and the molecule has no levels above the energy U_0.

particular, the vibrational motion of the two atoms is one-dimensional (along the line joining the atoms) and the potential energy approximates the SHO potential. Therefore, the allowed values of the vibrational energy should approximate those of an SHO, and this is amply borne out by observation, as illustrated in Fig. 7.20.

The molecular potential energy $U(r)$ in Fig. 7.20 deviates from the parabolic shape of the SHO at higher energies. Therefore, we would expect the higher energy levels to depart from the uniform spacing of the SHO. This, too, is what is observed.

The observation of photons emitted when molecules make transitions between different vibrational levels is an important source of information on interatomic forces, as we discuss further in Chapter 12. These same photons can also be used to identify the molecule that emitted them. For example, the H_2 molecule emits infrared photons of frequency 1.2×10^{14} Hz when it drops from one vibrational level to the next. This radiation is used by astronomers to locate clouds of H_2 molecules in our galaxy.

7.10   Tunneling⋆

⋆The phenomenon of tunneling is perhaps second only to quantization of energy as a uniquely quantum phenomenon. It has many important applications, as we will mention here and in Chapters 14 and 17. However, we will not be using this material again until Chapter 14, so you could omit this section for now.

So far in this chapter, we have focused mainly on a particle that is confined inside a potential well, such as the rigid box of Section 7.6, or the harmonic oscillator well of Section 7.9. We have seen that for these confined, or bound, particles, the Schrödinger equation implies quantization of the allowed energies — one of the most dramatic differences between classical and quantum mechanics. We have also discussed one example of an unconfined particle, the free particle of Section 7.7, for which we found that the Schrödinger equation does not imply any quantization of energy. In this section we discuss a second example of an unconfined particle, for which the Schrödinger equation has implications almost as dramatic as the quantization of energy for bound states. Specifically, we will consider a particle whose potential energy has a "barrier" (to be defined in a moment). In classical mechanics such barriers are impenetrable and a particle on either side of the barrier cannot cross over to the other side. In quantum mechanics we will find that the particle can "tunnel" through the barrier and emerge on the other side. This **barrier penetration,** or **tunneling,** has dramatic consequences in several natural phenomena, such as radioactive decay (Chapter 17), and is the basis of several modern electronic devices, such as the scanning tunneling microscope (Chapter 14).

FIGURE 7.21

A rectangular barrier of height U_0 and width L.

A simple example of a barrier is shown in Fig. 7.21, which is a plot of the potential energy of an electron moving along an x-axis consisting of two identical conducting wires separated by a small gap from x_0 to x_1. The gap between

the two conductors could be just an air gap, or it could be a thin layer of dirt in a poorly made electrical connection. In either case the gap forms a barrier of thickness $L = x_1 - x_0$ between the two wires. Inside either wire the potential energy is a constant, which we can take to be zero, but in the barrier it has a higher value $U_0 > 0$. We will be interested in the case that the particle's energy is less than the barrier height, $0 < E < U_0$, as shown in Fig. 7.21. Under these conditions a classical particle is excluded from the barrier since with $E < U_0$ its kinetic energy between x_0 and x_1 would be negative — an impossibility in classical mechanics. Thus, a classical particle could approach the barrier from the left (for example) but would inevitably rebound straight back on arrival at x_0; it could certainly not emerge on the right of x_1 unless we gave it more energy. To see in detail what happens to a quantum particle when it hits this barrier, one must solve the Schrödinger equation with this potential-energy function $U(x)$. Although the solution is not especially difficult, we do not need to go through it since we can already understand its main features from our discussion of the finite square well in Section 7.8.

Consider first a barrier whose length L is *infinite*. This extreme case is shown in Fig. 7.22. It is sometimes called a *potential step* and is precisely the same as the right wall of the finite square well of Section 7.8 (Fig. 7.17). In Fig. 7.22 we have also shown the wave function $\psi(x)$ for an energy $E < U_0$. To the left of x_0, the kinetic energy $K = (E - U)$ is positive and $\psi(x)$ is an oscillating sinusoidal wave, some combination of $\sin kx$ and $\cos kx$. To the right of x_0, $(E - U)$ is negative and $\psi(x)$ is a decreasing exponential with the form

$$\psi(x) = Be^{-\alpha x} \tag{7.101}$$

where, you may recall [see (7.82) if you don't],

$$\alpha = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}} \tag{7.102}$$

As we emphasized in Section 7.8, the quantum particle has a nonzero probability of being found in the classically forbidden region where $E - U$ is negative.

In the infinitely long barrier of Fig. 7.22, $\psi(x)$ goes steadily to zero as x increases. But if the barrier has finite length, the situation is as shown in Fig. 7.23. Just as in Fig. 7.22, $\psi(x)$ is sinusoidal (with amplitude A_L) to the left

of x_0; and just as in Fig. 7.22, it decreases exponentially within the barrier ($x_0 < x < x_1$). But when we reach x_1 the barrier stops and, once again, ($E - U$) is positive. Therefore, before $\psi(x)$ has decreased to zero, it starts oscillating again with amplitude A_R. The probability that the particle is to the left of x_0, approaching the barrier, is proportional to A_L^2; the probability that it is to the right of the barrier is proportional to A_R^2. Therefore, there is a nonzero probability P that a particle striking the barrier from the left will escape to the right*:

$$P = \left(\frac{A_R}{A_L}\right)^2 \tag{7.103}$$

From Fig. 7.23, we see that A_R is less than A_L because of the exponential decrease of $\psi(x)$ within the barrier. Specifically[†]

$$\frac{A_R}{A_L} \approx \frac{e^{-\alpha x_1}}{e^{-\alpha x_0}} = e^{-\alpha L} \tag{7.104}$$

Therefore, the probability that a particle which strikes the rectangular barrier of Fig. 7.23 with energy $E < U_0$ will tunnel through and emerge on the other side is

$$P \approx e^{-2\alpha L} \tag{7.105}$$

where α is given by (7.102).
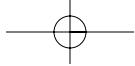
The probability (7.105) that a quantum particle will tunnel through the classically impenetrable barrier depends on the two variables: α, as given by (7.102), and L, the thickness of the barrier. In many applications the product αL is very large and the probability (7.105) is therefore very small. Nevertheless, if the particle keeps bumping against the barrier, it will eventually pass through it. This is what happens in the α decay of certain radioactive nuclei, as we will see in Section 17.10.

A modern application of quantum tunneling is the scanning tunneling microscope (STM). Here the surface of a sample is explored by measuring the electric current between the surface and a conducting probe that is scanned across the surface, just above it at a fixed height. This current is possible only because of quantum tunneling and the magnitude of the current is proportional to the probability (7.105) of tunneling through the barrier. This probability is sensitively dependent on L, the barrier thickness, that is, the distance between the probe and the surface. This means that by measuring the current, one can get a sensitive picture of the surface's topography, as we describe in detail in Chapter 14. (Meanwhile, see the beautiful picture of the surface of graphite made with an STM in Fig. 13.6.)

There are many other examples of quantum tunneling, but the two mentioned here are among the most important: The first is historically important

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*Our discussion here is a little oversimplified. Strictly speaking, we should be using wave functions e^{ikx} that travel in a definite direction, rather than sinusoidal functions. Nevertheless, the result (7.103) is a good enough approximation.

[†] Here, too, we are oversimplifying. In Fig. 7.23 you can see that the value of the exponential wave function at x_0 is not quite the same as the amplitude A_L. (Similarly, the value at x_1 is not quite equal to A_R.) Nevertheless, under the conditions of interest, (7.104) is a satisfactory approximation.

as the first application of quantum mechanics to a subatomic process, and the second is the basis for a modern and widely used experimental technique. Curiously, barrier penetration will not play an important role in our further development of quantum theory, and our focus for the next several chapters will be on bound states similar to those described in Sections 7.4 through 7.9. However, we will return to barrier penetration in Chapters 14 and 17.

Example 7.5

Consider two identical conducting wires, lying on the x axis and separated by an air gap of thickness $L = 1$ nm, (that is, a few atomic diameters). An electron that is moving inside either conductor has potential energy zero, whereas in the gap its potential energy is $U_0 > 0$. Thus the gap is a barrier of the type illustrated in Fig. 7.21. The electron approaches the barrier from the left with energy E such that $U_0 - E = 1$ eV; that is, the electron is 1 eV below the top of the barrier. What is the probability that the electron will emerge on the other side of the barrier? How different would this be if the barrier were twice as wide?

The required probability is given by Equation (7.105) with

$$\alpha = \frac{\sqrt{2m(U_0 - E)}}{\hbar} = \frac{\sqrt{2mc^2(U_0 - E)}}{\hbar c}$$
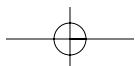
$$\approx \frac{\sqrt{2 \times (5 \times 10^5 \, \text{eV}) \times (1 \, \text{eV})}}{197 \, \text{eV} \cdot \text{nm}} \approx 5.1 \, \text{nm}^{-1}$$
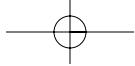
Thus $\alpha L = 5.1$ and the transmission probability is $P = e^{-2\alpha L} = e^{-10.2} = 3.7 \times 10^{-5}$ or about 0.004%. This probability is not large, but if we send enough electrons at the barrier, some will certainly get through. If we double L, this will give a transmission probability $P' = e^{-4\alpha L} = e^{-20.4} = 1.4 \times 10^{-9}$ — a dramatically smaller result. This illustrates the extreme sensitivity of the transmission probability to the width of the gap — a property that is exploited in the scanning tunneling microscope.

7.11 The Time-Dependent Schrödinger Equation*

*The time-dependent Schrödinger equation is one of the principal cornerstones of quantum theory. Nevertheless, it is used surprisingly little in practical calculations, and we will use it only in Chapter 11. Thus, you could skip this section on a first reading without significant loss of continuity.

As we mentioned at the start of this chapter, there are in fact two Schrödinger equations — the time-independent Schrödinger equation, which has been our main subject up to now, and the time-*dependent* Schrödinger equation. The latter is one of the basic equations of quantum mechanics: It determines the time evolution of any quantum system and is the analog of Newton's second law, $\mathbf{F} = m\mathbf{a}$, in classical mechanics. Among all the many solutions of the time-dependent Schrödinger equation, the most important are the stationary states (or states of definite energy); and for these, the time-dependent Schrödinger equation reduces to the time-independent equation, as we will prove in this section. Because the stationary states are by far the most important states in practice, it is the time-independent Schrödinger equation that one uses in

almost all practical problems. Nevertheless, you should have some acquaintance with the time-dependent equation, and that is the purpose of this section.

Before we write down the time-dependent Schrödinger equation, it is helpful to note that the time-independent Schrödinger equation (7.39) can be rewritten (as you should check) in the form

$$E\psi(x) = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)\right)\psi(x) \qquad (7.106)$$

This is the equation that (we have claimed) determines the possible energies E and the corresponding spatial wave functions $\psi(x)$ for a particle whose potential energy is $U(x)$. The full wave function for the same particle, including its time dependence, is denoted $\Psi(x, t)$ and the time dependence of any such wave function is determined by the time-dependent Schrödinger equation,

$$ih\frac{\partial}{\partial t}\Psi(x, t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right)\Psi(x, t) \qquad (7.107)$$

There is no way to *prove* that this equation is correct. Just like its counterpart $\mathbf{F} = m\mathbf{a}$ in classical mechanics, it is ultimately an axiom, an assumption, that is justified by the success of its many predictions. Nevertheless, we can motivate the form of this equation with the following plausibility argument.

We are searching for a wave equation, a differential equation that wave functions must obey, and we can use the free-particle wave function as a test case. We assume that a free particle has the wave function $\Psi(x, t) = e^{i(kx-\omega t)}$ and has a (purely kinetic) energy given by $E = \hbar\omega = \hbar^2 k^2/2m$. Any candidate wave equation must have this wave function as its solution for the special case $U(x) = 0$. Guided by the energy equation $\hbar\omega = \hbar^2 k^2/2m$, we seek differential operators that produce factors of ω and k^2, and we find that the operators $\partial/\partial t$ and $\partial^2/\partial x^2$ do just that:

$$\frac{\partial}{\partial t}e^{i(kx-\omega t)} = -i\omega e^{i(kx-\omega t)} \quad \text{and} \quad \frac{\partial^2}{\partial x^2}e^{i(kx-\omega t)} = -k^2 e^{i(kx-\omega t)}$$

And so we can construct an equation,

$$-i\hbar\frac{\partial}{\partial t}\left[e^{i(kx-\omega t)}\right] = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left[e^{i(kx-\omega t)}\right]$$
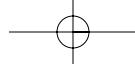
which can be viewed as a reflection of the relation $E = K$ for a free particle. We have just demonstrated that the equation

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

is correct for the special case of a free particle (potential $U = 0$). Schrödinger generalized this equation by adding a potential energy term, producing his famous result:

$$-i\hbar\frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + U(x)\Psi$$

Thus, Schrödinger's time-dependent equation can be viewed as an energy equation: The total energy is kinetic plus potential, $E = K + U$.

Notice that the time-dependent Schrödinger equation involves derivatives with respect to t and x. Since $\Psi(x, t)$ depends on two variables, these derivatives are *partial derivatives*, and the time-dependent Schrödinger equation is a *partial differential equation*.* It has a vast array of solutions, some of which are very complicated, but by far its most important solutions are the stationary states, and these are relatively simple. Recall that we claimed earlier that these are standing waves, with the form (7.11)

$$\Psi(x, t) = \psi(x)e^{-i\omega t} \qquad (7.108)$$

and that the spatial wave function $\psi(x)$ had to satisfy the time-*independent* Schrödinger equation. We can now prove these claims.

Let us suppose first that the function (7.108) does satisfy the time-dependent Schrödinger equation (7.107). Substituting into (7.107), we find that

$$i\hbar\frac{\partial}{\partial t}\Psi(x, t) = \hbar\omega\psi(x)e^{-i\omega t} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right)\psi(x)e^{-i\omega t}$$

Recognizing that $\hbar\omega = E$ (the de Broglie hypothesis) and canceling the common factor of $e^{-i\omega t}$, we see that

$$E\psi(x) = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)\right)\psi(x) \qquad (7.109)$$

which is precisely the time-independent Schrödinger equation (7.106). Thus, if the standing wave (7.108) satisfies the time-dependent Schrödinger equation, its spatial part must satisfy the time-independent Schrödinger equation. Conversely, if $\psi(x)$ satisfies the time-independent equation (7.109), we can follow the same steps backward and conclude that the standing wave (7.108) satisfies the time-dependent equation.

Although stationary states, given by the standing waves (7.108), are solutions — and very important solutions — of the time-dependent Schrödinger equation, they are by no means the only solutions. To see this, suppose that we have two stationary states,
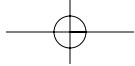
$$\Psi_1(x, t) = \psi_1(x)e^{-i\omega_1 t} \quad \text{and} \quad \Psi_2(x, t) = \psi_2(x)e^{-i\omega_2 t} \qquad (7.110)$$

where $\hbar\omega_1 = E_1$ and $\hbar\omega_2 = E_2$ are the corresponding energies. To be definite, we could consider ψ_1 and ψ_2 to be the lowest two wave functions of the rigid box as given in Equation (7.60) with $n = 1$ and 2. Because each of these functions satisfies the time-dependent Schrödinger equation, it is easy to see that the same is true of any linear combination of the form

$$\Psi(x, t) = \alpha\Psi_1(x, t) + \beta\Psi_2(x, t) \qquad (7.111)$$

for any two fixed numbers α and β. (That is, the superposition principle applies to the time-dependent Schrödinger equation.) To prove this, just

*There is a brief review of partial derivatives in Section 8.2. If your knowledge of this kind of derivative needs a little refreshing, you might want to read that section before coming back to this.

substitute the proposed solution into the left side of the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \Psi(x,t) = \alpha i\hbar \frac{\partial}{\partial t} \Psi_1(x,t) + \beta i\hbar \frac{\partial}{\partial t} \Psi_2(x,t)$$

$$= \alpha \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right) \Psi_1(x,t) + \beta \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right) \Psi_2(x,t)$$

$$= \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right) \Psi(x,t).$$

$|\Psi_1(x,t)|^2$

$n = 1$

x

0 a

$|\Psi_2(x,t)|^2$

$n = 2$

x

0 a
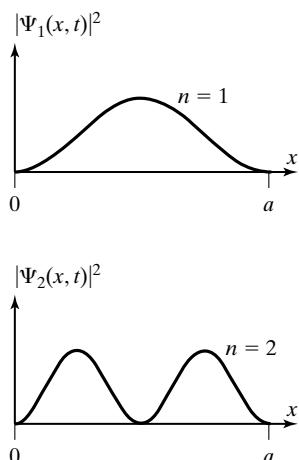
FIGURE 7.24

The probability density $|\Psi(x,t)|^2$ for each of the lowest two energy levels of the rigid box. Because these are stationary states, the probability densities are constant in time.

The special feature of the separate stationary-state wave functions of (7.110) is that the corresponding probability densities are independent of t (that is, stationary). This is because when we form $|\Psi(x,t)|^2$, the time-dependent exponential factor drops out (since $|e^{-i\omega t}| = 1$). The two probability densities (for the case of the lowest two stationary states of the rigid box) are shown in Fig. 7.24, where each picture is frozen and unchanging in time.

It is perhaps a little surprising that when we form a linear combination of two stationary-state wave functions, as in (7.111), the resulting state is not a stationary state. To see this, we can rewrite (7.111) as

$$\Psi(x,t) = \alpha \psi_1(x) e^{-i\omega_1 t} + \beta \psi_2(x) e^{-i\omega_2 t}$$
$$= e^{-i\omega_1 t} [\alpha \psi_1(x) + \beta \psi_2(x) e^{-i\omega_{21} t}] \qquad (7.112)$$

where, in the second line, we have factored out the first exponential $e^{-i\omega_1 t}$ and replaced ω_2 in the second exponential by $\omega_2 - \omega_1$, which we have abbreviated as $\omega_{21} = (\omega_2 - \omega_1)$. When we form the absolute value squared of $\Psi(x,t)$, the first exponential disappears in the now-familiar way, but the second does not.

$$|\Psi(x,t)|^2 = |\alpha \psi_1(x) + \beta \psi_2(x) e^{-i\omega_{21} t}|^2 \qquad (7.113)$$

It is fairly easy to see that since one of the terms on the right is oscillatory while the other is not, the right side is definitely not independent of time. The only exception to this statement is if one of the two coefficients α or β is zero, in which case the state is just one of the original stationary states. Rather than prove these statements in general, we examine one particular case in the following example. (But see also Problem 7.59.)

Example 7.6
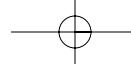
For a particle in a rigid box, consider the nonstationary state with wave function (7.112) for the special case that $\alpha = \beta = 1/\sqrt{2}$. (The particular value $1/\sqrt{2}$ is chosen to guarantee that Ψ is normalized — see Problem 7.58.) Evaluate $|\Psi(x,t)|^2$ and plot it for several different times.

With the given values of α and β, the wave function is

$$\Psi(x,t) = \frac{1}{\sqrt{2}} [\psi_1(x) e^{-i\omega_1 t} + \psi_2(x) e^{-i\omega_2 t}] \qquad (7.114)$$

and from (7.113), we find

$$|\Psi(x,t)|^2 = \tfrac{1}{2} |\psi_1(x) + \psi_2(x) e^{-i\omega_{21} t}|^2 \qquad (7.115)$$

where the explicit forms of ψ_1 and ψ_2 can be found in (7.60) and $\omega_{21} = (\omega_2 - \omega_1) = (E_2 - E_1)/\hbar$ with the energies given by (7.23). The absolute value on the right can be evaluated in several ways. If you think of it as $|u + ve^{-i\theta}|^2$, then

$$|u + ve^{-i\theta}|^2 = |u + v\cos\theta - iv\sin\theta|^2$$
$$= (u + v\cos\theta)^2 + (v\sin\theta)^2 = u^2 + v^2 + 2uv\cos\theta \quad (7.116)$$

where in the first line we used the Euler relation for $e^{-i\theta}$ and in the second we used $\cos^2 + \sin^2 = 1$. Thus,

$$|\Psi(x,t)|^2 = \tfrac{1}{2}[\psi_1(x)^2 + \psi_2(x)^2 + 2\psi_1(x)\psi_2(x)\cos(\omega_{21}t)]. \quad (7.117)$$
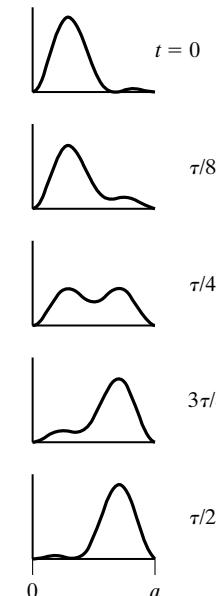
The most obvious thing about this result is that, because of the factor $\cos(\omega_{21}t)$, the probability density *does* vary with time. Notice that in this case the time dependence is actually periodic, with period $\tau = 2\pi/\omega_{21}$.

We have plotted (7.117) for five equally spaced times, $\tau/8$ apart, in Fig. 7.25, where it is quite clear that the probability density is moving around inside the box. At $t = 0$, the probability is concentrated in the left half of the box, with almost no probability of finding the particle on the right. As t advances, the probability shifts across to the right, and by the time $t = \tau/2$, the particle is almost certainly in the right half. If we had shown a few more plots (at the same spacing of t), they would have shown the probability shifting back to the left, and by $t = \tau$ the density would be the same as at $t = 0$ again.
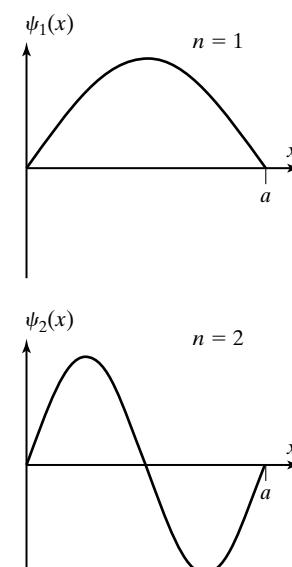
Some features of Fig. 7.25 can be understood if we examine the wave functions carefully. At $t = 0$, the term inside the absolute value signs in (7.115) is just $\psi_1(x) + \psi_2(x)$. If you look at the plots in Fig. 7.26, you will see that $\psi_1(x)$ and $\psi_2(x)$ are both positive on the left of the box but have opposite signs on the right. Therefore, when we add them, they interfere constructively on the left, but destructively on the right. Thus, at $t = 0$, the probability density $|\Psi(x,0)|^2$ is large on the left and very small on the right, as in the first of the plots of Fig. 7.25. By the time $t = \tau/2$, the exponential factor in (7.115) is* $e^{-i\pi} = -1$ and the term inside the absolute value signs is $\psi_1(x) - \psi_2(x)$. Referring again to Fig. 7.26, you will see that now the two waves interfere destructively on the left and constructively on the right, as seen in the last of the plots in Fig. 7.25.

Looking back at (7.114), we can now understand why any linear combination of stationary-state wave functions is itself not stationary: The time dependence of each separate term in (7.114) is contained in a simple exponential factor $e^{-i\omega t}$ (which disappears when we form $|\Psi_1|^2$ or $|\Psi_2|^2$), but these two factors have *different* frequencies ω_1 and ω_2. Thus, as time goes by, they vary at different rates and the interference between the two terms in the sum keeps changing, as is evident in Fig. 7.25.

The time dependence of nonstationary states, as determined by the time-dependent Schrödinger equation, is fascinating and theoretically very important. Nevertheless — and perhaps fortunately for us — it plays no role in the majority of elementary quantum problems. For the most part, our main concern will be solving the time-independent Schrödinger equation to find the allowed energies and the corresponding stationary-state wave functions for
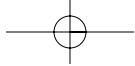

FIGURE 7.25

The probability density $|\Psi(x,t)|^2$ for the non-stationary state (7.114) at five equally spaced times.


FIGURE 7.26

The two lowest stationary-state wave functions $\psi_1(x)$ and $\psi_2(x)$ for the rigid box.

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*If you're not familiar with this result, check it using Euler's formula (7.10).
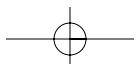
electrons in atoms, molecules, and solids and for nucleons in nuclei. The one exception to this statement concerns the following problem, which we will address in Chapter 11: If the solutions of the time-independent Schrödinger equation were really *perfectly* stationary states, then they would represent states of an atom (or other system) that *never* change. This would imply that an atom in one of its energy levels would never make a transition to another energy level — in flagrant contradiction to the observed transitions made by most atoms. As we will see in Chapter 11, atomic transitions result from various outside influences, such as electromagnetic fields, which mean that the stationary states calculated for the isolated atom are not in fact exactly stationary states for the real system, which must include the outside influences. To calculate how these influences cause the observed transitions, we will need to use the time-dependent Schrödinger equation.

CHECKLIST FOR CHAPTER 7

CONCEPT	DETAILS
Superposition principle	If Ψ_1 and Ψ_2 are possible waves, so is $A\Psi_1 + B\Psi_2$
Classical standing wave	$\Psi(x,t) = \psi(x)\cos\omega t$ (7.5) (does not move right or left)
Nodes	Points at which the disturbance remains zero for all times
Time dependence of quantum standing waves	$\Psi(x,t) = \psi(x)e^{-i\omega t}$ (7.11) (fixed spatial part, oscillatory time part)
Time-independent Schrödinger equation	$\dfrac{d^2\psi}{dx^2} = \dfrac{2m}{\hbar^2}[U(x) - E]\psi$ (7.39)
Particle in a one-dimensional rigid box	Moves freely inside $0 \leq x \leq a$ but cannot escape outside
Boundary conditions	$\psi(0) = \psi(a) = 0$ (7.16)
Allowed energies	$E_n = n^2(\pi^2\hbar^2/2ma^2)$ (7.23)
Wave functions	$\psi(x) = \sqrt{2/a}\,\sin(n\pi x/a)$ (7.60)
Normalization condition	$\int |\psi(x)|^2\,dx = 1$ (7.55)
Behavior of wave functions	
In classically forbidden zone $(E < U)$	Curves away from axis, $\psi \to 0$ exponentially as $x \to \pm\infty$
In classically allowed zone $(E > U)$	Curves toward the axis and oscillates sinusoidally
Allowed energies and well-behaved functions	Section 7.8
Simple harmonic oscillator ★	$U = \frac{1}{2}kx^2$ (7.97)
Allowed energies	$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_c$ (7.98)
Tunneling ★	Ability of a quantum particle to penetrate into a classically forbidden zone
Probability of tunneling	$P = e^{-2\alpha L}$ (7.105)
Time-dependent Schrödinger equation ★	$i\hbar\dfrac{\partial}{\partial t}\Psi(x,t) = \left(-\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} + U(x)\right)\Psi(x,t)$ (7.107)

PROBLEMS FOR CHAPTER 7

SECTION 7.2 (Classical Standing Waves)

7.1 • A string is oscillating with wave function

$$y(x, t) = A \sin kx \cos \omega t \qquad (7.118)$$

with $A = 3$ cm, $k = 0.2\pi$ rad/cm, and $\omega = 10\pi$ rad/s. For each of the times $t = 0$, 0.05, and 0.07 s, sketch the string for $0 \le x \le 10$ cm.

7.2 • A standing wave of the form (7.118) has amplitude 2 m, wavelength 10 m, and period $T = 2$ s. Write down the expression for $y(x, t)$.

7.3 • A string is clamped at the points $x = 0$ and $x = 30$ cm. It is oscillating sinusoidally with amplitude 2 cm, wavelength 20 cm, and frequency $f = 40$ Hz. Write an expression for its wave function $y(x, t)$.

7.4 • For the standing wave of Eq. (7.118) calculate the string's transverse velocity at any fixed position x. [That is, differentiate (7.118) with respect to t, treating x as a constant.] At certain times the string's displacement is zero for all x, and an instantaneous snapshot of the string would show no wave at all. Sketch the string at such a moment, and indicate, with several small arrows, the velocity of several points on the string at that moment.

7.5 • In Fig. 7.27 are sketched three successive snapshots of a standing wave on a string. The first (solid) curve shows the string at maximum displacement. Were these snapshots taken at equally spaced times? If not, make a sketch in which they were. (Use the same first and third curves.)

FIGURE 7.27

(Problems 7.5 and 7.6)

7.6 • Figure 7.27 shows a standing wave on a string. In any position other than the dotted one, the string has potential energy because it is stretched (compared to the straight, dotted position). Let U_0 denote this potential energy at the position of the solid curve (which shows the maximum displacement). What is the potential energy when the string reaches the position of the dotted line? What is the kinetic energy at this position?

7.7 • Consider a standing wave on a string, clamped at the points $x = 0$ and $x = 40$ cm. It is oscillating with amplitude 3 cm and wavelength 80 cm, and its maximum transverse velocity is 60 cm/s. Write an expression for its displacement $y(x, t)$ as a function of x and t.

7.8 • Rewrite the expression (7.118) for a standing wave, eliminating the wave number k and angular frequency ω in favor of the wavelength λ and period T. Use

your answer to explain clearly why the wave repeats itself if we move from any point x_0 to $x_0 + \lambda$ (with t fixed). Show similarly what happens if we increase t from any t_0 to $t_0 + T$.

7.9 •• A string is oscillating with wave function of the form (7.118) but with $A = 2.5$ cm, $k = 1$ rad/cm, and $\omega = 10\pi$ rad/s. **(a)** Sketch two complete wavelengths of the wave at each of the times $t = 0.05$ s and $t = 0.1$ s. **(b)** For a fixed value of x, differentiate (7.118) with respect to t to give the string's transverse velocity at any position x. Graph this velocity as a function of x for each of the two times in part (a).

SECTION 7.3 (Standing Waves in Quantum Mechanics)

7.10 • Prove that any complex number $z = x + iy$ (with x and y real) can be written as $z = re^{i\theta}$ (with r and θ real). Give expressions for x and y in terms of r and θ, and vice versa. [*Hint:* Use Euler's formula, (7.10).]

7.11 • **(a)** Show for any complex number $z = x + iy$, that $|z|^2 = zz^*$ where $z^* = x - iy$ is the complex conjugate of z. **(b)** Hence, prove the useful identity, $|zw| = |z| \cdot |w|$. **(c)** Show for any standing wave, with the form (7.11), $|\Psi(x, t)| = |\psi(x)|$, and hence that the probability density is independent of time.

7.12 • Consider a complex function of time, $z = re^{-i\omega t}$, where r is a real constant. **(a)** Write z in terms of its real and imaginary parts, x, and y, and show that they oscillate sinusoidally and 90° out of phase. **(b)** Show that $|z| = \sqrt{x^2 + y^2}$ is constant.

7.13 •• We claimed in connection with Eq. (7.7) that the general (real) sinusoidal wave has time dependence

$$a \cos \omega t + b \sin \omega t \qquad (7.119)$$

Another way to say this is that the general sinusoidal time dependence is
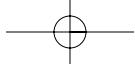
$$A \sin(\omega t + \phi) \qquad (7.120)$$

(a) Show that these two forms are equivalent; that is, prove that the function (7.119) can be expressed in the form (7.120) and vice versa. Give expressions for a and b in terms of A and ϕ and vice versa. (Remember the trig identities in Appendix B.) **(b)** Show that by changing the origin of time (that is, rewriting everything in terms of $t' = t +$ constant, with a suitably chosen constant) you can eliminate the constant ϕ from (7.120) [that is, rewrite (7.120) as $A \sin \omega t'$.]

7.14 •• The function e^z is defined for any z, real or complex, by its *power series*

$$e^z = 1 + z + \frac{z^2}{2!} + \frac{z^3}{3!} + \cdots$$

Write down this series for the case that z is purely imaginary, $z = i\theta$. Note that the terms in this series are alternately real and imaginary. Group together all

the real terms and all the imaginary terms, and prove the important identity, called Euler's formula,

$$e^{i\theta} = \cos\theta + i\sin\theta \qquad (7.121)$$

[*Hint:* You will need to remember the power series for $\cos\theta$ and $\sin\theta$ given in Appendix B. You may wonder whether it is legitimate to regroup the terms of an infinite series as recommended here; for power series like those in this problem, it is legitimate.]

7.15 •• Use the identity $e^{i(\theta+\phi)} = e^{i\theta}e^{i\phi}$ to prove the trig identities for $\cos(\theta + \phi)$ and $\sin(\theta + \phi)$.

7.16 •• Use the result (7.121) to prove that

$$\cos\theta = \frac{e^{i\theta} + e^{-i\theta}}{2} \quad \text{and} \quad \sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2}$$

SECTION 7.4 (The Particle in a Rigid Box)

7.17 • Find the lowest three energies, in eV, for an electron in a one-dimensional box of length $a = 0.2$ nm (about the size of an atom).

7.18 • Find the lowest three energies, in MeV, of a proton in a one-dimensional rigid box of length $a = 5$ fm (a typical nuclear size).

7.19 • What is the spacing, in eV, between the lowest two levels of an electron confined in a one-dimensional wire of length 1 cm?

7.20 • Sketch the energy levels and wave functions for the levels $n = 5, 6, 7$ for a particle in a one-dimensional rigid box. (See Fig. 7.5.)

7.21 • For the ground state of a particle in a rigid box, we have seen that the momentum has a definite magnitude $\hbar k$ but is equally likely to be in either direction. This means that the uncertainty in p is $\Delta p \approx \hbar k$. The uncertainty in position is $\Delta x \approx a/2$. Verify that these uncertainties are consistent with the Heisenberg uncertainty principle (6.34).

SECTION 7.6 (The Rigid Box Again)

7.22 • Prove that the function $\psi = Ae^{\alpha x} + Be^{-\alpha x}$ satisfies the equation $\psi'' = \alpha^2\psi$ for any two constants A and B.

7.23 • We saw that the coefficients A and B in the wave function for a negative-energy state in the rigid box would have to satisfy $A + B = 0$ and $Ae^{\alpha a} + Be^{-\alpha a} = 0$. Show that this is possible only if $A = B = 0$ and hence, that there are no negative-energy states.

7.24 • Prove that the function $\psi = Ae^{ikx} + Be^{-ikx}$ satisfies the equation $\psi'' = -k^2\psi$ for any two constants A and B.

7.25 •• We have seen that second-order differential equations like the Schrödinger equation have two independent solutions. Consider the *fourth*-order equation $d^4\psi/dx^4 = \beta^4\psi$, where β is a positive constant. Prove that each of the four functions $e^{\pm\beta x}$ and $e^{\pm i\beta x}$ is a solution. (It is a fact — though harder to prove — that any solution of the equation can be expressed as a linear combination of these four solutions.)

7.26 •• A second-order differential equation like the Schrödinger equation has two independent solutions $\psi_1(x)$ and $\psi_2(x)$. These two solutions can be chosen in many ways, but once they are chosen, any solution can be expressed as a linear combination $A\psi_1(x) + B\psi_2(x)$ (where A and B are constants, real or complex). **(a)** To illustrate this property, consider the differential equation $\psi'' = -k^2\psi$ where k is a constant. Prove that each of the three functions $\sin kx$, $\cos kx$, and e^{ikx} is a solution. **(b)** Show that each can be expressed as a combination of the other two.

7.27 •• Many physical problems lead to a differential equation of the form

$$a\psi''(x) + b\psi'(x) + c\psi(x) = 0$$

where a, b, c are constants. [An example was given in (7.30).] **(a)** Prove that this equation has two solutions of the form $\psi(x) = e^{\gamma x}$, where γ is either solution of the quadratic equation $a\gamma^2 + b\gamma + c = 0$. **(b)** Prove that any linear combination of these two solutions is itself a solution.

7.28 •• Consider the second-order differential equation

$$f(x)\psi''(x) + b(x)\psi'(x) + h(x)\psi(x) = 0$$

where f, g, and h are known functions of x. Prove that if $\psi_1(x)$ and $\psi_2(x)$ are both solutions of this equation, the linear combination $A\psi_1(x) + B\psi_2(x)$ is also a solution for any two constants A and B — the result known as the superposition principle.

7.29 •• Show that the integral which appears in the normalization condition for a particle in a rigid box has the value

$$\int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{a}{2}$$

[*Hint:* Use the identity for $\sin^2\theta$ in terms of $\cos 2\theta$ given in Appendix B.]

7.30 •• **(a)** Write down and sketch the probability distribution $|\psi(x)|^2$ for the second excited state $(n = 3)$ of a particle in a rigid box of length a. **(b)** What are the most probable positions, x_{mp}? **(c)** What are the probabilities of finding the particle in the intervals $[0.50a, 0.51a]$ and $[0.75a, 0.76a]$?

7.31 •• Answer the same questions as in Problem 7.30 but for the third excited state $(n = 4)$.

7.32 •• If a particle has wave function $\psi(x)$, the probability of finding the particle between any two points b and c is

$$P(b \leq x \leq c) = \int_b^c |\psi(x)|^2 \, dx \qquad (7.122)$$

For a particle in the ground state of a rigid box, calculate the probability of finding it between $x = 0$ and $x = a/3$ (where a is the width of the box). Use the hint in Problem 7.29.

7.33 •• Evaluate the integral (7.65) to give the average result $\langle x \rangle$ (the expectation value) found when the position of a particle in the ground state of a rigid box is measured many times. [*Hint:* Rewrite $\sin^2(\pi x/a)$ in terms of $\cos(2\pi x/a)$ and use integration by parts.]

7.34 •• Do Problem 7.33 for the case of the second excited state ($n = 3$) of a rigid box.

7.35 ••• Consider a particle in the ground state of a rigid box of length a. **(a)** Evaluate the integral (7.122) to give the probability of finding the particle between $x = 0$ and $x = c$ for any $c \leq a$. **(b)** What does your result give when $c = a$? Explain. **(c)** What if $c = a/2$? **(d)** What if $c = a/4$? **(e)** The answer to part (c) is half that for part (b), whereas that to part (d) is *not* half that for part (c). Explain.

SECTION 7.8 (The Nonrigid Box)

7.36 • Consider the potential-energy function $U(x) = \frac{1}{2}kx^2$. **(a)** Sketch U as a function of x. **(b)** For a classical particle of energy E, find the turning points in terms of E and k. **(c)** If we double the energy, what happens to the length of the classically allowed region?

7.37 •• Consider the potential-energy function (the Gaussian well)

$$U(x) = U_0(1 - e^{-x^2/a^2})$$

where U_0 and a are positive constants. **(a)** Sketch $U(x)$. **(b)** For $0 < E < U_0$, find the classical turning points (in terms of U_0, E, and a).

7.38 •• Give an argument that a particle moving in either of the finite wells of Figs. 7.8(b) and (c) can have no states with $E < 0$. [*Hint:* Remember that whenever $U(x) - E$ is positive, $\psi(x)$ must bend away from the axis; show that a wave function that is well behaved as $x \rightarrow -\infty$ (that is, behaves like $e^{\alpha x}$) necessarily blows up as $x \rightarrow \infty$.]

7.39 •• Make sketches of the probability density $|\psi(x)|^2$ for the first four energy levels of a particle in a nonrigid box. Draw next to each graph the corresponding graph for the rigid box.

7.40 •• Consider the potential well shown in Fig. 7.28(a). Sketch the wave function for the eighth excited level of this well, assuming that it has energy $E > U_0$. [*Hint:* The wave function has eight nodes — not counting the nodes at the walls of the well.]
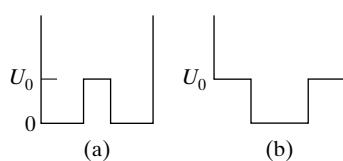

FIGURE 7.28

(Problems 7.40 to 7.43)

7.41 •• Do the same task as in Problem 7.40, but for the well in Fig. 7.28(b).

7.42 •• Sketch the wave function for the fourth excited level of the well of Fig. 7.28(a), assuming that it has energy in the interval $0 < E < U_0$.

7.43 •• Do Problem 7.42, but for the well of Fig. 7.28(b).

7.44 •• Consider the infinitely deep potential well shown in Fig. 7.29. **(a)** Argue that this is the potential energy of a particle of mass m above a hard surface in a uniform gravitational field with x measured vertically up. **(b)** Sketch the wave functions for the ground state and the first two excited states of this well.
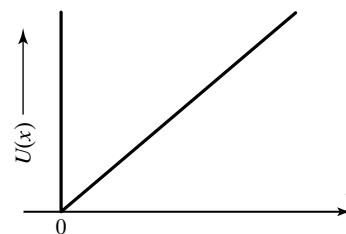

FIGURE 7.29

(Problem 7.44)

7.45 •• **(a)** Derive an approximate expression for the number of bound states in a finite square well of depth U_0. To do this, make the assumption that the energy of the highest state of the finite well is close to the corresponding energy of the infinite well. This state is the one that has an energy E near the top of the well, that is, $E = U_0$. **(b)** Compute the approximate number of bound states for the case of an electron in a well of depth $U_0 = 10$ eV, and width $a = 0.3$ nm. These numbers crudely approximate valence electrons in a solid.

7.46 •• In a region where the potential energy $U(x)$ varies, the Schrödinger equation must usually be solved by numerical methods — generally with the help of a computer. The simplest such method, though not the most efficient, is called Euler's method and can be described as follows: In solving the Schrödinger equation numerically, one needs to know the values of $\psi(x)$ and $\psi'(x)$ at one point x_0. For example, for the finite wells of Fig. 7.8 we know these values at $x_0 = 0$ since we know that $\psi(x)$ has the form $\psi(x) = e^{\alpha x}$ for $x \leq 0$. Suppose now we want to find $\psi(x)$ at some point $x > 0$. We first divide the interval from x_0 to x into n equal intervals each of width Δx:
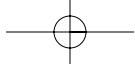
$$x_0 < x_1 < x_2 < \cdots < x_n = x$$

Knowing $\psi(x)$ and $\psi'(x)$ at $x = x_0$, we can use the Schrödinger equation to find approximate values of these two functions at x_1, and from these, we can find values at x_2 and so on until we know both functions at $x_n = x$. To do this, we use the approximations

$$\psi(x_{i+1}) \approx \psi(x_i) + \psi'(x_i)\, \Delta x$$

and

$$\psi'(x_{i+1}) \approx \psi'(x_i) + \psi''(x_i)\, \Delta x$$

[The first approximation is just the definition of the derivative, and the second is the same approximation applied to $\psi'(x)$.] Consider the equation $\psi''(x) = -\psi(x)$, with the starting values $\psi(0) = 0$ and $\psi'(0) = 1$, and do the following (for which you don't need a computer): **(a)** What is the exact solution of this equation with these initial conditions? What is the exact value of $\psi(x)$ at $x = 1$? **(b)** Divide the interval from $x = 0$ to 1 into two equal intervals ($n = 2$), and use the Euler's method to find an approximate value for $\psi(1)$. **(c)** Repeat with $n = 3$ and $n = 4$. Compare your results with the exact answer, and make a plot of the exact and approximate values for the case that $n = 4$. Note well how the approximate solution improves as you increase n.

7.47 •• Do Problem 7.46, but for the differential equation $\psi''(x) = +\psi(x)$, with the starting values $\psi(0) = 0$ and $\psi'(0) = 1$.

SECTION 7.9 (The Simple Harmonic Oscillator)

7.48 • Show that the length parameter b defined for the SHO in Eq. (7.99) is equal to the value of x at the classical turning point for a particle with the energy of the quantum ground state.

7.49 • Verify that the $n = 0$ wave function for the SHO, given in Table 7.1, satisfies the Schrödinger equation with $E = \frac{1}{2}\hbar\omega_c$. (The potential-energy function is $U = \frac{1}{2}kx^2$.)

7.50 • The wave function $\psi_0(x)$ for the ground state of a harmonic oscillator is given in Table 7.1. Show that its normalization constant A_0 is

$$A_0 = (\pi b^2)^{-1/4} \qquad (7.123)$$

You will need to know the integral $\int_{-\infty}^{\infty} e^{-\lambda x^2}\, dx$, which can be found in Appendix B.

7.51 • Show that the normalization constant A_1 for the wave function of the first excited state of the SHO is $A_1 = (4/\pi b^2)^{1/4}$. (The wave function is given in Table 7.1. You will need to know the integral $\int_{-\infty}^{\infty} x^2 e^{-\lambda x^2}\, dx$, which is given in Appendix B.)

7.52 •• Verify that the $n = 2$ wave function for the SHO, given in Table 7.1, satisfies the Schrödinger equation with energy $\frac{5}{2}\hbar\omega_c$.

7.53 ••• The wave functions of the harmonic oscillator, like those of a particle in a finite well, are nonzero in the classically forbidden regions, outside the classical turning points. In this question you will find the probability that a quantum particle which is in the ground state of an SHO will be found outside its classical turning points. The wave function for this state is in Table 7.1, and its normalization constant A_0 is given in Problem 7.50. **(a)** What are the turning points for a classical particle with the ground-state energy $\frac{1}{2}\hbar\omega_c$ in an SHO with $U = \frac{1}{2}kx^2$? Relate your answer to the constant b in Eq. (7.99). **(b)** For a quantum particle in the ground state, write down the integral that gives the total probability for finding the particle between the two classical turning points. The form of the required integral is given in Problem 7.32, Eq. (7.122).

To evaluate it, change variables until you get an integral of the form $\int_{-1}^{1} e^{-y^2}\, dy$; this is a standard integral of mathematical physics (called the error function) with the known value 1.49. What is the probability of finding the particle between the classical turning points? **(c)** What is the probability of finding it *outside* the classical turning points?

SECTION 7.10 (Tunneling)

7.54 • Consider two straight wires lying on the x axis, separated by a gap of 4 nanometers. The potential energy U_0 in the gap is about 3 eV higher than the energy of a conduction electron in either wire. What is the probability that a conduction electron in one wire arriving at the gap will pass through the gap into the other wire?

7.55 •• The radioactive decay of certain heavy nuclei by emission of an alpha particle is a result of quantum tunneling, as described in detail in Section 17.10. Meanwhile, here is a simplified model: Imagine an alpha particle moving around inside a nucleus, such as thorium 232. When the alpha bounces against the surface of the nucleus, it meets a barrier caused by the attractive nuclear force. The dimensions of this barrier vary a lot from one nucleus to another, but as representative numbers you can assume that the barrier's width is $L \approx 35$ fm (1 fm $= 10^{-15}$ m) and the average barrier height is $U_0 - E \approx 5$ MeV. Find the probability that an alpha hitting the nuclear surface will escape. Given that the alpha hits the nuclear surface about 5×10^{21} times per second, what is the probability that it will escape in a day?

SECTION 7.11 (The Time-Dependent Schrödinger Equation)

7.56 • Verify that $e^{i\pi} = -1$.

7.57 • If $\psi(x)$ satisfies the time-independent Schrödinger equation (7.106), verify that the function $\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$ satisfies the time-dependent Schrödinger equation (7.107).

7.58 •• Assuming the wave functions ψ_1 and ψ_2 are normalized, verify that the superposition (7.114) is also normalized. [*Hint:* It will help if you can prove that $\int \psi_1\psi_2\, dx = 0$.]

7.59 •• Verify that for the wave function (7.111),

$$|\Psi(x,t)|^2 = |\alpha|^2|\psi_1(x)|^2 + |\beta|^2|\psi_2(x)|^2 +$$
$$2\mathrm{Re}(\alpha^*\beta)\psi_1(x)\psi_2(x)\cos(\omega_{21}t)$$

assuming that $\psi_1(x)$ and $\psi_2(x)$ are real.

COMPUTER PROBLEMS

7.60 • (Section 7.2) Use appropriate software to draw five graphs (all on the same plot) of the standing wave (7.2) for $0 < x < 2$ and for the five times $t = 0$, 0.05, 0.1, 0.15, and 0.2. Take $A = \lambda = T = 1$. Using your plots, describe clearly the behavior of the standing wave.

7.61 • (Section 7.9) Use appropriate software to plot the lowest two wave functions of the simple harmonic oscillator. The functions are given in Table 7.1, and the normalization constants in Problems 7.50 and 7.51. For the purposes of your plot, you may as well choose your unit of length such that $b = 1$.

7.62 •• (Section 7.2) If you have access to graphing software that lets you animate graphics, make 20 separate plots of the standing wave of Problem 7.60 at equally spaced times $t = 0, 0.05, 0.01, \ldots, 0.95$ and animate them to make a movie of the standing wave. Describe the behavior of the wave.

7.63 •• (Section 7.11) Make plots similar to Fig. 7.25, but for eight different times, $t = 0, \frac{1}{8}, \frac{2}{8}, \frac{3}{8}, \ldots, \frac{7}{8}$. If possible, animate these pictures to show the movement of the distribution in the well.

7.64 ••• (Section 7.8) If you haven't already done so, do Problem 7.46, then using a programmable calculator or computer software such as MathCad, extend your answers to the cases that the number of steps n is 5, 10, and 50. Make a plot showing the exact solution and the values of your approximate solution for $n = 50$.

7.65 ••• (Section 7.8) If you haven't already done so, do Problem 7.47, then using a programmable calculator or computer software such as MathCad, extend your answers to the cases that the number of steps n is 5, 10, and 50. Make a plot showing the exact solution and the values of your approximate solution for $n = 50$.

7.66 ••• (Section 7.8) If you have access to computer software with preprogrammed numerical solution of differential equations (for example, the function NDSolve in Mathematica), do the following: **(a)** Plot the Gaussian well of Problem 7.37, using units such that $U_0 = a = \hbar = 1$ and taking $m = 36$. (The first three choices simply define a convenient system of units — for instance, a is the unit of length — and the last is chosen so that the well supports several bound states.) **(b)** We know that to be acceptable, the wave function must be proportional to $e^{\alpha x}$ far to the left of the well. To ensure this, use the boundary conditions $\psi(-3) = 1$ and $\psi'(-3) = \alpha$, and solve the Schrödinger differential equation for energy $E = 0.1$. Plot your solution, and confirm that it does not behave acceptably as $x \to \infty$. **(c)** Repeat for $E = 0.2$. What can you conclude about the energy of the ground state from the plots of parts (b) and (c)? **(d)** Repeat for two or three intermediate energies until you know the ground-state energy to two significant figures.

7.67 ••• (Section 7.8) Consider the problem of a particle in finite square well of depth U_0, as described in Section 7.8. To solve this problem, use a coordinate system centered on the box, with the left edge of the well at $x = -a/2$ and the right edge at $x = +a/2$. From the symmetry of the potential, one can argue that the stationary states should have symmetric probability distributions, that is, $|\psi(x)|^2 = |\psi(-x)|^2$. This implies that solutions are either *symmetric* and satisfy $\psi(x) = \psi(-x)$ or are *antisymmetric* and satisfy $\psi(x) = -\psi(-x)$. Thus, with our choice of coordinates, the solutions within the well are either of the form $\cos(kx)$ (for $n = 1, 3, 5, \ldots$) or of the form $\sin(kx)$ (for $n = 2, 4, 6, \ldots$). **(a)** For the case of the symmetric solutions, derive an equation relating k and α. [*Hint:* Using the boundary conditions that both $\psi(x)$ and $\psi'(x)$ are continuous at $x = -a/2$, you can produce two equations that relate k, α, and the arbitrary coefficients A and G in Section 7.8. By dividing these equations, you can eliminate the coefficients. The final equation you produce is a *transcendental equation* relating E and U_0; it cannot be solved for E using elementary methods.] **(b)** Show that the equation derived in (a) produces the correct stationary-state energies in the limit $U_0 \to \infty$. **(c)** Using numerical techniques, find the ground-state energy E_1 of a square well of depth $U_0 = 3 E_1$. [*Hint:* A simple trial-and-error search for the solution works surprisingly well.]