



? These containers hold solutions of microscopic semiconductor particles of different sizes. The particles glow when exposed to ultraviolet light; the smallest particles glow blue and the largest particles glow red. This is because the energy levels of electrons (i) are spaced farther apart in smaller particles; (ii) are spaced farther apart in larger particles; (iii) have the same spacing in all particles but have higher energies in smaller particles; (iv) have the same spacing in all particles but have higher energies in larger particles; (v) depend on the wavelength of ultraviolet light used.

# 40 Quantum Mechanics I: Wave Functions

In Chapter 39 we found that particles can behave like waves. In fact, it turns out that we can use the wave picture to completely describe the behavior of a particle. This approach, called *quantum mechanics*, is the key to understanding the behavior of matter on the molecular, atomic, and nuclear scales. In this chapter we'll see how to find the *wave function* of a particle by solving the *Schrödinger equation*, which is as fundamental to quantum mechanics as Newton's laws are to mechanics or as Maxwell's equations are to electromagnetism.

We'll begin with a quantum-mechanical analysis of a *free particle* that moves along a straight line without being acted on by forces of any kind. We'll then consider particles that are acted on by forces and are trapped in *bound states*, just as electrons are bound within an atom. We'll see that solving the Schrödinger equation automatically gives the possible energy levels for the system.

Besides energies, solving the Schrödinger equation gives us the probabilities of finding a particle in various regions. One surprising result is that there is a nonzero probability that microscopic particles will pass through thin barriers, even though such a process is forbidden by Newtonian mechanics.

In this chapter we'll consider the Schrödinger equation for one-dimensional motion only. In Chapter 41 we'll see how to extend this equation to three-dimensional problems such as the hydrogen atom. The hydrogen-atom wave functions will in turn form the foundation for our analysis of more complex atoms, of the periodic table of the elements, of x-ray energy levels, and of other properties of atoms.

## 40.1 WAVE FUNCTIONS AND THE ONE-DIMENSIONAL SCHRÖDINGER EQUATION

We have now seen compelling evidence that on an atomic or subatomic scale, an object such as an electron cannot be described simply as a classical, Newtonian point particle. Instead, we must take into account its *wave* characteristics. In the Bohr model

### LEARNING OUTCOMES

#### In this chapter, you'll learn...

- 40.1 The wave function that describes the behavior of a particle and the Schrödinger equation that this function must satisfy.
- 40.2 How to calculate the wave functions and energy levels for a particle confined to a box.
- 40.3 How to analyze the quantum-mechanical behavior of a particle in a potential well.
- 40.4 How quantum mechanics makes it possible for particles to go where Newtonian mechanics says they cannot.
- 40.5 How to use quantum mechanics to analyze a harmonic oscillator.
- 40.6 How measuring a quantum-mechanical system can change that system's state.

#### You'll need to review...

- 7.5 Potential wells.
- 14.2, 14.3 Harmonic oscillators.
- 15.3, 15.7, 15.8 Wave functions for waves on a string; standing waves.
- 32.3 Wave functions for electromagnetic waves.
- 38.1, 38.4 Work function; photon interpretation of interference and diffraction.
- 39.1, 39.3, 39.5, 39.6 De Broglie relationships; Bohr model for hydrogen; Planck radiation law; Heisenberg uncertainty principle.

Figure 40.1 These children are talking over a cup-and-string “telephone.” The displacement of the string is completely described by a wave function  $y(x, t)$ . In an analogous way, a particle is completely described by a quantum-mechanical wave function  $\Psi(x, y, z, t)$ .



**CAUTION Particle waves vs. mechanical waves** Unlike waves on a string or sound waves in air, the wave function for a particle is *not* a mechanical wave that needs a material medium in order to propagate. The wave function describes the particle, but we cannot define the function itself in terms of anything material. We can describe only how it is related to physically observable effects. ■

of the hydrogen atom (Section 39.3) we tried to have it both ways: We pictured the electron as a classical particle in a circular orbit around the nucleus, and used the de Broglie relationship between particle momentum and wavelength to explain why only orbits of certain radii are allowed. As we saw in Section 39.6, however, the Heisenberg uncertainty principle tells us that a hybrid description of this kind can’t be wholly correct. In this section we’ll explore how to describe the state of a particle by using *only* the language of waves. This new description, called **quantum mechanics**, replaces the classical scheme of describing the state of a particle by its coordinates and velocity components.

Our new quantum-mechanical scheme for describing a particle has a lot in common with the language of classical wave motion. In Section 15.3 of Chapter 15, we described transverse waves on a string by specifying the position of each point in the string at each instant of time by means of a *wave function*  $y(x, t)$  that represents the displacement from equilibrium, at time  $t$ , of a point on the string at a distance  $x$  from the origin (Fig. 40.1). Once we know the wave function for a particular wave motion, we know everything there is to know about the motion. For example, we can find the velocity and acceleration of any point on the string at any time. We worked out specific forms for these functions for *sinusoidal* waves, in which each particle undergoes simple harmonic motion.

We followed a similar pattern for sound waves in Chapter 16. The wave function  $p(x, t)$  for a wave traveling along the  $x$ -direction represented the pressure variation at any point  $x$  and any time  $t$ . In Section 32.3 we used *two* wave functions to describe the  $\vec{E}$  and  $\vec{B}$  fields in an electromagnetic wave.

Thus it’s natural to use a wave function as the central element of our new language of quantum mechanics. The customary symbol for this wave function is the Greek letter psi,  $\Psi$  or  $\psi$ . In general, we’ll use an uppercase  $\Psi$  to denote a function of all the space coordinates and time, and a lowercase  $\psi$  for a function of the space coordinates only—*not* of time. Just as the wave function  $y(x, t)$  for mechanical waves on a string provides a complete description of the motion, so the wave function  $\Psi(x, y, z, t)$  for a particle contains all the information that can be known about the particle.

## Waves in One Dimension: Waves on a String

The wave function of a particle depends in general on all three dimensions of space. For simplicity, however, we’ll begin our study of these functions by considering *one-dimensional* motion, in which a particle of mass  $m$  moves parallel to the  $x$ -axis and the wave function  $\Psi$  depends on the coordinate  $x$  and the time  $t$  only. (In the same way, we studied one-dimensional kinematics in Chapter 2 before going on to study two- and three-dimensional motion in Chapter 3.)

What does a one-dimensional quantum-mechanical wave look like, and what determines its properties? We can answer this question by first recalling the properties of a wave on a string. We saw in Section 15.3 that any wave function  $y(x, t)$  that describes a wave on a string must satisfy the *wave equation*:

$$\frac{\partial^2 y(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y(x, t)}{\partial t^2} \quad (\text{wave equation for waves on a string}) \quad (40.1)$$

In Eq. (40.1)  $v$  is the speed of the wave, which is the same no matter what the wavelength. As an example, consider the following wave function for a wave of wavelength  $\lambda$  and frequency  $f$  moving in the positive  $x$ -direction along a string:

$$y(x, t) = A \cos(kx - \omega t) + B \sin(kx - \omega t) \quad \begin{array}{l} \text{(sinusoidal wave} \\ \text{on a string)} \end{array} \quad (40.2)$$

Here  $k = 2\pi/\lambda$  is the *wave number* and  $\omega = 2\pi f$  is the *angular frequency*. (We used these same quantities for mechanical waves in Chapter 15 and electromagnetic waves in Chapter 32.) The quantities  $A$  and  $B$  are constants that determine the amplitude and phase of the wave. The expression in Eq. (40.2) is a valid wave function if and only if it satisfies the wave equation, Eq. (40.1). To check this, take the first and second

derivatives of  $y(x, t)$  with respect to  $x$  and take the first and second derivatives with respect to  $t$ :

$$\frac{\partial y(x, t)}{\partial x} = -kA \sin(kx - \omega t) + kB \cos(kx - \omega t) \quad (40.3a)$$

$$\frac{\partial^2 y(x, t)}{\partial x^2} = -k^2 A \cos(kx - \omega t) - k^2 B \sin(kx - \omega t) \quad (40.3b)$$

$$\frac{\partial y(x, t)}{\partial t} = \omega A \sin(kx - \omega t) - \omega B \cos(kx - \omega t) \quad (40.3c)$$

$$\frac{\partial^2 y(x, t)}{\partial t^2} = -\omega^2 A \cos(kx - \omega t) - \omega^2 B \sin(kx - \omega t) \quad (40.3d)$$

If we substitute Eqs. (40.3b) and (40.3d) into the wave equation, Eq. (40.1), we get

$$\begin{aligned} & -k^2 A \cos(kx - \omega t) - k^2 B \sin(kx - \omega t) \\ &= \frac{1}{v^2} [-\omega^2 A \cos(kx - \omega t) - \omega^2 B \sin(kx - \omega t)] \end{aligned} \quad (40.4)$$

For Eq. (40.4) to be satisfied at all coordinates  $x$  and all times  $t$ , the coefficients of  $\cos(kx - \omega t)$  must be the same on both sides of the equation, and likewise for the coefficients of  $\sin(kx - \omega t)$ . Both of these conditions will be satisfied if

$$k^2 = \frac{\omega^2}{v^2} \quad \text{or} \quad \omega = vk \quad (\text{waves on a string}) \quad (40.5)$$

Since  $\omega = 2\pi f$  and  $k = 2\pi/\lambda$ , Eq. (40.5) is equivalent to

$$2\pi f = v \frac{2\pi}{\lambda} \quad \text{or} \quad v = \lambda f \quad (\text{waves on a string})$$

This equation is just the familiar relationship among wave speed, wavelength, and frequency for waves on a string. So our calculation shows that Eq. (40.2) is a valid wave function for waves on a string for any values of  $A$  and  $B$ , provided that  $\omega$  and  $k$  are related by Eq. (40.5).

## Waves in One Dimension: Particle Waves

What we need is a quantum-mechanical version of the wave equation, Eq. (40.1), valid for particle waves. We expect this equation to involve partial derivatives of the wave function  $\Psi(x, t)$  with respect to  $x$  and with respect to  $t$ . However, this new equation *cannot* be the same as Eq. (40.1) for waves on a string because the relationship between  $\omega$  and  $k$  is different. We can show this by considering a **free particle**, one that experiences no force at all as it moves along the  $x$ -axis. For such a particle the potential energy  $U(x)$  has the same value for all  $x$  (recall from Chapter 7 that  $F_x = -dU(x)/dx$ , so zero force means the potential energy has zero derivative). For simplicity let  $U = 0$  for all  $x$ . Then the energy of the free particle is equal to its kinetic energy, which we can express in terms of its momentum  $p$ :

$$E = \frac{1}{2}mv^2 = \frac{m^2v^2}{2m} = \frac{(mv)^2}{2m} = \frac{p^2}{2m} \quad (\text{energy of a free particle}) \quad (40.6)$$

The de Broglie relationships (Section 39.1) tell us that the energy  $E$  is proportional to the angular frequency  $\omega$  and the momentum  $p$  is proportional to the wave number  $k$ :

$$E = hf = \frac{h}{2\pi} 2\pi f = \hbar\omega \quad (40.7a)$$

$$p = \frac{h}{\lambda} = \frac{h}{2\pi} \frac{2\pi}{\lambda} = \hbar k \quad (40.7b)$$

Remember that  $\hbar = h/2\pi$ . If we substitute Eqs. (40.7) into Eq. (40.6), we find that the relationship between  $\omega$  and  $k$  for a free particle is

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \quad (\text{free particle}) \quad (40.8)$$

Equation (40.8) is *very* different from the corresponding relationship for waves on a string, Eq. (40.5): The angular frequency  $\omega$  for particle waves is proportional to the *square* of the wave number, while for waves on a string  $\omega$  is directly proportional to  $k$ . Our task is therefore to construct a quantum-mechanical version of the wave equation whose free-particle solutions satisfy Eq. (40.8).

We'll attack this problem by assuming a sinusoidal wave function  $\Psi(x, t)$  of the same form as Eq. (40.2) for a sinusoidal wave on a string. For a wave on a string, Eq. (40.2) represents a wave of wavelength  $\lambda = 2\pi/k$  and frequency  $f = \omega/2\pi$  propagating in the positive  $x$ -direction. By analogy, our sinusoidal wave function  $\Psi(x, t)$  represents a free particle of mass  $m$ , momentum  $p = \hbar k$ , and energy  $E = \hbar\omega$  moving in the positive  $x$ -direction:

$$\Psi(x, t) = A \cos(kx - \omega t) + B \sin(kx - \omega t) \quad \begin{array}{l} \text{(sinusoidal wave} \\ \text{function representing} \\ \text{a free particle)} \end{array} \quad (40.9)$$

The wave number  $k$  and angular frequency  $\omega$  in Eq. (40.9) must satisfy Eq. (40.8). If you look at Eq. (40.3b), you'll see that taking the second derivative of  $\Psi(x, t)$  in Eq. (40.9) with respect to  $x$  gives us  $\Psi(x, t)$  multiplied by  $-k^2$ . Hence if we multiply  $\partial^2 \Psi(x, t)/\partial x^2$  by  $-\hbar^2/2m$ , we get

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} &= -\frac{\hbar^2}{2m} [-k^2 A \cos(kx - \omega t) - k^2 B \sin(kx - \omega t)] \\ &= \frac{\hbar^2 k^2}{2m} [A \cos(kx - \omega t) + B \sin(kx - \omega t)] \\ &= \frac{\hbar^2 k^2}{2m} \Psi(x, t) \end{aligned} \quad (40.10)$$

Equation (40.10) suggests that  $(-\hbar^2/2m)\partial^2 \Psi(x, t)/\partial x^2$  should be one side of our quantum-mechanical wave equation, with the other side equal to  $\hbar\omega\Psi(x, t)$  in order to satisfy Eq. (40.8). If you look at Eq. (40.3c), you'll see that taking the *first* time derivative of  $\Psi(x, t)$  in Eq. (40.9) brings out a factor of  $\omega$ . So we'll make the educated guess that the right-hand side of our quantum-mechanical wave equation involves  $\hbar = h/2\pi$  times  $\partial\Psi(x, t)/\partial t$ . So our tentative equation is

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} = C\hbar \frac{\partial \Psi(x, t)}{\partial t} \quad (40.11)$$

At this point we include a constant  $C$  as a “fudge factor” to make sure that everything turns out right. Now let's substitute the wave function from Eq. (40.9) into Eq. (40.11). From Eq. (40.10) and Eq. (40.3c), we get

$$\begin{aligned} \frac{\hbar^2 k^2}{2m} [A \cos(kx - \omega t) + B \sin(kx - \omega t)] \\ = C\hbar\omega [A \sin(kx - \omega t) - B \cos(kx - \omega t)] \end{aligned} \quad (40.12)$$

From Eq. (40.8),  $\hbar\omega = \hbar^2 k^2/2m$ , so we can cancel these factors on the two sides of Eq. (40.12). What remains is

$$\begin{aligned} A \cos(kx - \omega t) + B \sin(kx - \omega t) \\ = CA \sin(kx - \omega t) - CB \cos(kx - \omega t) \end{aligned} \quad (40.13)$$



As in our discussion above of the wave equation for waves on a string, in order for Eq. (40.13) to be satisfied for all values of  $x$  and all values of  $t$ , the coefficients of  $\cos(kx - \omega t)$  must be the same on both sides of the equation, and likewise for the coefficients of  $\sin(kx - \omega t)$ . Hence we have the following relationships among the coefficients  $A$ ,  $B$ , and  $C$  in Eqs. (40.9) and (40.11):

$$A = -CB \quad (40.14a)$$

$$B = CA \quad (40.14b)$$

If we use Eq. (40.14b) to eliminate  $B$  from Eq. (40.14a), we get  $A = -C^2A$ , which means that  $C^2 = -1$ . Thus  $C$  is equal to the *imaginary* number  $i = \sqrt{-1}$ , and Eq. (40.11) becomes

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} = i\hbar \frac{\partial \Psi(x, t)}{\partial t} \quad \text{(one-dimensional Schrödinger equation for a free particle)} \quad (40.15)$$

Equation (40.15) is the one-dimensional **Schrödinger equation** for a free particle, developed in 1926 by the Austrian physicist Erwin Schrödinger (**Fig. 40.2**). The presence of the imaginary number  $i$  in Eq. (40.15) means that the solutions to the Schrödinger equation are complex quantities, with a real part and an imaginary part. (The imaginary part of  $\Psi(x, t)$  is a real function multiplied by the imaginary number  $i = \sqrt{-1}$ .) An example is our free-particle wave function from Eq. (40.9). Since we found that  $C = i$  in Eqs. (40.14), it follows from Eq. (40.14b) that  $B = iA$ . Then Eq. (40.9) becomes

$$\Psi(x, t) = A[\cos(kx - \omega t) + i\sin(kx - \omega t)] \quad \begin{array}{l} \text{(sinusoidal wave} \\ \text{function representing} \\ \text{a free particle)} \end{array} \quad (40.16)$$

The real part of  $\Psi(x, t)$  is  $\text{Re}\Psi(x, t) = A\cos(kx - \omega t)$  and the imaginary part is  $\text{Im}\Psi(x, t) = A\sin(kx - \omega t)$ . **Figure 40.3** graphs the real and imaginary parts of  $\Psi(x, t)$  at  $t = 0$ , so  $\Psi(x, 0) = A\cos kx + iA\sin kx$ .

We can rewrite Eq. (40.16) with *Euler's formula*, which states that for any angle  $\theta$ ,

$$\begin{aligned} e^{i\theta} &= \cos\theta + i\sin\theta \\ e^{-i\theta} &= \cos(-\theta) + i\sin(-\theta) = \cos\theta - i\sin\theta \end{aligned} \quad (40.17)$$

Thus our sinusoidal free-particle wave function becomes

$$\Psi(x, t) = Ae^{i(kx - \omega t)} = Ae^{ikx}e^{-i\omega t} \quad \begin{array}{l} \text{(sinusoidal wave function} \\ \text{representing a free particle)} \end{array} \quad (40.18)$$

If  $k$  is positive in Eq. (40.16), the wave function represents a free particle moving in the positive  $x$ -direction with momentum  $p = \hbar k$  and energy  $E = \hbar\omega = \hbar^2 k^2 / 2m$ . If  $k$  is negative, the momentum and hence the motion are in the negative  $x$ -direction. (With a negative value of  $k$ , the wavelength is  $\lambda = 2\pi/|k|$ .)

## Interpreting the Wave Function

The complex nature of the wave function for a free particle makes this function challenging to interpret. (We certainly haven't needed imaginary numbers before this point to describe real physical phenomena.) Here's how to think about this function:  $\Psi(x, t)$  describes the *distribution* of a particle in space, just as the wave functions for an electromagnetic wave describe the distribution of the electric and magnetic fields. When we worked out interference and diffraction patterns in Chapters 35 and 36, we found that the intensity  $I$  of the radiation at any point in a pattern is proportional to the square of the electric-field magnitude—that is, to  $E^2$ . In the photon interpretation of interference and diffraction (see Section 38.4), the intensity at each point is proportional to the number of photons striking around that point or, alternatively, to the *probability* that any individual

Figure 40.2 Erwin Schrödinger (1887–1961) developed the equation that bears his name in 1926, an accomplishment for which he shared (with the British physicist P. A. M. Dirac) the 1933 Nobel Prize in physics. His grave marker is adorned with a version of Eq. (40.15).



Figure 40.3 The spatial wave function  $\Psi(x, t) = Ae^{i(kx - \omega t)}$  for a free particle of definite momentum  $p = \hbar k$  is a complex function: It has both a real part and an imaginary part. These are graphed here as functions of  $x$  for  $t = 0$ .

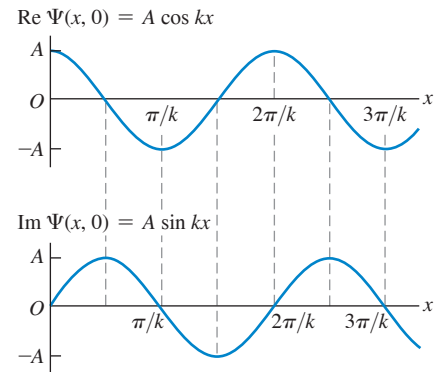
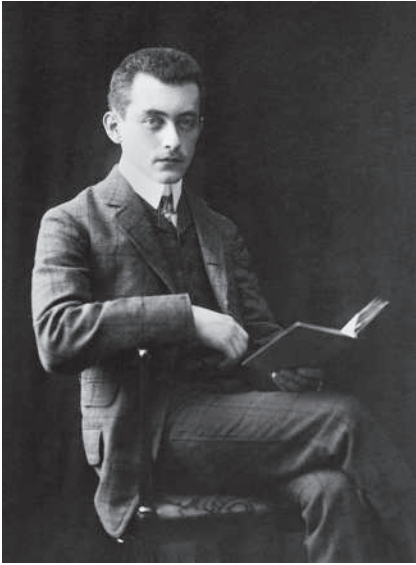


Figure 40.4 In 1926, the German physicist Max Born (1882–1970) devised the interpretation that  $|\Psi|^2$  is the probability distribution function for a particle that is described by the wave function  $\Psi$ . He also coined the term “quantum mechanics” (in the original German, *Quantenmechanik*). For his contributions, Born shared (with Walther Bothe) the 1954 Nobel Prize in physics.



photon will strike around the point. Thus the square of the electric-field magnitude at each point is proportional to the probability of finding a photon around that point.

In exactly the same way, the square of the wave function of a particle at each point tells us about the probability of finding the particle around that point. More precisely, we should say the square of the *absolute value* of the wave function,  $|\Psi|^2$ . This is necessary because, as we have seen, the wave function is a complex quantity with real and imaginary parts.

For a particle that can move only along the  $x$ -direction, the quantity  $|\Psi(x, t)|^2 dx$  is the probability that the particle will be found at time  $t$  at a coordinate in the range from  $x$  to  $x + dx$ . The particle is most likely to be found in regions where  $|\Psi|^2$  is large, and so on. This interpretation, first made by the German physicist Max Born (Fig. 40.4), requires that the wave function  $\Psi$  be *normalized*. That is, the integral of  $|\Psi(x, t)|^2 dx$  over all possible values of  $x$  must equal exactly 1. In other words, the probability is exactly 1, or 100%, that the particle is *somewhere*.

**CAUTION Interpreting  $|\Psi|^2$**  Note that  $|\Psi(x, t)|^2$  itself is *not* a probability. Rather,  $|\Psi(x, t)|^2 dx$  is the probability of finding the particle between position  $x$  and position  $x + dx$  at time  $t$ . If the length  $dx$  is made smaller, it becomes less likely that the particle will be found within that length, so the probability decreases. A better name for  $|\Psi(x, t)|^2$  is the **probability distribution function**, since it describes how the probability of finding the particle at different locations is distributed over space. Another common name for  $|\Psi(x, t)|^2$  is the *probability density*.

We can use the probability interpretation of  $|\Psi|^2$  to get a better understanding of Eq. (40.18), the wave function for a free particle. This function describes a particle that has a definite momentum  $p = \hbar k$  in the  $x$ -direction and *no* uncertainty in momentum:  $\Delta p_x = 0$ . The Heisenberg uncertainty principle for position and momentum, Eqs. (39.29), says that  $\Delta x \Delta p_x \geq \hbar/2$ . If  $\Delta p_x$  is zero, then  $\Delta x$  must be infinite, and we have no idea where along the  $x$ -axis the particle can be found. (We saw a similar result for photons in Section 38.4.) We can show this by calculating the probability distribution function  $|\Psi(x, t)|^2$ : the product of  $\Psi$  and its *complex conjugate*  $\Psi^*$ . To find the complex conjugate of a complex number, we replace all  $i$  with  $-i$ . For example, the complex conjugate of  $c = a + ib$ , where  $a$  and  $b$  are real, is  $c^* = a - ib$ , so  $|c|^2 = c^* c = (a + ib)(a - ib) = a^2 + b^2$  (recall that  $i^2 = -1$ ). The complex conjugate of Eq. (40.18) is

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

(We have to allow for the possibility that the coefficient  $A$  is itself a complex number.) Hence the probability distribution function is

$$\begin{aligned} |\Psi(x, t)|^2 &= \Psi^*(x, t) \Psi(x, t) = (A^* e^{-ikx} e^{i\omega t})(A e^{ikx} e^{-i\omega t}) \\ &= A^* A e^0 = |A|^2 \end{aligned}$$

The probability distribution function doesn't depend on position, which says that we are equally likely to find the particle *anywhere* along the  $x$ -axis! Mathematically, this is because the sinusoidal wave function  $\Psi(x, t) = A e^{i(kx - \omega t)} = A [\cos(kx - \omega t) + i \sin(kx - \omega t)]$  extends all the way from  $x = -\infty$  to  $x = +\infty$  with the same amplitude  $A$ . This also means that the wave function can't be normalized: The integral of  $|\Psi(x, t)|^2$  over all space is infinite for any value of  $A$ .

Note also that the wave function in Eq. (40.18) describes a particle with a definite energy  $E = \hbar\omega$ , so there is zero uncertainty in energy:  $\Delta E = 0$ . The Heisenberg uncertainty principle for energy and time interval,  $\Delta t \Delta E \geq \hbar/2$  [Eq. (39.30)], tells us that the time uncertainty  $\Delta t$  for this particle is infinite. In other words, we can have no idea *when* the particle will pass a given point on the  $x$ -axis. That also agrees with our result  $|\Psi(x, t)|^2 = |A|^2$ ; the probability distribution function has the same value at all times.

Since we always have some idea of where a particle is, the wave function given in Eq. (40.18) isn't a realistic description. In our study of light in Section 38.4, we saw that we can make a wave function that's more *localized* in space by superposing two or more sinusoidal functions. (This would be a good time to review that section.) As an illustration, let's calculate  $|\Psi(x, t)|^2$  for a wave function of this kind.

**EXAMPLE 40.1** A localized free-particle wave function

The wave function  $\Psi(x, t) = Ae^{i(k_1x - \omega_1t)} + Ae^{i(k_2x - \omega_2t)}$  is a superposition of *two* free-particle wave functions of the form given by Eq. (40.18). Both  $k_1$  and  $k_2$  are positive. (a) Show that this wave function satisfies the Schrödinger equation for a free particle of mass  $m$ . (b) Find the probability distribution function for  $\Psi(x, t)$ .

**IDENTIFY and SET UP** Both wave functions  $Ae^{i(k_1x - \omega_1t)}$  and  $Ae^{i(k_2x - \omega_2t)}$  represent a particle moving in the positive  $x$ -direction, but with different momenta and kinetic energies:  $p_1 = \hbar k_1$  and  $E_1 = \hbar\omega_1 = \hbar^2 k_1^2/2m$  for the first function,  $p_2 = \hbar k_2$  and  $E_2 = \hbar\omega_2 = \hbar^2 k_2^2/2m$  for the second function. To test whether a superposition of these is also a valid wave function for a free particle, we'll see whether our function  $\Psi(x, t)$  satisfies the free-particle Schrödinger equation, Eq. (40.15). We'll use the derivatives of the exponential function:  $(d/du)e^{au} = ae^{au}$  and  $(d^2/du^2)e^{au} = a^2e^{au}$ . The probability distribution function  $|\Psi(x, t)|^2$  is the product of  $\Psi(x, t)$  and its complex conjugate.

**EXECUTE** (a) If we substitute  $\Psi(x, t)$  into Eq. (40.15), the left-hand side of the equation is

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} &= -\frac{\hbar^2}{2m} \frac{\partial^2 (Ae^{i(k_1x - \omega_1t)} + Ae^{i(k_2x - \omega_2t)})}{\partial x^2} \\ &= -\frac{\hbar^2}{2m} [(ik_1)^2 Ae^{i(k_1x - \omega_1t)} + (ik_2)^2 Ae^{i(k_2x - \omega_2t)}] \\ &= \frac{\hbar^2 k_1^2}{2m} Ae^{i(k_1x - \omega_1t)} + \frac{\hbar^2 k_2^2}{2m} Ae^{i(k_2x - \omega_2t)} \end{aligned}$$

The right-hand side is

$$\begin{aligned} i\hbar \frac{\partial \Psi(x, t)}{\partial t} &= i\hbar \frac{\partial (Ae^{i(k_1x - \omega_1t)} + Ae^{i(k_2x - \omega_2t)})}{\partial t} \\ &= i\hbar [(-i\omega_1)Ae^{i(k_1x - \omega_1t)} + (-i\omega_2)Ae^{i(k_2x - \omega_2t)}] \\ &= \hbar\omega_1 Ae^{i(k_1x - \omega_1t)} + \hbar\omega_2 Ae^{i(k_2x - \omega_2t)} \end{aligned}$$

The two sides *are* equal, provided that  $\hbar\omega_1 = \hbar^2 k_1^2/2m$  and  $\hbar\omega_2 = \hbar^2 k_2^2/2m$ . These are just the relationships that we noted above. So we conclude that  $\Psi(x, t) = Ae^{i(k_1x - \omega_1t)} + Ae^{i(k_2x - \omega_2t)}$  is a valid free-particle wave function. In general, if we take any two wave functions that are solutions of the Schrödinger equation and then make a superposition of these to create a third wave function  $\Psi(x, t)$ , then  $\Psi(x, t)$  is also a solution of the Schrödinger equation.

(b) The complex conjugate of  $\Psi(x, t)$  is

$$\Psi^*(x, t) = A^* e^{-i(k_1x - \omega_1t)} + A^* e^{-i(k_2x - \omega_2t)}$$

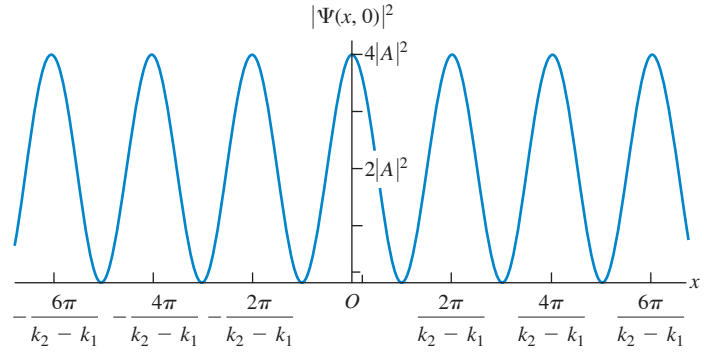
Hence

$$\begin{aligned} |\Psi(x, t)|^2 &= \Psi^*(x, t)\Psi(x, t) \\ &= (A^* e^{-i(k_1x - \omega_1t)} + A^* e^{-i(k_2x - \omega_2t)})(Ae^{i(k_1x - \omega_1t)} + Ae^{i(k_2x - \omega_2t)}) \\ &= A^* A \left[ e^{-i(k_1x - \omega_1t)} e^{i(k_1x - \omega_1t)} + e^{-i(k_2x - \omega_2t)} e^{i(k_2x - \omega_2t)} \right. \\ &\quad \left. + e^{-i(k_1x - \omega_1t)} e^{i(k_2x - \omega_2t)} + e^{-i(k_2x - \omega_2t)} e^{i(k_1x - \omega_1t)} \right] \\ &= |A|^2 [e^0 + e^0 + e^{i[(k_2 - k_1)x - (\omega_2 - \omega_1)t]} + e^{-i[(k_2 - k_1)x - (\omega_2 - \omega_1)t]}] \end{aligned}$$

To simplify this expression, recall that  $e^0 = 1$ . From Euler's formula,  $e^{i\theta} = \cos\theta + i\sin\theta$  and  $e^{-i\theta} = \cos\theta - i\sin\theta$ , so  $e^{i\theta} + e^{-i\theta} = 2\cos\theta$ . Hence

$$\begin{aligned} |\Psi(x, t)|^2 &= |A|^2 \{ 2 + 2\cos[(k_2 - k_1)x - (\omega_2 - \omega_1)t] \} \\ &= 2|A|^2 \{ 1 + \cos[(k_2 - k_1)x - (\omega_2 - \omega_1)t] \} \end{aligned}$$

**Figure 40.5** The probability distribution function at  $t = 0$  for  $\Psi(x, t) = Ae^{i(k_1x - \omega_1t)} + Ae^{i(k_2x - \omega_2t)}$ .



**EVALUATE** Figure 40.5 is a graph of the probability distribution function  $|\Psi(x, t)|^2$  at  $t = 0$ . The value of  $|\Psi(x, t)|^2$  varies between 0 and  $4|A|^2$ ; probabilities can never be negative! The particle has become *some-what* localized: The particle is most likely to be found near a point where  $|\Psi(x, t)|^2$  is maximum (where the functions  $Ae^{i(k_1x - \omega_1t)}$  and  $Ae^{i(k_2x - \omega_2t)}$  interfere constructively) and is very unlikely to be found near a point where  $|\Psi(x, t)|^2 = 0$  (where  $Ae^{i(k_1x - \omega_1t)}$  and  $Ae^{i(k_2x - \omega_2t)}$  interfere destructively).

Note also that the probability distribution function is not stationary: It moves in the positive  $x$ -direction like the particle that it represents. To see this, recall from Section 15.3 that a sinusoidal wave given by  $y(x, t) = A\cos(kx - \omega t)$  moves in the positive  $x$ -direction with speed  $v = \omega/k$ ; since  $|\Psi(x, t)|^2$  includes a term  $\cos[(k_2 - k_1)x - (\omega_2 - \omega_1)t]$ , the probability distribution moves at a speed  $v_{av} = (\omega_2 - \omega_1)/(k_2 - k_1)$ . The subscript “av” reminds us that  $v_{av}$  represents the *average* value of the particle's speed.

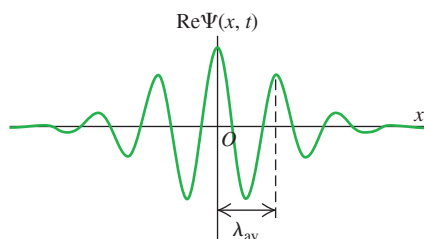
The price we pay for localizing the particle somewhat is that, unlike a particle represented by Eq. (40.18), it no longer has either a definite momentum or a definite energy. That's consistent with the Heisenberg uncertainty principles: If we decrease the uncertainties about where a particle is and when it passes a certain point, the uncertainties in its momentum and energy must increase.

The average momentum of the particle is  $p_{av} = (\hbar k_2 + \hbar k_1)/2$ , which is the average of the momenta associated with the free-particle wave functions we added to create  $\Psi(x, t)$ . This corresponds to the particle having an average speed  $v_{av} = p_{av}/m = (\hbar k_2 + \hbar k_1)/2m$ . Can you show that this is equal to the expression  $v_{av} = (\omega_2 - \omega_1)/(k_2 - k_1)$  that we found above?

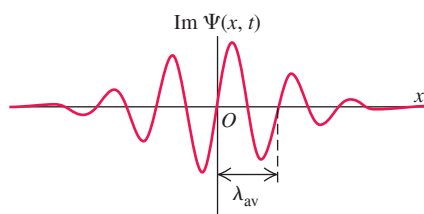
**KEYCONCEPT** A free particle (one on which no forces act) that moves in the  $x$ -direction only is described by a wave function  $\Psi(x, t)$  that obeys the free-particle Schrödinger equation [Eq. (40.15)]. A wave function with definite momentum and energy is completely delocalized; to write a wave function that is localized in space, you must superpose wave functions with different values of momentum and energy.

Figure 40.6 Superposing a large number of sinusoidal waves with different wave numbers and appropriate amplitudes can produce a wave pulse that has a wavelength  $\lambda_{\text{av}} = 2\pi/k_{\text{av}}$  and is localized within a region of space of length  $\Delta x$ . This localized pulse has aspects of both particle and wave.

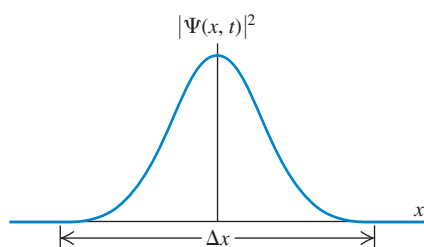
(a) Real part of the wave function at time  $t$



(b) Imaginary part of the wave function at time  $t$



(c) Probability distribution function at time  $t$



## Wave Packets

The wave function that we examined in Example 40.1 is not very well localized: The probability distribution function still extends from  $x = -\infty$  to  $x = +\infty$ . Hence this wave function can't be normalized. To make a wave function that's more highly localized, imagine superposing two additional sinusoidal waves with different wave numbers and amplitudes so as to reinforce alternate maxima of  $|\Psi(x, t)|^2$  in Fig. 40.5 and cancel out the in-between ones. If we continue this process and superpose a very large number of waves with different wave numbers, we can construct a wave with only *one* maximum of  $|\Psi(x, t)|^2$  (Fig. 40.6). Then we have something that begins to look like both a particle and a wave. It is a particle in the sense that it is localized in space; if we look from a distance, it may look like a point. But it also has a periodic structure that is characteristic of a wave.

A localized wave pulse like that shown in Fig. 40.6 is called a **wave packet**. We can represent a wave packet by an expression such as

$$\Psi(x, t) = \int_{-\infty}^{\infty} A(k) e^{i(kx - \omega t)} dk \quad (40.19)$$

This integral represents a superposition of a very large number of waves, each with a different wave number  $k$  and angular frequency  $\omega = \hbar k^2/2m$ , and each with an amplitude  $A(k)$  that depends on  $k$ .

There is an important relationship between the two functions  $\Psi(x, t)$  and  $A(k)$ , which we show qualitatively in Fig. 40.7. If the function  $A(k)$  is sharply peaked, as in Fig. 40.7a, we are superposing only a narrow range of wave numbers. The resulting wave pulse is then relatively broad (Fig. 40.7b). But if we use a wider range of wave numbers, so that the function  $A(k)$  is broader (Fig. 40.7c), then the wave pulse is more narrowly localized (Fig. 40.7d). This is simply the uncertainty principle in action. A narrow range of  $k$  means a narrow range of  $p_x = \hbar k$  and thus a small  $\Delta p_x$ ; the result is a relatively large  $\Delta x$ . A broad range of  $k$  corresponds to a large  $\Delta p_x$ , and the resulting  $\Delta x$  is smaller. You can see that the uncertainty principle for position and momentum,  $\Delta x \Delta p_x \geq \hbar/2$ , is really just a consequence of the properties of integrals like Eq. (40.19).

**CAUTION Matter waves versus light waves in vacuum** We can regard both a wave packet that represents a particle and a short pulse of light from a laser as superpositions of waves of different wave numbers and angular frequencies. An important difference is that the speed of light in vacuum is the same for all wavelengths  $\lambda$  and hence all wave numbers  $k = 2\pi/\lambda$ , but the speed of a matter wave is *different* for different wavelengths. You can see this from the formula for the speed of the wave crests in a periodic wave,  $v = \lambda f = \omega/k$ . For a matter wave,  $\omega = \hbar k^2/2m$ , so  $v = \hbar k/2m = h/2m\lambda$ . Hence matter waves with longer wavelengths and smaller wave numbers travel more slowly than those with short wavelengths and large wave numbers. (This shouldn't be too surprising. The de Broglie relationships that we learned in Section 39.1 tell us that shorter wavelength corresponds to greater momentum and hence a greater speed.) Since the individual sinusoidal waves that make up a wave packet travel at different speeds, the shape of the packet changes as it moves. That's why we've specified the time for which the wave packets in Figs. 40.6 and 40.7 are drawn; at later times, the packets become more spread out. By contrast, a pulse of light waves in vacuum retains the same shape at all times because all of its constituent sinusoidal waves travel together at the same speed. ■

## The One-Dimensional Schrödinger Equation with Potential Energy

The one-dimensional Schrödinger equation that we presented in Eq. (40.15) is valid only for free particles, for which the potential-energy function is zero:  $U(x) = 0$ . But for an electron within an atom, a proton within an atomic nucleus, and many other real situations, the potential energy plays an important role. To study the behavior of matter waves in these situations, we need a version of the Schrödinger equation that describes a particle moving in the presence of a nonzero potential-energy function  $U(x)$ . This equation is



General one-dimensional Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + U(x) \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t} \quad (40.20)$$

Planck's constant divided by  $2\pi$  (pointing to  $\hbar$ )  
Particle's mass (pointing to  $m$ )  
Particle's wave function (pointing to  $\Psi(x, t)$ )  
Potential-energy function (pointing to  $U(x)$ )

Note that if  $U(x) = 0$ , Eq. (40.20) reduces to the free-particle Schrödinger equation given in Eq. (40.15).

Here's the motivation behind Eq. (40.20). If  $\Psi(x, t)$  is a sinusoidal wave function for a free particle,  $\Psi(x, t) = Ae^{i(kx - \omega t)} = Ae^{ikx}e^{-i\omega t}$ , the derivative terms in Eq. (40.20) become

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} (Ae^{ikx}e^{-i\omega t}) = -\frac{\hbar^2}{2m} (ik)^2 (Ae^{ikx}e^{-i\omega t}) \\ &= \frac{\hbar^2 k^2}{2m} \Psi(x, t) \\ i\hbar \frac{\partial \Psi(x, t)}{\partial t} &= i\hbar \frac{\partial}{\partial t} (Ae^{ikx}e^{-i\omega t}) = i\hbar(-i\omega)(Ae^{ikx}e^{-i\omega t}) = \hbar\omega \Psi(x, t) \end{aligned}$$

In these expressions  $(\hbar^2 k^2/2m)\Psi(x, t)$  is just the kinetic energy  $K = p^2/2m = \hbar^2 k^2/2m$  multiplied by the wave function, and  $\hbar\omega \Psi(x, t)$  is the total energy  $E = \hbar\omega$  multiplied by the wave function. So for a wave function of this kind, Eq. (40.20) says that kinetic energy times  $\Psi(x, t)$  plus potential energy times  $\Psi(x, t)$  equals total energy times  $\Psi(x, t)$ . That's equivalent to the statement in classical physics that the sum of kinetic energy and potential energy equals total mechanical energy:  $K + U = E$ .

The observations we've just made certainly aren't a *proof* that Eq. (40.20) is correct. The real reason we know this equation *is* correct is that it works: Predictions made with this equation agree with experimental results. Later in this chapter we'll apply Eq. (40.20) to several physical situations, each with a different form of the function  $U(x)$ .

## Stationary States

We saw in our discussion of wave packets that any free-particle wave function can be built up as a superposition of sinusoidal wave functions of the form  $\Psi(x, t) = Ae^{ikx}e^{-i\omega t}$ . Each such sinusoidal wave function corresponds to a state of definite energy  $E = \hbar\omega = \hbar^2 k^2/2m$  and definite angular frequency  $\omega = E/\hbar$ , so we can rewrite these functions as  $\Psi(x, t) = Ae^{ikx}e^{-iEt/\hbar}$ . If the potential-energy function  $U(x)$  is nonzero, these sinusoidal wave functions do not satisfy the Schrödinger equation, Eq. (40.20), and so these functions cannot be the basic “building blocks” of more complicated wave functions. However, we can still write the wave function for a state of definite energy  $E$  in the form

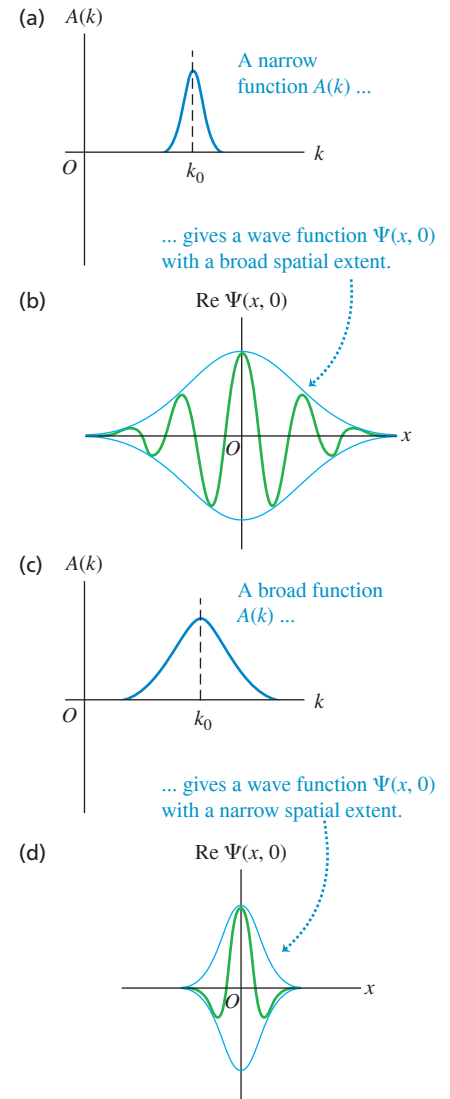
Time-dependent wave function for a state of definite energy

$$\Psi(x, t) = \psi(x) e^{-iEt/\hbar} \quad (40.21)$$

Time-independent wave function (pointing to  $\psi(x)$ )  
Energy of state (pointing to  $E$ )  
Planck's constant divided by  $2\pi$  (pointing to  $\hbar$ )

That is, the wave function  $\Psi(x, t)$  for a state of definite energy is the product of a *time-independent* wave function  $\psi(x)$  and a factor  $e^{-iEt/\hbar}$ . (For the free-particle sinusoidal wave function,  $\psi(x) = Ae^{ikx}$ .) States of definite energy are of tremendous importance in quantum mechanics. For example, for each energy level in a hydrogen atom (Section 39.3) there is a specific wave function. It is possible for an atom to be in a state that does not have a definite energy. The wave function for any such state can be written as a combination of definite-energy wave functions, in precisely the same way that a free-particle wave packet can be written as a superposition of sinusoidal wave functions of definite energy as in Eq. (40.19).

Figure 40.7 How varying the function  $A(k)$  in the wave-packet expression, Eq. (40.19), changes the character of the wave function  $\Psi(x, t)$  (shown here at a specific time  $t = 0$ ).



A state of definite energy is commonly called a **stationary state**. To see where this name comes from, let's multiply Eq. (40.21) by its complex conjugate to find the probability distribution function  $|\Psi|^2$ :

$$\begin{aligned} |\Psi(x, t)|^2 &= \Psi^*(x, t)\Psi(x, t) = [\psi^*(x)e^{+iEt/\hbar}] [\psi(x)e^{-iEt/\hbar}] \\ &= \psi^*(x)\psi(x)e^{(+iEt/\hbar)+(-iEt/\hbar)} = |\psi(x)|^2 e^0 \\ &= |\psi(x)|^2 \end{aligned} \quad (40.22)$$

Since  $|\psi(x)|^2$  does not depend on time, Eq. (40.22) shows that the same must be true for the probability distribution function  $|\Psi(x, t)|^2$ . This justifies the term “stationary state” for a state of definite energy.

**CAUTION** A stationary state does not mean a stationary particle. Saying that a particle is in a stationary state does *not* mean that the particle is at rest. It's the *probability distribution* (that is, the relative likelihood of finding the particle at various positions), not the particle itself, that's stationary. ■

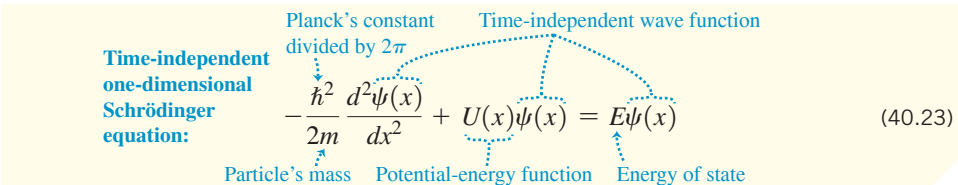
The Schrödinger equation, Eq. (40.20), becomes quite a bit simpler for stationary states. To see this, we substitute Eq. (40.21) into Eq. (40.20):

$$-\frac{\hbar^2}{2m} \frac{\partial^2 [\psi(x)e^{-iEt/\hbar}]}{\partial x^2} + U(x)\psi(x)e^{-iEt/\hbar} = i\hbar \frac{\partial [\psi(x)e^{-iEt/\hbar}]}{\partial t}$$

The derivative in the first term on the left-hand side is with respect to  $x$ , so the factor  $e^{-iEt/\hbar}$  comes outside of the derivative. Now we take the derivative with respect to  $t$  on the right-hand side of the equation:

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} e^{-iEt/\hbar} + U(x)\psi(x)e^{-iEt/\hbar} &= i\hbar \left( \frac{-iE}{\hbar} \right) [\psi(x)e^{-iEt/\hbar}] \\ &= E\psi(x)e^{-iEt/\hbar} \end{aligned}$$

If we divide both sides of this equation by  $e^{-iEt/\hbar}$ , we get



The diagram shows the equation  $-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x)$  with several labels and arrows pointing to its parts:

- Time-independent one-dimensional Schrödinger equation:** Points to the entire equation.
- Planck's constant divided by  $2\pi$ :** Points to  $\hbar$  in the first term.
- Particle's mass:** Points to  $m$  in the first term.
- Potential-energy function:** Points to  $U(x)$ .
- Time-independent wave function:** Points to  $\psi(x)$  in the second term.
- Energy of state:** Points to  $E$  on the right-hand side.

(40.23)

This is called the **time-independent one-dimensional Schrödinger equation**. The time-dependent factor  $e^{-iEt/\hbar}$  does not appear, and Eq. (40.23) involves only the time-independent wave function  $\psi(x)$ . We'll devote much of this chapter to solving this equation to find the definite-energy, stationary-state wave functions  $\psi(x)$  and the corresponding values of  $E$ —that is, the energies of the allowed levels—for different physical situations.

## EXAMPLE 40.2 A stationary state

Consider the wave function  $\psi(x) = A_1 e^{ikx} + A_2 e^{-ikx}$ , where  $k$  is positive. Is this a valid time-independent wave function for a free particle in a stationary state? What is the energy corresponding to this wave function?

**IDENTIFY and SET UP** A valid stationary-state wave function for a free particle must satisfy the time-independent Schrödinger equation, Eq. (40.23), with  $U(x) = 0$ . To test the given function  $\psi(x)$ , we simply substitute it into the left-hand side of the equation. If the result is a constant times  $\psi(x)$ , then the wave function is indeed a solution and the constant is equal to the particle energy  $E$ .

**EXECUTE** Substituting  $\psi(x) = A_1 e^{ikx} + A_2 e^{-ikx}$  and  $U(x) = 0$  into Eq. (40.23), we obtain

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} &= -\frac{\hbar^2}{2m} \frac{d^2(A_1 e^{ikx} + A_2 e^{-ikx})}{dx^2} \\ &= -\frac{\hbar^2}{2m} [(ik)^2 A_1 e^{ikx} + (-ik)^2 A_2 e^{-ikx}] \\ &= \frac{\hbar^2 k^2}{2m} (A_1 e^{ikx} + A_2 e^{-ikx}) = \frac{\hbar^2 k^2}{2m} \psi(x) \end{aligned}$$

The result is a constant times  $\psi(x)$ , so this  $\psi(x)$  is indeed a valid stationary-state wave function for a free particle. Comparing with Eq. (40.23) shows that the constant on the right-hand side is the particle energy:  $E = \hbar^2 k^2 / 2m$ .

**EVALUATE** Note that  $\psi(x)$  is a *superposition* of two different wave functions: one function ( $A_1 e^{ikx}$ ) that represents a particle with magnitude of momentum  $p = \hbar k$  moving in the positive  $x$ -direction, and one function ( $A_2 e^{-ikx}$ ) that represents a particle with the same magnitude of momentum moving in the negative  $x$ -direction. So while the

combined wave function  $\psi(x)$  represents a stationary state with a definite energy, this state does *not* have a definite momentum. We'll see in Section 40.2 that such a wave function can represent a *standing wave*, and we'll explore situations in which such standing matter waves can arise.

**KEYCONCEPT** A quantum-mechanical state of definite energy  $E$  has a wave function of the form  $\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$ . It is called a stationary state because the associated probability distribution function  $|\Psi(x, t)|^2 = |\psi(x)|^2$  does not depend on time.

**TEST YOUR UNDERSTANDING OF SECTION 40.1** Does a wave packet given by Eq. (40.19) represent a stationary state?

**ANSWER** Equation (40.19) represents a superposition of wave functions with different values of wave number  $k$  and hence different values of energy  $E = \hbar^2 k^2 / 2m$ . The state that this combined wave function represents is not a state of definite energy, and therefore not a stationary state. Another way to see this is to note that there is a factor  $e^{-iEt/\hbar}$  inside the integral in Eq. (40.19), with a different value of  $E$  for each value of  $k$ . This wave function therefore has a very complicated time dependence, and the probability distribution function  $|\Psi(x, t)|^2$  does depend on time.

## 40.2 PARTICLE IN A BOX

An important problem in quantum mechanics is how to use the time-independent Schrödinger equation, Eq. (40.23), to determine the possible energy levels and the corresponding wave functions for various systems. That is, for a given potential-energy function  $U(x)$ , what are the possible stationary-state wave functions  $\psi(x)$ , and what are the corresponding energies  $E$ ?

In Section 40.1 we solved this problem for the case  $U(x) = 0$ , corresponding to a *free* particle. The allowed wave functions and corresponding energies are

$$\psi(x) = A e^{ikx} \quad E = \frac{\hbar^2 k^2}{2m} \quad (\text{free particle}) \quad (40.24)$$

The wave number  $k$  is equal to  $2\pi/\lambda$ , where  $\lambda$  is the wavelength. We found that  $k$  can have any real value, so the energy  $E$  of a free particle can have any value from zero to infinity. Furthermore, the particle can be found with equal probability at any value of  $x$  from  $-\infty$  to  $+\infty$ .

Now let's look at a simple model in which a particle is *bound* so that it cannot escape to infinity, but rather is confined to a restricted region of space. Our system consists of a particle confined between two rigid walls separated by a distance  $L$  (**Fig. 40.8**). The motion is purely one dimensional, with the particle moving along the  $x$ -axis only and the walls at  $x = 0$  and  $x = L$ . The potential energy corresponding to the rigid walls is infinite, so the particle cannot escape; between the walls, the potential energy is zero (**Fig. 40.9**). This situation is often described as a “**particle in a box**.” This model might represent an electron that is free to move within a long, straight molecule or along a very thin wire.

### Wave Functions for a Particle in a Box

To solve the Schrödinger equation for this system, we begin with some restrictions on the particle's stationary-state wave function  $\psi(x)$ . Because the particle is confined to the region  $0 \leq x \leq L$ , we expect the probability distribution function  $|\Psi(x, t)|^2 = |\psi(x)|^2$  and the wave function  $\psi(x)$  to be zero outside that region. This agrees with the Schrödinger equation: If the term  $U(x)\psi(x)$  in Eq. (40.23) is to be finite, then  $\psi(x)$  must be zero where  $U(x)$  is infinite.

Furthermore,  $\psi(x)$  must be a *continuous* function to be a mathematically well-behaved solution to the Schrödinger equation. This implies that  $\psi(x)$  must be zero at the region's boundary,  $x = 0$  and  $x = L$ . These two conditions serve as *boundary conditions* for the

Figure 40.8 The Newtonian view of a particle in a box.

A particle with mass  $m$  moves along a straight line at constant speed, bouncing between two rigid walls a distance  $L$  apart.

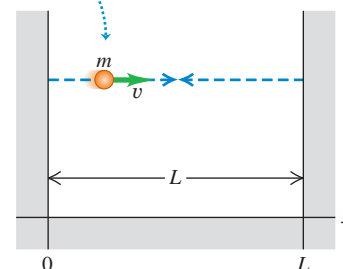


Figure 40.9 The potential-energy function for a particle in a box.

The potential energy  $U$  is zero in the interval  $0 < x < L$  and is infinite everywhere outside this interval.

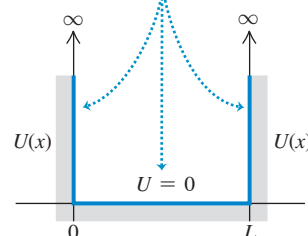
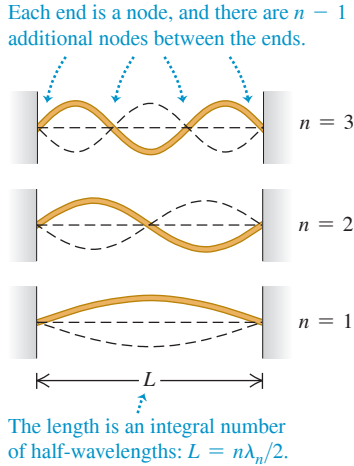


Figure 40.10 Normal modes of vibration for a string with length  $L$ , held at both ends.



problem. They should look familiar, because they are the same conditions that we used to find the normal modes of a vibrating string in Section 15.8 (Fig. 40.10); you should review that discussion.

An additional condition is that to calculate the second derivative  $d^2\psi(x)/dx^2$  in Eq. (40.23), the *first* derivative  $d\psi(x)/dx$  must also be continuous except at points where the potential energy becomes infinite (as it does at the walls of the box). This is analogous to the requirement that a vibrating string, like those shown in Fig. 40.10, can't have any kinks in it (which would correspond to a discontinuity in the first derivative of the wave function) except at the ends of the string.

We now solve for the wave functions in the region  $0 \leq x \leq L$  subject to the above conditions. In this region  $U(x) = 0$ , so  $\psi(x)$  in this region must satisfy

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad (\text{particle in a box}) \quad (40.25)$$

Equation (40.25) is the *same* Schrödinger equation as for a free particle, so it is tempting to conclude that the wave functions and energies are given by Eq. (40.24). It is true that  $\psi(x) = Ae^{ikx}$  satisfies the Schrödinger equation with  $U(x) = 0$ , is continuous, and has a continuous first derivative  $d\psi(x)/dx = ikAe^{ikx}$ . However, this wave function does *not* satisfy the boundary conditions that  $\psi(x)$  must be zero at  $x = 0$  and  $x = L$ : At  $x = 0$  the wave function in Eq. (40.24) is equal to  $Ae^0 = A$ , and at  $x = L$  it is equal to  $Ae^{ikL}$ . (These would be equal to zero if  $A = 0$ , but then the wave function would be zero and there would be no particle at all!)

The way out of this dilemma is to recall Example 40.2 (Section 40.1), in which we found that a more general stationary-state solution to the time-independent Schrödinger equation with  $U(x) = 0$  is

$$\psi(x) = A_1e^{ikx} + A_2e^{-ikx} \quad (40.26)$$

This wave function is a superposition of two waves: one traveling in the  $+x$ -direction of amplitude  $A_1$ , and one traveling in the  $-x$ -direction with the same wave number but amplitude  $A_2$ . This is analogous to a standing wave on a string (Fig. 40.10), which we can regard as the superposition of two sinusoidal waves propagating in opposite directions (see Section 15.7). The energy that corresponds to Eq. (40.26) is  $E = \hbar^2k^2/2m$ , just as for a single wave.

To see whether the wave function given by Eq. (40.26) can satisfy the boundary conditions, let's first rewrite it in terms of sines and cosines by using Euler's formula, Eq. (40.17):

$$\begin{aligned} \psi(x) &= A_1(\cos kx + i\sin kx) + A_2[\cos(-kx) + i\sin(-kx)] \\ &= A_1(\cos kx + i\sin kx) + A_2(\cos kx - i\sin kx) \\ &= (A_1 + A_2)\cos kx + i(A_1 - A_2)\sin kx \end{aligned} \quad (40.27)$$

At  $x = 0$  this is equal to  $\psi(0) = A_1 + A_2$ , which must equal zero to satisfy the boundary condition at that point. Hence  $A_2 = -A_1$ , and Eq. (40.27) becomes

$$\psi(x) = 2iA_1\sin kx = C\sin kx \quad (40.28)$$

We have simplified the expression by introducing the constant  $C = 2iA_1$ . (We'll come back to this constant later.) We can also satisfy the second boundary condition that  $\psi = 0$  at  $x = L$  by choosing values of  $k$  such that  $kL = n\pi$  ( $n = 1, 2, 3, \dots$ ). Hence Eq. (40.28) does indeed give the stationary-state wave functions for a particle in a box in the region  $0 \leq x \leq L$ . (Outside this region,  $\psi(x) = 0$ .) The possible values of  $k$  and the wavelength  $\lambda = 2\pi/k$  are

$$k = \frac{n\pi}{L} \quad \text{and} \quad \lambda = \frac{2\pi}{k} = \frac{2L}{n} \quad (n = 1, 2, 3, \dots) \quad (40.29)$$

Just as for the string in Fig. 40.10, the length  $L$  of the region is an integral number of half-wavelengths.



## Energy Levels for a Particle in a Box

The possible energy levels for a particle in a box are given by  $E = \hbar^2 k^2 / 2m = p^2 / 2m$ , where  $p = \hbar k = (h/2\pi)(2\pi/\lambda) = h/\lambda$  is the magnitude of momentum of a free particle with wave number  $k$  and wavelength  $\lambda$ . This makes sense, since inside the region  $0 \leq x \leq L$  the potential energy is zero and the energy is all kinetic. For each value of  $n$ , there are corresponding values of  $p$ ,  $\lambda$ , and  $E$ ; let's call them  $p_n$ ,  $\lambda_n$ , and  $E_n$ . Putting the pieces together, we get

$$p_n = \frac{h}{\lambda_n} = \frac{nh}{2L} \quad (40.30)$$

and so the energy levels for a particle in a box are

$$E_n = \frac{p_n^2}{2m} = \frac{n^2 h^2}{8mL^2} = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad (n = 1, 2, 3, \dots) \quad (40.31)$$

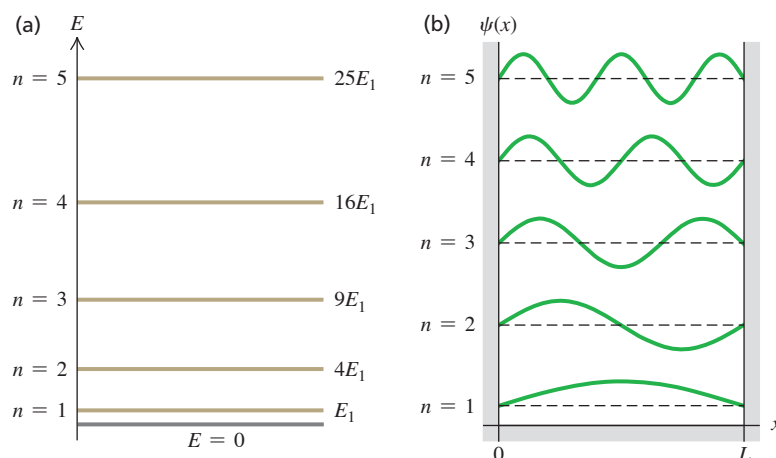
Energy levels for a particle in a box Magnitude of momentum Planck's constant Planck's constant divided by  $2\pi$   
Particle's mass Width of box Quantum number

Each energy level has its own value of the quantum number  $n$  and a corresponding wave function, which we denote by  $\psi_n$ . When we replace  $k$  in Eq. (40.28) by  $n\pi/L$  from Eq. (40.29), we find

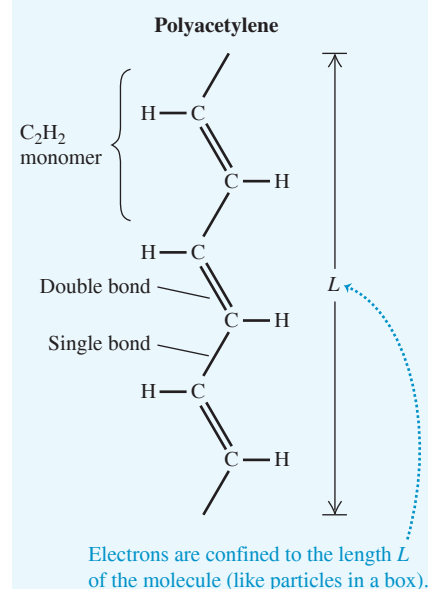
$$\psi_n(x) = C \sin \frac{n\pi x}{L} \quad (n = 1, 2, 3, \dots) \quad (40.32)$$

The energy-level diagram in **Fig. 40.11a** shows the five lowest levels for a particle in a box. The energy levels are proportional to  $n^2$ , so successively higher levels are spaced farther and farther apart. There are an infinite number of levels because the walls are perfectly rigid; even a particle of infinitely great kinetic energy is confined within the box. Figure 40.11b shows graphs of the wave functions  $\psi_n(x)$  for  $n = 1, 2, 3, 4$ , and 5. Note that these functions look identical to those for a standing wave on a string (see Fig. 40.10).

**CAUTION** A particle in a box cannot have zero energy The energy of a particle in a box *cannot* be zero. Equation (40.31) shows that  $E = 0$  would require  $n = 0$ , but substituting  $n = 0$  into Eq. (40.32) gives a zero wave function. Since a particle is described by a *nonzero* wave function, there cannot be a particle with  $E = 0$ . This is a consequence of the Heisenberg uncertainty principle: A particle in a zero-energy state would have a definite value of momentum (precisely zero), so its position uncertainty would be infinite and the particle could be found anywhere along the  $x$ -axis. But this is impossible, since a particle in a box can be found only between  $x = 0$  and  $x = L$ . Hence  $E = 0$  is not allowed. By contrast, the allowed stationary-state wave functions with  $n = 1, 2, 3, \dots$  do not represent states of definite momentum (each is an equal mixture of a state of  $x$ -momentum  $+p_n = nh/2L$  and a state of  $x$ -momentum  $-p_n = -nh/2L$ ). Hence each stationary state has a nonzero momentum uncertainty, consistent with having a finite position uncertainty. ■



**APPLICATION** **Particles in a Polymer “Box”** Polyacetylene is one of a class of long-chain organic molecules that conduct electricity along their length. The molecule is made up of a large number of ( $C_2H_2$ ) units, called *monomers* (only three monomers are shown here). Electrons can move freely along the length of the molecule but not perpendicular to the length, so the molecule is like a one-dimensional “box” for electrons. The length  $L$  of the molecule depends on the number of monomers. Experiment shows that the allowed energy levels agree well with Eq. (40.31): The greater the number of monomers and the greater the length  $L$ , the lower the energy levels and the smaller the spacing between these levels.



**Figure 40.11** (a) Energy-level diagram for a particle in a box. Each energy is  $n^2 E_1$ , where  $E_1$  is the ground-level energy. (b) Wave functions for a particle in a box, with  $n = 1, 2, 3, 4$ , and 5. **CAUTION:** The five graphs have been displaced vertically for clarity, as in Fig. 40.10. Each of the horizontal dashed lines represents  $\psi = 0$  for the respective wave function.

## EXAMPLE 40.3 Electron in an atom-size box

## WITH VARIATION PROBLEMS

Find the first two energy levels for an electron confined to a one-dimensional box  $5.0 \times 10^{-10}$  m across (about the diameter of an atom).

**IDENTIFY and SET UP** This problem uses what we have learned in this section about a particle in a box. The first two energy levels correspond to  $n = 1$  and  $n = 2$  in Eq. (40.31).

**EXECUTE** From Eq. (40.31),

$$E_1 = \frac{h^2}{8mL^2} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2}{8(9.109 \times 10^{-31} \text{ kg})(5.0 \times 10^{-10} \text{ m})^2} \\ = 2.4 \times 10^{-19} \text{ J} = 1.5 \text{ eV}$$

$$E_2 = \frac{2^2 h^2}{8mL^2} = 4E_1 = 9.6 \times 10^{-19} \text{ J} = 6.0 \text{ eV}$$

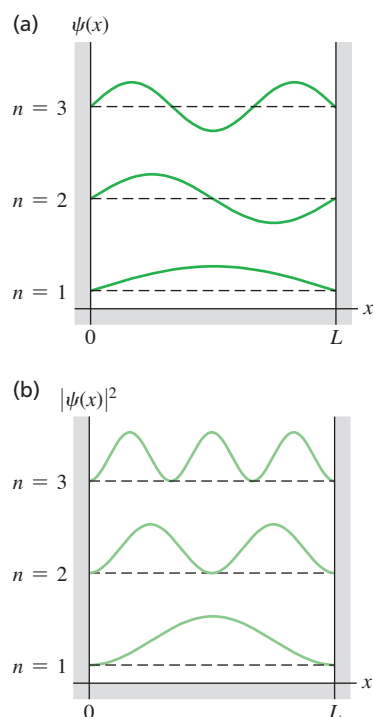
**EVALUATE** The difference between the first two energy levels is  $E_2 - E_1 = 4.5$  eV. An electron confined to a box is different from an electron bound in an atom, but it is reassuring that this result is of the same order of magnitude as the difference between actual atomic energy levels.

You can show that for a proton or neutron ( $m = 1.67 \times 10^{-27}$  kg) confined to a box  $1.1 \times 10^{-14}$  m across (the width of a medium-sized atomic nucleus), the energies of the first two levels are about a million times larger:  $E_1 = 1.7 \times 10^6$  eV = 1.7 MeV,  $E_2 = 4E_1 = 6.8$  MeV,  $E_2 - E_1 = 5.1$  MeV. This suggests why nuclear reactions (which involve transitions between energy levels in nuclei) release so much more energy than chemical reactions (which involve transitions between energy levels of electrons in atoms).

Finally, you can show (see Exercise 40.9) that the energy levels of a billiard ball ( $m = 0.2$  kg) confined to a box 1.3 m across—the width of a billiard table—are separated by about  $5 \times 10^{-67}$  J. Quantum effects won't disturb a game of billiards.

**KEYCONCEPT** The wave functions for the stationary states of a particle confined to a one-dimensional box are sinusoidal standing waves inside the box with a node at each end; the wave function is zero outside the box. The  $n$ th stationary state has a wave function with  $n$  half-wavelengths within the length of the box, and has an energy equal to  $n^2$  times the energy of the lowest-energy ( $n = 1$ ) state. There are an infinite number of these stationary states.

Figure 40.12 Graphs of (a)  $\psi(x)$  and (b)  $|\psi(x)|^2$  for the first three wave functions ( $n = 1, 2, 3$ ) for a particle in a box. The horizontal dashed lines represent  $\psi(x) = 0$  and  $|\psi(x)|^2 = 0$  for each of the three levels. The value of  $|\psi(x)|^2 dx$  at each point is the probability of finding the particle in a small interval  $dx$  about the point. As in Fig. 40.11b, the three graphs in each part have been displaced vertically for clarity.



## Probability and Normalization

Let's look a bit more closely at the wave functions for a particle in a box, keeping in mind the *probability* interpretation of the wave function  $\psi$  that we discussed in Section 40.1. In our one-dimensional situation the quantity  $|\psi(x)|^2 dx$  is proportional to the probability that the particle will be found within a small interval  $dx$  about  $x$ . For a particle in a box,

$$|\psi(x)|^2 dx = C^2 \sin^2 \frac{n\pi x}{L} dx$$

Figure 40.12 shows graphs of both  $\psi(x)$  and  $|\psi(x)|^2$  for  $n = 1, 2$ , and 3. Note that not all positions are equally likely. By contrast, in classical mechanics the particle is equally likely to be found at any position between  $x = 0$  and  $x = L$ . We see from Fig. 40.12b that  $|\psi(x)|^2 = 0$  at some points, so there is zero probability of finding the particle at exactly these points. Don't let that bother you; the uncertainty principle has already shown us that we can't measure position exactly. The particle is localized only to be somewhere between  $x = 0$  and  $x = L$ .

The particle must be *somewhere* on the  $x$ -axis—that is, somewhere between  $x = -\infty$  and  $x = +\infty$ . So the *sum* of the probabilities for all the  $dx$ 's everywhere (the *total* probability of finding the particle) must equal 1. That's the normalization condition that we discussed in Section 40.1:

$$\text{Normalization condition, time-independent wave function:} \quad \int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1 \quad \text{Time-independent wave function} \quad (40.33)$$

Probability distribution function      Probability that particle is somewhere on  $x$ -axis

A wave function is said to be *normalized* if it has a constant such as  $C$  in Eq. (40.32) that is calculated to make the total probability equal 1 in Eq. (40.33). For a normalized wave function,  $|\psi(x)|^2 dx$  is not merely proportional to, but *equals*, the probability of finding the particle between the coordinates  $x$  and  $x + dx$ . That's why we call  $|\psi(x)|^2$  the probability distribution function. (In Section 40.1 we called  $|\Psi(x, t)|^2$  the probability distribution function. For the case of a stationary-state wave function, however,  $|\Psi(x, t)|^2$  is equal to  $|\psi(x)|^2$ .)

Let's normalize the particle-in-a-box wave functions  $\psi_n(x)$  given by Eq. (40.32). Since  $\psi_n(x)$  is zero except between  $x = 0$  and  $x = L$ , Eq. (40.33) becomes

$$\int_0^L C^2 \sin^2 \frac{n\pi x}{L} dx = 1 \quad (40.34)$$

You can evaluate this integral by using the trigonometric identity  $\sin^2 \theta = \frac{1}{2}(1 - \cos 2\theta)$ ; the result is  $C^2 L/2$ . Thus our probability interpretation of the wave function demands that  $C^2 L/2 = 1$ , or  $C = (2/L)^{1/2}$ ; the constant  $C$  is *not* arbitrary. (This is in contrast to the classical vibrating string problem, in which  $C$  represents an amplitude that depends on initial conditions.) Thus the normalized stationary-state wave functions for a particle in a box are

Stationary-state wave functions for a particle in a box

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad (n = 1, 2, 3, \dots)$$

Quantum number  $n$   
Width of box  $L$

(40.35)

#### EXAMPLE 40.4 A nonsinusoidal wave function?

#### WITH VARIATION PROBLEMS

(a) Show that  $\psi(x) = Ax + B$ , where  $A$  and  $B$  are constants, is a solution of the Schrödinger equation for an  $E = 0$  energy level of a particle in a box. (b) What constraints do the boundary conditions at  $x = 0$  and  $x = L$  place on the constants  $A$  and  $B$ ?

**IDENTIFY and SET UP** To be physically reasonable, a wave function must satisfy both the Schrödinger equation and the appropriate boundary conditions. In part (a) we'll substitute  $\psi(x)$  into the Schrödinger equation for a particle in a box, Eq. (40.25), to determine whether it is a solution. In part (b) we'll see what restrictions on  $\psi(x)$  arise from applying the boundary conditions that  $\psi(x) = 0$  at  $x = 0$  and  $x = L$ .

**EXECUTE** (a) From Eq. (40.25), the Schrödinger equation for an  $E = 0$  energy level of a particle in a box is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x) = 0$$

in the region  $0 \leq x \leq L$ . Differentiating  $\psi(x) = Ax + B$  twice with respect to  $x$  gives  $d^2\psi(x)/dx^2 = 0$ , so the left side of the equation is

zero, and so  $\psi(x) = Ax + B$  is a solution of this Schrödinger equation for  $E = 0$ . (Note that both  $\psi(x)$  and its derivative  $d\psi(x)/dx = A$  are continuous functions, as they must be.)

(b) Applying the boundary condition at  $x = 0$  gives  $\psi(0) = B = 0$ , and so  $\psi(x) = Ax$ . Applying the boundary condition at  $x = L$  gives  $\psi(L) = AL = 0$ , so  $A = 0$ . Hence  $\psi(x) = 0$  both inside the box ( $0 \leq x \leq L$ ) and outside: There is *zero* probability of finding the particle anywhere with this wave function, and so  $\psi(x) = Ax + B$  is *not* a physically valid wave function.

**EVALUATE** The moral is that there are many functions that satisfy the Schrödinger equation for a given physical situation, but most of these—including the function considered here—have to be rejected because they don't satisfy the appropriate boundary conditions.

**KEYCONCEPT** To be physically reasonable, a stationary-state wave function for a given situation must satisfy both the Schrödinger equation and any boundary conditions that apply to that situation.

## Time Dependence

The wave functions  $\psi_n(x)$  in Eq. (40.35) depend only on the *spatial* coordinate  $x$ . Equation (40.21) shows that if  $\psi(x)$  is the wave function for a state of definite energy  $E$ , the full time-dependent wave function is  $\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$ . Hence the *time-dependent* stationary-state wave functions for a particle in a box are

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{-iE_n t/\hbar} \quad (n = 1, 2, 3, \dots) \quad (40.36)$$

In this expression the energies  $E_n$  are given by Eq. (40.31). The higher the quantum number  $n$ , the greater the angular frequency  $\omega_n = E_n/\hbar$  at which the wave function oscillates. Note that since  $|e^{-iE_n t/\hbar}|^2 = e^{+iE_n t/\hbar} e^{-iE_n t/\hbar} = e^0 = 1$ , the probability distribution function  $|\Psi_n(x, t)|^2 = (2/L) \sin^2(n\pi x/L)$  is independent of time and does *not* oscillate. (Remember, this is why we say that these states of definite energy are *stationary*.)

**TEST YOUR UNDERSTANDING OF SECTION 40.2** If a particle in a box is in the  $n$ th energy level, what is the average value of its  $x$ -component of momentum  $p_x$ ? (i)  $nh/2L$ ; (ii)  $(\sqrt{2}/2)nh/L$ ; (iii)  $(1/\sqrt{2})nh/L$ ; (iv)  $[1/(2\sqrt{2})]nh/L$ ; (v) zero.

**ANSWER** (v) Our derivation of the stationary-state wave functions for a particle in a box shows that they are superpositions of waves propagating in opposite directions, just like a standing wave on a string. One wave has momentum in the positive  $x$ -direction, while the other wave has an equal magnitude of momentum in the negative  $x$ -direction. The total  $x$ -component of momentum is zero.

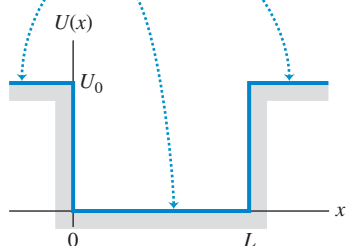
### 40.3 POTENTIAL WELLS

A **potential well** is a potential-energy function  $U(x)$  that has a minimum. We introduced this term in Section 7.5, and we also used it in our discussion of periodic motion in Chapter 14. In Newtonian mechanics a particle trapped in a potential well can vibrate back and forth with periodic motion. Our first application of the Schrödinger equation, the particle in a box, involved a rudimentary potential well with a function  $U(x)$  that is zero within a certain interval and infinite everywhere else. As we mentioned in Section 40.2, this function corresponds to a few situations found in nature, but the correspondence is only approximate.

A better approximation to several physical situations is a **finite well**, which is a potential well that has straight sides but *finite* height. **Figure 40.13** shows a potential-energy function that is zero in the interval  $0 \leq x \leq L$  and has the value  $U_0$  outside this interval. This function is often called a **square-well potential**. It could serve as a simple model of an electron within a metallic sheet with thickness  $L$ , moving perpendicular to the surfaces of the sheet. The electron can move freely inside the metal but has to climb a potential-energy barrier with height  $U_0$  to escape from either surface of the metal. The energy  $U_0$  is related to the *work function* that we discussed in Section 38.1 in connection with the photoelectric effect. In three dimensions, a spherical version of a finite well gives an approximate description of the motions of protons and neutrons within a nucleus.

Figure 40.13 A square-well potential.

The potential energy  $U$  is zero within the potential well (in the interval  $0 \leq x \leq L$ ) and has the constant value  $U_0$  outside this interval.



#### Bound States of a Square-Well Potential

In Newtonian mechanics, the particle is trapped (localized) in a well if the total mechanical energy  $E$  is less than  $U_0$ . In quantum mechanics, such a trapped state is often called a **bound state**. All states are bound for an infinitely deep well like the one we described in Section 40.2. For a finite well like that shown in Fig. 40.13, if  $E$  is greater than  $U_0$ , the particle is *not* bound.

Let's see how to solve the Schrödinger equation for the bound states of a square-well potential. Our goal is to find the energies and wave functions for which  $E < U_0$ . It's easiest to consider separately the regions where  $U = 0$  and where  $U = U_0$ . Inside the square well ( $0 \leq x \leq L$ ), where  $U = 0$ , the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad \text{or} \quad \frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2} \psi(x) \quad (40.37)$$

This is the same as Eq. (40.25) from Section 40.2, which describes a particle in a box. As in Section 40.2, we can express the solutions of this equation as combinations of  $\cos kx$  and  $\sin kx$ , where  $E = \hbar^2 k^2 / 2m$ . We can rewrite the relationship between  $E$  and  $k$  as  $k = \sqrt{2mE}/\hbar$ . Hence inside the square well we have

$$\psi(x) = A \cos\left(\frac{\sqrt{2mE}}{\hbar} x\right) + B \sin\left(\frac{\sqrt{2mE}}{\hbar} x\right) \quad (\text{inside the well}) \quad (40.38)$$

where  $A$  and  $B$  are constants. So far, this looks a lot like the particle-in-a-box analysis in Section 40.2. The difference is that for the square-well potential, the potential energy outside the well is not infinite, so the wave function  $\psi(x)$  outside the well is *not* zero.



For the regions outside the well ( $x < 0$  and  $x > L$ ) the potential-energy function in the time-independent Schrödinger equation is  $U = U_0$ :

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + U_0\psi(x) = E\psi(x) \quad \text{or} \quad \frac{d^2\psi(x)}{dx^2} = \frac{2m(U_0 - E)}{\hbar^2}\psi(x) \quad (40.39)$$

The quantity  $U_0 - E$  is positive, so the solutions of this equation are exponential functions rather than sines or cosines. Using  $\kappa$  (the Greek letter kappa) to represent the quantity  $[2m(U_0 - E)]^{1/2}/\hbar$  and taking  $\kappa$  as positive, we can write the solutions as

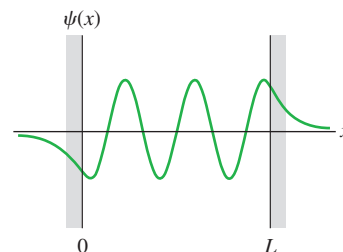
$$\psi(x) = Ce^{\kappa x} + De^{-\kappa x} \quad (\text{outside the well}) \quad (40.40)$$

where  $C$  and  $D$  are constants with different values in the two regions  $x < 0$  and  $x > L$ . Note that  $\psi$  can't be allowed to approach infinity as  $x \rightarrow +\infty$  or  $x \rightarrow -\infty$ . [If it did, we wouldn't be able to satisfy the normalization condition, Eq. (40.33).] This means that in Eq. (40.40), we must have  $D = 0$  for  $x < 0$  and  $C = 0$  for  $x > L$ .

Our calculations so far show that the bound-state wave functions for a finite well are sinusoidal inside the well [Eq. (40.38)] and exponential outside it [Eq. (40.40)]. We have to *match* the wave functions inside and outside the well so that they satisfy the boundary conditions that we mentioned in Section 40.2:  $\psi(x)$  and  $d\psi(x)/dx$  must be continuous at the boundary points  $x = 0$  and  $x = L$ . If the wave function  $\psi(x)$  or the slope  $d\psi(x)/dx$  were to change discontinuously at a point, the second derivative  $d^2\psi(x)/dx^2$  would be *infinite* at that point. That would violate the time-independent Schrödinger equation, Eq. (40.23), which says that at every point  $d^2\psi(x)/dx^2$  is proportional to  $U - E$ . For a finite well  $U - E$  is finite everywhere, so  $d^2\psi(x)/dx^2$  must also be finite everywhere.

Matching the sinusoidal and exponential functions at the boundary points so that they join smoothly is possible only for certain specific values of the total energy  $E$ , so this requirement determines the possible energy levels of the finite square well. There is no simple formula for the energy levels as there was for the infinitely deep well. Finding the levels is a fairly complex mathematical problem that requires solving a transcendental equation by numerical approximation; we won't go into the details. **Figure 40.14** shows the general shape of a possible wave function. The most striking features of this wave function are the “exponential tails” that extend outside the well into regions that are forbidden by Newtonian mechanics (because in those regions the particle would have negative kinetic energy). We see that there is some probability for finding the particle *outside* the potential well, which would be impossible in classical mechanics. In Section 40.4 we'll discuss an amazing result of this effect.

**Figure 40.14** A possible wave function for a particle in a finite potential well. The function is sinusoidal inside the well ( $0 \leq x \leq L$ ) and exponential outside it. It approaches zero asymptotically at large  $|x|$ . The functions must join smoothly at  $x = 0$  and  $x = L$ ; the wave function and its derivative must be continuous.



### EXAMPLE 40.5 Outside a finite well

(a) Show that Eq. (40.40),  $\psi(x) = Ce^{\kappa x} + De^{-\kappa x}$ , is indeed a solution of the time-independent Schrödinger equation outside a finite well of height  $U_0$ . (b) What happens to  $\psi(x)$  in the limit  $U_0 \rightarrow \infty$ ?

**IDENTIFY and SET UP** In part (a), we try the given function  $\psi(x)$  in the time-independent Schrödinger equation for  $x < 0$  and for  $x > L$ , Eq. (40.39). In part (b), we note that in the limit  $U_0 \rightarrow \infty$  the finite well becomes an *infinite* well, like that for a particle in a box (Section 40.2). So in this limit the wave functions outside a finite well must reduce to the wave functions outside the box.

**EXECUTE** (a) We must show that  $\psi(x) = Ce^{\kappa x} + De^{-\kappa x}$  satisfies  $d^2\psi(x)/dx^2 = [2m(U_0 - E)/\hbar^2]\psi(x)$ . We recall that  $(d/du)e^{au} = ae^{au}$  and  $(d^2/du^2)e^{au} = a^2e^{au}$ ; the left-hand side of the Schrödinger equation is then

$$\begin{aligned} \frac{d^2\psi(x)}{dx^2} &= \frac{d^2}{dx^2}(Ce^{\kappa x}) + \frac{d^2}{dx^2}(De^{-\kappa x}) \\ &= C\kappa^2 e^{\kappa x} + D(-\kappa)^2 e^{-\kappa x} \\ &= \kappa^2(Ce^{\kappa x} + De^{-\kappa x}) = \kappa^2\psi(x) \end{aligned}$$

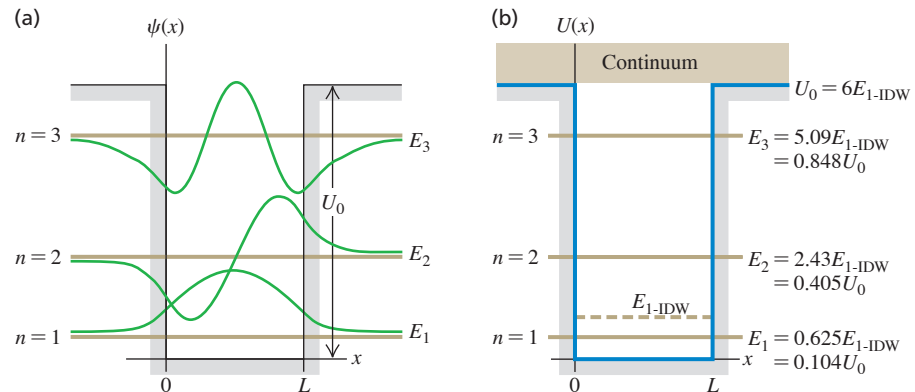
Since from Eq. (40.40)  $\kappa^2 = 2m(U_0 - E)/\hbar^2$ , this is equal to the right-hand side of the equation. The equation is satisfied, and  $\psi(x)$  is a solution.

(b) As  $U_0$  approaches infinity,  $\kappa$  also approaches infinity. In the region  $x < 0$ ,  $\psi(x) = Ce^{\kappa x}$ ; as  $\kappa \rightarrow \infty$ ,  $\kappa x \rightarrow -\infty$  (since  $x$  is negative) and  $e^{\kappa x} \rightarrow 0$ , so the wave function approaches zero for all  $x < 0$ . Likewise, we can show that the wave function also approaches zero for all  $x > L$ . This is just what we found in Section 40.2; the wave function for a particle in a box must be zero outside the box.

**EVALUATE** Our result in part (b) shows that the infinite square well is a *limiting case* of the finite well. We've seen many cases in Newtonian mechanics where it's important to consider limiting cases [such as Examples 5.11 (Section 5.2) and 5.13 (Section 5.3)]. Limiting cases are no less important in quantum mechanics.

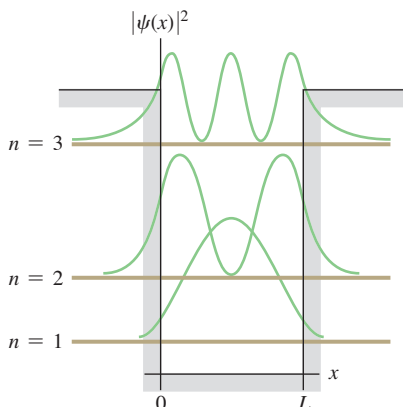
**KEYCONCEPT** A finite potential well is a region where the potential energy is constant and less than the constant value outside that region. If a particle is in a bound state, so that in Newtonian mechanics it would not have enough energy to escape from the well, its stationary-state wave function is sinusoidal within the well and exponential outside the well.

Figure 40.15 (a) Wave functions for the three bound states for a particle in a finite potential well of depth  $U_0 = 6E_{1\text{-IDW}}$ . (Here  $E_{1\text{-IDW}}$  is the ground-level energy for an infinite well of the same width.) The horizontal brown line for each wave function corresponds to  $\psi = 0$ ; the vertical placement of these lines indicates the energy of each bound state (compare Fig. 40.11). (b) Energy-level diagram for this system. All energies greater than  $U_0$  are possible; states with  $E > U_0$  form a continuum.



**CAUTION Misconceptions about the finite potential well** Note that in our notation the energy of a particle in a finite potential well is given relative to the *bottom* of the well, which we take to be  $E = 0$ . (We did the same for the particle in a box, or infinite potential well, in Section 40.2.) If the depth of a finite square well is  $U_0$ , a bound state has an energy that is greater than zero but less than  $U_0$ . Note also that how far the exponential part of a bound state wave function extends outside a finite potential well depends on the energy of the bound state. The greater the bound state energy, the farther outside the well the wave function extends and the farther outside the particle is likely to be found (Fig. 40.15). **I**

Figure 40.16 Probability distribution functions  $|\psi(x)|^2$  for the square-well wave functions shown in Fig. 40.15. The horizontal brown line for each wave function corresponds to  $|\psi|^2 = 0$ .



### Comparing Finite and Infinite Square Wells

Let's continue the comparison of the finite-depth potential well with the infinitely deep well, which we began in Example 40.5. First, because the wave functions for the finite well don't go to zero at  $x = 0$  and  $x = L$ , the wavelength of the sinusoidal part of each wave function is *longer* than it would be with an infinite well. This increase in  $\lambda$  corresponds to a reduced magnitude of momentum  $p = h/\lambda$  and therefore a reduced energy. Thus each energy level, including the ground level, is *lower* for a finite well than for an infinitely deep well with the same width.

Second, a well with finite depth  $U_0$  has only a *finite* number of bound states and corresponding energy levels, compared to the *infinite* number for an infinitely deep well. How many levels there are depends on the magnitude of  $U_0$  in comparison with the ground-level energy for the infinitely deep well (IDW), which we call  $E_{1\text{-IDW}}$ . From Eq. (40.31),

$$E_{1\text{-IDW}} = \frac{\pi^2 \hbar^2}{2mL^2} \quad (\text{ground-level energy, infinitely deep well}) \quad (40.41)$$

When the well is very deep so  $U_0$  is much larger than  $E_{1\text{-IDW}}$ , there are many bound states and the energies of the lowest few are nearly the same as the energies for the infinitely deep well. When  $U_0$  is only a few times as large as  $E_{1\text{-IDW}}$  there are only a few bound states. (There is always at least *one* bound state, no matter how shallow the well.) As with the infinitely deep well, there is no state with  $E = 0$ ; such a state would violate the uncertainty principle.

**Figure 40.15** shows the case  $U_0 = 6E_{1\text{-IDW}}$ , for which there are three bound states. In the figure, we express the energy levels both as fractions of the well depth  $U_0$  and as multiples of  $E_{1\text{-IDW}}$ . If the well were infinitely deep, the lowest three levels, as given by Eq. (40.31), would be  $E_{1\text{-IDW}}$ ,  $4E_{1\text{-IDW}}$ , and  $9E_{1\text{-IDW}}$ . Figure 40.15 also shows the wave functions for the three bound states.

It turns out that when  $U_0$  is less than  $E_{1\text{-IDW}}$ , there is only one bound state. In the limit when  $U_0$  is *much smaller* than  $E_{1\text{-IDW}}$  (a very shallow well), the energy of this single state is approximately  $E = 0.68U_0$ .

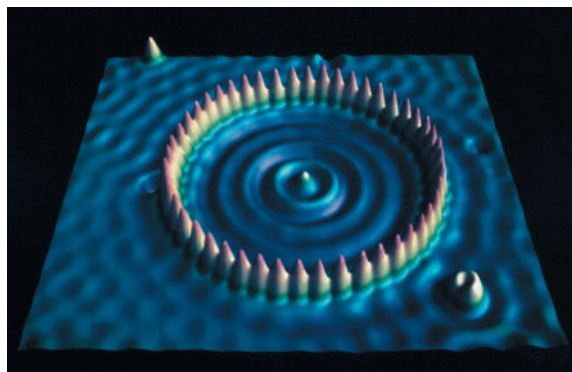
**Figure 40.16** shows graphs of the probability distributions—that is, the values of  $|\psi|^2$ —for the wave functions shown in Fig. 40.15a. As with the infinite well, not all positions are equally likely. Unlike the infinite well, there is some probability of finding the particle outside the well in the classically forbidden regions.

There are also states for which  $E$  is *greater* than  $U_0$ . In these *free-particle states* the particle is not bound but is free to move through all values of  $x$ . Any energy  $E$  greater than  $U_0$  is possible, so the free-particle states form a *continuum* rather than a discrete set

of states with definite energy levels. The free-particle wave functions are sinusoidal both inside and outside the well. The wavelength is shorter inside the well than outside, corresponding to greater kinetic energy inside the well than outside it.

**Figure 40.17** shows particles in a *two-dimensional* finite potential well. Example 40.6 describes another application of the square-well potential.

**Figure 40.17** To make this image, 48 iron atoms (shown as yellow peaks) were placed in a circle on a copper surface. The “elevation” at each point inside the circle indicates the electron density within the circle. The standing-wave pattern is very similar to the probability distribution function for a particle in a one-dimensional finite potential well. (This image was made with a scanning tunneling microscope, discussed in Section 40.4.)



### EXAMPLE 40.6 An electron in a finite well

### WITH VARIATION PROBLEMS

An electron is trapped in a square well 0.50 nm across (roughly five times a typical atomic diameter). (a) Find the ground-level energy  $E_{1-IDW}$  if the well is infinitely deep. (b) Find the energy levels if the actual well depth  $U_0$  is six times the ground-level energy found in part (a). (c) Find the wavelength of the photon emitted when the electron makes a transition from the  $n = 2$  level to the  $n = 1$  level. In what region of the electromagnetic spectrum does the photon wavelength lie? (d) If the electron is in the  $n = 1$  (ground) level and absorbs a photon, what is the minimum photon energy that will free the electron from the well? In what region of the spectrum does the wavelength of this photon lie?

**IDENTIFY and SET UP** Equation (40.41) gives the ground-level energy  $E_{1-IDW}$  for an infinitely deep well, and Fig. 40.15b shows the energies for a square well with  $U_0 = 6E_{1-IDW}$ . The energy of the photon emitted or absorbed in a transition is equal to the difference in energy between two levels involved in the transition; the photon wavelength is given by  $E = hc/\lambda$  (see Chapter 38).

**EXECUTE** (a) From Eq. (40.41),

$$E_{1-IDW} = \frac{\pi^2 \hbar^2}{2mL^2} = \frac{\pi^2 (1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2(9.11 \times 10^{-31} \text{ kg})(0.50 \times 10^{-9} \text{ m})^2} = 2.4 \times 10^{-19} \text{ J} = 1.5 \text{ eV}$$

(b) We have  $U_0 = 6E_{1-IDW} = 6(1.5 \text{ eV}) = 9.0 \text{ eV}$ . We can read off the energy levels from Fig. 40.15b:

$$\begin{aligned} E_1 &= 0.625E_{1-IDW} = 0.625(1.5 \text{ eV}) = 0.94 \text{ eV} \\ E_2 &= 2.43E_{1-IDW} = 2.43(1.5 \text{ eV}) = 3.6 \text{ eV} \\ E_3 &= 5.09E_{1-IDW} = 5.09(1.5 \text{ eV}) = 7.6 \text{ eV} \end{aligned}$$

(c) The photon energy and wavelength for the  $n = 2$  to  $n = 1$  transition are

$$\begin{aligned} E_2 - E_1 &= 3.6 \text{ eV} - 0.94 \text{ eV} = 2.7 \text{ eV} \\ \lambda &= \frac{hc}{E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{2.7 \text{ eV}} = 460 \text{ nm} \end{aligned}$$

in the blue region of the visible spectrum.

(d) We see from Fig. 40.15b that the minimum energy needed to free the electron from the well from the  $n = 1$  level is  $U_0 - E_1 = 9.0 \text{ eV} - 0.94 \text{ eV} = 8.1 \text{ eV}$ , which is three times the 2.7 eV photon energy found in part (c). Hence the corresponding photon wavelength is one-third of 460 nm, or (to two significant figures) 150 nm, which is in the ultraviolet region of the spectrum.

**EVALUATE** As a check, you can calculate the bound-state energies by using the formulas  $E_1 = 0.104U_0$ ,  $E_2 = 0.405U_0$ , and  $E_3 = 0.848U_0$  given in Fig. 40.15b. As an additional check, note that the first three energy levels of an infinitely deep well of the same width are  $E_{1-IDW} = 1.5 \text{ eV}$ ,  $E_{2-IDW} = 4E_{1-IDW} = 6.0 \text{ eV}$ , and  $E_{3-IDW} = 9E_{1-IDW} = 13.5 \text{ eV}$ . The energies we found in part (b) are less than these values: As we mentioned earlier, the finite depth of the well lowers the energy levels compared to the levels for an infinitely deep well.

One application of these ideas is *quantum dots*, which are **?** nanometer-sized particles of a semiconductor such as cadmium selenide (CdSe). An electron within a quantum dot behaves much like a particle in a finite potential well of width  $L$  equal to the size of the dot. When quantum dots are illuminated with ultraviolet light, the electrons absorb the ultraviolet photons and are excited into high energy levels, such as the  $n = 3$  level described in this example. If the electron returns to the ground level ( $n = 1$ ) in two or more steps (for example,

*Continued*

from  $n = 3$  to  $n = 2$  and from  $n = 2$  to  $n = 1$ ), one step will involve emitting a visible-light photon, as we have calculated here. (We described this process of *fluorescence* in Section 39.3.) Increasing the value of  $L$  decreases the energies of the levels and hence the spacing between them, and thus decreases the energy and increases the wavelength of the emitted photons. The photograph that opens this chapter shows quantum dots of different sizes in solution: Each emits a characteristic wavelength that depends on the dot size. Quantum dots can

be injected into living tissue and their fluorescent glow used as a tracer for biological research and for medicine. They may also be the key to a new generation of lasers and ultrafast computers.

**KEYCONCEPT** A finite square well has a finite number of bound states. The energies of these bound states are determined by the boundary conditions that the wave function and its derivative are both continuous at the edges of the well.

**TEST YOUR UNDERSTANDING OF SECTION 40.3** Suppose that the width of the finite potential well shown in Fig. 40.15 is reduced by one-half. How must the value of  $U_0$  change so that there are still just three bound energy levels whose energies are the fractions of  $U_0$  shown in Fig. 40.15b?  $U_0$  must (i) increase by a factor of four; (ii) increase by a factor of two; (iii) remain the same; (iv) decrease by a factor of one-half; (v) decrease by a factor of one-fourth.

### ANSWER

(i) The energy levels are arranged as shown in Fig. 40.15b if  $U_0 = 6E_1$ , where  $E_1$  is the ground-level energy of an infinite well. If the well width  $L$  is reduced to one-half of its initial value,  $E_1$  increases by a factor of four and so  $U_0$  must also increase by a factor of four. The energies  $E_1$ ,  $E_2$ , and  $E_3$  shown in Fig. 40.15b are all specific fractions of  $U_0$ , so they will also increase by a factor of four.

Figure 40.18 A potential-energy barrier. According to Newtonian mechanics, if the total energy of the system is  $E_1$ , a particle to the left of the barrier can go no farther than  $x = a$ . If the total energy is greater than  $E_2$ , the particle can pass over the barrier.

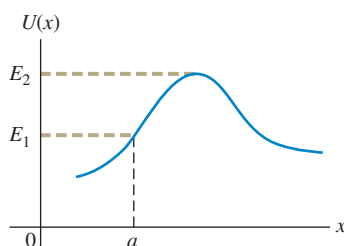
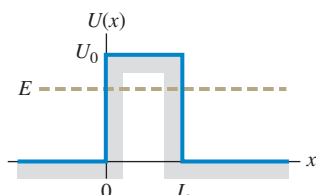


Figure 40.19 A rectangular potential-energy barrier with width  $L$  and height  $U_0$ . According to Newtonian mechanics, if the total energy  $E$  is less than  $U_0$ , a particle cannot pass over this barrier but is confined to the side where it starts.



## 40.4 POTENTIAL BARRIERS AND TUNNELING

A **potential barrier** is the opposite of a potential well; it is a potential-energy function with a *maximum*. Figure 40.18 shows an example. In classical Newtonian mechanics, if a particle (such as a roller coaster) is located to the left of the barrier (which might be a hill), and if the total mechanical energy of the system is  $E_1$ , the particle cannot move farther to the right than  $x = a$ . If it did, the potential energy  $U$  would be greater than the total mechanical energy  $E$  and the kinetic energy  $K = E - U$  would be negative. This is impossible in classical mechanics since  $K = \frac{1}{2}mv^2$  can never be negative.

A quantum-mechanical particle behaves differently: If it encounters a barrier like the one in Fig. 40.18 and has energy less than  $E_2$ , it *may* appear on the other side. This phenomenon is called *tunneling*. In quantum-mechanical tunneling, unlike macroscopic, mechanical tunneling, the particle does not actually push through the barrier and loses no energy in the process.

### Tunneling Through a Rectangular Barrier

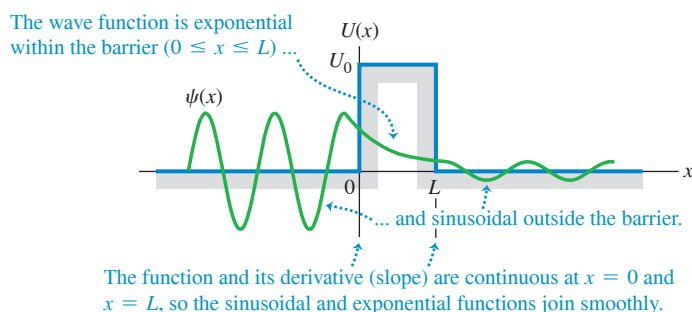
To understand how tunneling can occur, let's look at the potential-energy function  $U(x)$  shown in Fig. 40.19. It's like Fig. 40.13 turned upside-down; the potential energy is zero everywhere except in the range  $0 \leq x \leq L$ , where it has the value  $U_0$ . This might represent a simple model for the potential energy of an electron in the presence of two slabs of metal separated by an air gap of thickness  $L$ . The potential energy is lower within either slab than in the gap between them.

Let's consider solutions of the Schrödinger equation for this potential-energy function for the case in which  $E$  is less than  $U_0$ . We can use our results from Section 40.3. In the regions  $x < 0$  and  $x > L$ , where  $U = 0$ , the solution is sinusoidal and is given by Eq. (40.38). Within the barrier ( $0 \leq x \leq L$ ),  $U = U_0$  and the solution is exponential as in Eq. (40.40). Just as with the finite potential well, the functions have to join smoothly at the boundary points  $x = 0$  and  $x = L$ , which means that both  $\psi(x)$  and  $d\psi(x)/dx$  have to be continuous at these points.

These requirements lead to a wave function like the one shown in Fig. 40.20. The function is *not* zero inside the barrier (the region forbidden by Newtonian mechanics). Even more remarkable, a particle that is initially to the *left* of the barrier has some probability of being found to the *right* of the barrier. How great this probability is depends on the width  $L$  of the barrier and the particle's energy  $E$  in comparison with the barrier height  $U_0$ .



Figure 40.20 A possible wave function for a particle tunneling through the potential-energy barrier shown in Fig. 40.19.



The **tunneling probability**  $T$  that the particle gets through the barrier is proportional to the square of the ratio of the amplitudes of the sinusoidal wave functions on the two sides of the barrier. These amplitudes are determined by matching wave functions and their derivatives at the boundary points, a fairly involved mathematical problem. When  $T$  is much smaller than unity, it is given approximately by

$$T = Ge^{-2\kappa L} \text{ where } G = 16 \frac{E}{U_0} \left(1 - \frac{E}{U_0}\right) \text{ and } \kappa = \frac{\sqrt{2m(U_0 - E)}}{\hbar} \quad (40.42)$$

(probability of tunneling)

The probability decreases rapidly with increasing barrier width  $L$ . It also depends critically on the energy difference  $U_0 - E$ , which in Newtonian physics is the additional kinetic energy the particle would need to be able to climb over the barrier.

### EXAMPLE 40.7 Tunneling through a barrier

### WITH VARIATION PROBLEMS

A 2.0 eV electron encounters a barrier 5.0 eV high. What is the probability that it will tunnel through the barrier if the barrier width is (a) 1.00 nm and (b) 0.50 nm?

**IDENTIFY and SET UP** This problem uses the ideas of tunneling through a rectangular barrier, as in Figs. 40.19 and 40.20. Our target variable is the tunneling probability  $T$  in Eq. (40.42), which we evaluate for the given values  $E = 2.0$  eV (electron energy),  $U = 5.0$  eV (barrier height),  $m = 9.11 \times 10^{-31}$  kg (mass of the electron), and  $L = 1.00$  nm or 0.50 nm (barrier width).

**EXECUTE** First we evaluate  $G$  and  $\kappa$  in Eq. (40.42), using  $E = 2.0$  eV:

$$G = 16 \left( \frac{2.0 \text{ eV}}{5.0 \text{ eV}} \right) \left( 1 - \frac{2.0 \text{ eV}}{5.0 \text{ eV}} \right) = 3.8$$

$$U_0 - E = 5.0 \text{ eV} - 2.0 \text{ eV} = 3.0 \text{ eV} = 4.8 \times 10^{-19} \text{ J}$$

$$\kappa = \frac{\sqrt{2(9.11 \times 10^{-31} \text{ kg})(4.8 \times 10^{-19} \text{ J})}}{1.055 \times 10^{-34} \text{ J} \cdot \text{s}} = 8.9 \times 10^9 \text{ m}^{-1}$$

(a) When  $L = 1.00 \text{ nm} = 1.00 \times 10^{-9} \text{ m}$ , we have  $2\kappa L = 2(8.9 \times 10^9 \text{ m}^{-1})(1.00 \times 10^{-9} \text{ m}) = 17.8$  and  $T = Ge^{-2\kappa L} = 3.8e^{-17.8} = 7.1 \times 10^{-8}$ .

(b) When  $L = 0.50 \text{ nm}$ , one-half of 1.00 nm,  $2\kappa L$  is one-half of 17.8, or 8.9. Hence  $T = 3.8e^{-8.9} = 5.2 \times 10^{-4}$ .

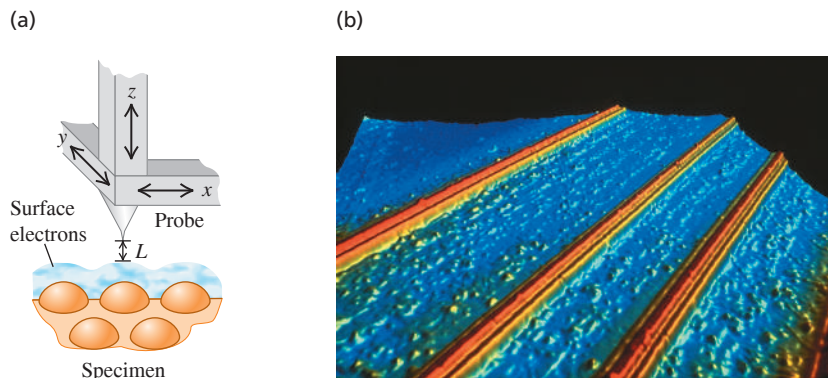
**EVALUATE** Halving the width of this barrier increases the tunneling probability  $T$  by a factor of  $(5.2 \times 10^{-4})/(7.1 \times 10^{-8}) = 7.3 \times 10^3$ , or nearly ten thousand. The tunneling probability is an *extremely* sensitive function of the barrier width. Note that our results for  $T$  in both part (a) and (b) are much less than 1, which is consistent with the assumptions that go into Eq. (40.42).

**KEYCONCEPT** Quantum-mechanical particles can be found in places where Newtonian mechanics would forbid them to be. An example is tunneling, in which a particle can pass through a barrier where its total mechanical energy is less than the potential energy. The probability that tunneling occurs depends on the width of the barrier and the additional energy the particle would need to “climb” over the barrier.

## Applications of Tunneling

Tunneling has a number of practical applications, some of considerable importance. When you twist two copper wires together or close the contacts of a switch, current passes from one conductor to the other despite a thin layer of nonconducting copper oxide between them. The electrons tunnel through this thin insulating layer. A *tunnel diode* is a semiconductor device in which electrons tunnel through a potential barrier. The current can be switched on and off very quickly (within a few picoseconds) by varying the height of the barrier.

Figure 40.21 (a) Schematic diagram of the probe of a scanning tunneling microscope (STM). As the sharp conducting probe is scanned across the surface in the  $x$ - and  $y$ -directions, it is also moved in the  $z$ -direction to maintain a constant tunneling current. The changing position of the probe is recorded and used to construct an image of the surface. (b) This colored STM image shows “quantum wires”: thin strips, just 10 atoms wide, of a conductive rare-earth silicide atop a silicon surface. Such quantum wires may one day be the basis of ultraminiaturized circuits.



### BIO APPLICATION Electron Tunneling in Enzymes

Protein molecules play essential roles as enzymes in living organisms. Enzymes like the one shown here are large molecules, and in many cases their function depends on the ability of electrons to tunnel across the space that separates one part of the molecule from another. Without tunneling, life as we know it would be impossible!

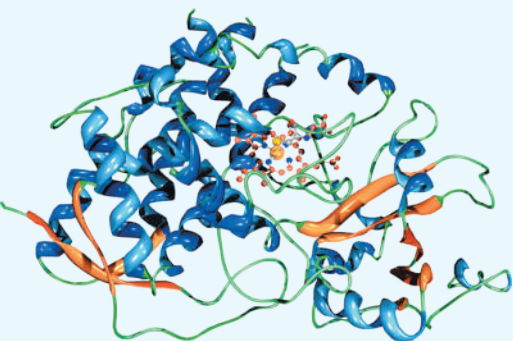
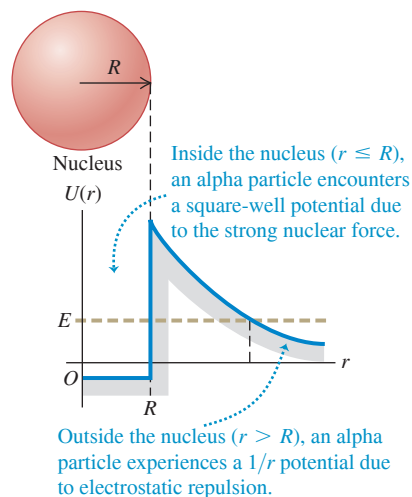


Figure 40.22 Approximate potential-energy function for an alpha particle interacting with a nucleus of radius  $R$ . If an alpha particle inside the nucleus has energy  $E$  greater than zero, it can tunnel through the barrier and escape from the nucleus.



A *Josephson junction* consists of two superconductors separated by an oxide layer a few atoms (1 to 2 nm) thick. Electron pairs in the superconductors can tunnel through the barrier layer, giving such a device unusual circuit properties. Josephson junctions are useful for establishing precise voltage standards and measuring tiny magnetic fields, and they play a crucial role in the developing field of quantum computing.

The *scanning tunneling microscope* (STM) uses electron tunneling to create images of surfaces down to the scale of individual atoms. An extremely sharp conducting needle is brought very close to the surface, within 1 nm or so (Fig. 40.21a). When the needle is at a positive potential with respect to the surface, electrons can tunnel through the surface potential-energy barrier and reach the needle. As Example 40.7 shows, the tunneling probability and hence the tunneling current are very sensitive to changes in the width  $L$  of the barrier (the distance between the surface and the needle tip). In one mode of operation the needle is scanned across the surface while being moved perpendicular to the surface to maintain a constant tunneling current. The needle motion is recorded; after many parallel scans, an image of the surface can be reconstructed. Extremely precise control of needle motion, including isolation from vibration, is essential. Figure 40.21b shows an STM image. (Figure 40.17 is also an STM image.)

Tunneling is also of great importance in nuclear physics. A fusion reaction can occur when two nuclei tunnel through the barrier caused by their electrical repulsion and approach each other closely enough for the attractive nuclear force to cause them to fuse. Fusion reactions occur in the cores of stars, including the sun; without tunneling, the sun wouldn't shine. The emission of alpha particles from unstable nuclei such as radium also involves tunneling. An alpha particle is a cluster of two protons and two neutrons (the same as a nucleus of the most common form of helium). Such clusters form naturally within larger atomic nuclei. An alpha particle trying to escape from a nucleus encounters a potential barrier that results from the combined effect of the attractive nuclear force and the electrical repulsion of the remaining part of the nucleus (Fig. 40.22). To escape, the alpha particle must tunnel through this barrier. Depending on the barrier height and width for a given kind of alpha-emitting nucleus, the tunneling probability can be low or high, and the alpha-emitting material will have low or high radioactivity. Recall from Section 39.2 that Ernest Rutherford used alpha particles from a radioactive source to discover the atomic nucleus. Although Rutherford did not know it, tunneling allowed these alpha particles to escape from their parent nuclei, which made his experiments possible! We'll learn more about alpha decay in Chapter 43.

**TEST YOUR UNDERSTANDING OF SECTION 40.4** Is it possible for a particle undergoing tunneling to be found *within* the barrier rather than on either side of it?

**ANSWER** Yes. Figure 40.20 shows a possible wave function  $\psi(x)$  for tunneling. Since  $\psi(x)$  is not zero within the barrier ( $0 \leq x \leq L$ ), there is some probability that the particle can be found there.

## 40.5 THE HARMONIC OSCILLATOR

Systems that *oscillate* are of tremendous importance in the physical world, from the oscillations of your eardrums in response to a sound wave to the vibrations of the ground caused by an earthquake. Oscillations are equally important on the microscopic scale where quantum effects dominate. The molecules of the air around you can be set into vibration when they collide with each other, the protons and neutrons in an excited atomic nucleus can oscillate in opposite directions, and a microwave oven transfers energy to food by making water molecules in the food flip back and forth. In this section we'll look at the solutions of the Schrödinger equation for the simplest kind of vibrating system, the quantum-mechanical harmonic oscillator.

As we learned in Section 14.2, a **harmonic oscillator** is a particle with mass  $m$  that moves along the  $x$ -axis under the influence of a conservative force  $F_x = -k'x$ . The constant  $k'$  is called the *force constant*. (In Section 14.2 we used the symbol  $k$  for the force constant. In this section we'll use the symbol  $k'$  instead to minimize confusion with the wave number  $k = 2\pi/\lambda$ .) The force is proportional to the particle's displacement  $x$  from its equilibrium position,  $x = 0$ . The corresponding potential-energy function is  $U = \frac{1}{2}k'x^2$  (**Fig. 40.23**). In Newtonian mechanics, when the particle is displaced from equilibrium, it undergoes sinusoidal motion with frequency  $f = (1/2\pi)(k'/m)^{1/2}$  and angular frequency  $\omega = 2\pi f = (k'/m)^{1/2}$ . The amplitude (that is, the maximum displacement from equilibrium) of these Newtonian oscillations is  $A$ , which is related to the energy  $E$  of the oscillator by  $E = \frac{1}{2}k'A^2$ .

Let's make an enlightened guess about the energy levels of a quantum-mechanical harmonic oscillator. In classical physics an electron oscillating with angular frequency  $\omega$  emits electromagnetic radiation with that same angular frequency. It's reasonable to guess that when an excited quantum-mechanical harmonic oscillator with angular frequency  $\omega = (k'/m)^{1/2}$  (according to Newtonian mechanics, at least) makes a transition from one energy level to a lower level, it would emit a photon with this same angular frequency  $\omega$ . The energy of such a photon is  $hf = (2\pi\hbar)(\omega/2\pi) = \hbar\omega$ . So we would expect that the spacing between adjacent energy levels of the harmonic oscillator would be

$$hf = \hbar\omega = \hbar \sqrt{\frac{k'}{m}} \quad (40.43)$$

That's the same spacing between energy levels that Planck assumed in deriving his radiation law (see Section 39.5). It was a good assumption; as we'll see, the energy levels are in fact half-integer  $(\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots)$  multiples of  $\hbar\omega$ .

### Wave Functions, Boundary Conditions, and Energy Levels

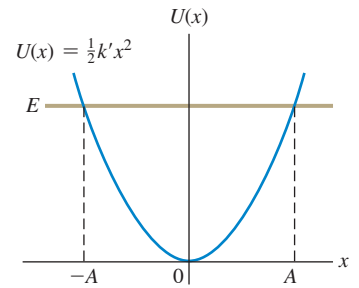
We'll begin our quantum-mechanical analysis of the harmonic oscillator by writing down the one-dimensional time-independent Schrödinger equation, Eq. (40.23), with  $\frac{1}{2}k'x^2$  in place of  $U$ :

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + \frac{1}{2}k'x^2\psi(x) = E\psi(x) \quad \text{(Schrödinger equation for the harmonic oscillator)} \quad (40.44)$$

The solutions of this equation are wave functions for the physically possible states of the system.

In the discussion of square-well potentials in Section 40.2 we found that the energy levels are determined by boundary conditions at the walls of the well. However, the harmonic-oscillator potential has no walls as such; what, then, are the appropriate boundary conditions? Classically,  $|x|$  cannot be greater than the amplitude  $A$  given by  $E = \frac{1}{2}k'A^2$ . Quantum mechanics does allow some penetration into classically forbidden regions, but the probability decreases as that penetration increases. Thus the wave functions must approach zero as  $|x|$  grows large.

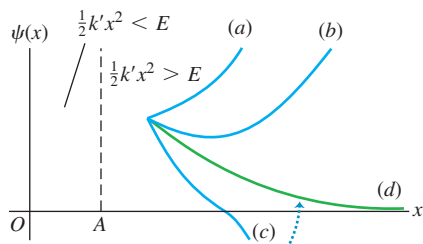
Figure 40.23 Potential-energy function for the harmonic oscillator. In Newtonian mechanics the amplitude  $A$  is related to the total energy  $E$  by  $E = \frac{1}{2}k'A^2$ , and the particle is restricted to the range from  $x = -A$  to  $x = A$ . In quantum mechanics the particle can be found at  $x > A$  or  $x < -A$ .



Satisfying the requirement that  $\psi(x) \rightarrow 0$  as  $|x| \rightarrow \infty$  is not as trivial as it may seem. To see why this is, let's rewrite Eq. (40.44) in the form

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2} \left( \frac{1}{2}k'x^2 - E \right) \psi(x) \quad (40.45)$$

**Figure 40.24** Possible behaviors of harmonic-oscillator wave functions in the region  $\frac{1}{2}k'x^2 > E$ . In this region,  $\psi(x)$  and  $d^2\psi(x)/dx^2$  have the same sign. The curve is concave upward when  $d^2\psi(x)/dx^2$  is positive and concave downward when  $d^2\psi(x)/dx^2$  is negative.



Only curve *d*, which approaches the *x*-axis asymptotically for large *x*, is an acceptable wave function for this system.

Equation (40.45) shows that when  $x$  is large enough (either positive or negative) to make the quantity  $(\frac{1}{2}k'x^2 - E)$  positive, the function  $\psi(x)$  and its second derivative  $d^2\psi(x)/dx^2$  have the same sign. **Figure 40.24** shows four possible kinds of behavior of  $\psi(x)$  beginning at a point where  $x$  is greater than the classical amplitude  $A$ , so that  $\frac{1}{2}k'x^2 - \frac{1}{2}k'A^2 = \frac{1}{2}k'x^2 - E > 0$ . Let's look at these four cases more closely. If  $\psi(x)$  is positive as shown in Fig. 40.24, Eq. (40.45) tells us that  $d^2\psi(x)/dx^2$  is also positive and the function is *concave upward*. Note also that  $d^2\psi(x)/dx^2$  is the rate of change of the *slope* of  $\psi(x)$ ; this will help us understand how our four possible wave functions behave.

- **Curve *a*:** The slope of  $\psi(x)$  is positive at point  $x$ . Since  $d^2\psi(x)/dx^2 > 0$ , the function curves upward increasingly steeply and goes to infinity. This violates the boundary condition that  $\psi(x) \rightarrow 0$  as  $|x| \rightarrow \infty$ , so this isn't a viable wave function.
- **Curve *b*:** The slope of  $\psi(x)$  is negative at point  $x$ , and  $d^2\psi(x)/dx^2$  has a large positive value. Hence the slope changes rapidly from negative to positive and keeps on increasing—so, again, the wave function goes to infinity. This wave function isn't viable either.
- **Curve *c*:** As for curve *b*, the slope is negative at point  $x$ . However,  $d^2\psi(x)/dx^2$  now has a *small* positive value, so the slope increases only gradually as  $\psi(x)$  decreases to zero and crosses over to negative values. Equation (40.45) tells us that once  $\psi(x)$  becomes negative,  $d^2\psi(x)/dx^2$  also becomes negative. Hence the curve becomes *concave downward* and heads for *negative* infinity. This wave function, too, fails to satisfy the requirement that  $\psi(x) \rightarrow 0$  as  $|x| \rightarrow \infty$  and thus isn't viable.
- **Curve *d*:** If the slope of  $\psi(x)$  at point  $x$  is negative, and the positive value of  $d^2\psi(x)/dx^2$  at this point is neither too large nor too small, the curve bends just enough to glide in asymptotically to the  $x$ -axis. In this case  $\psi(x)$ ,  $d\psi(x)/dx$ , and  $d^2\psi(x)/dx^2$  all approach zero at large  $x$ . This case offers the only hope of satisfying the boundary condition that  $\psi(x) \rightarrow 0$  as  $|x| \rightarrow \infty$ , and it occurs only for certain very special values of the energy  $E$ .

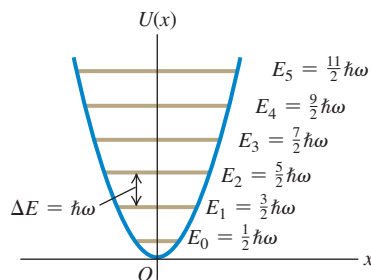
This qualitative discussion suggests how the boundary conditions as  $|x| \rightarrow \infty$  determine the possible energy levels for the quantum-mechanical harmonic oscillator. It turns out that these boundary conditions are satisfied only if the energy  $E$  is equal to one of the values  $E_n$ :

$$E_n = \left(n + \frac{1}{2}\right) \hbar \sqrt{\frac{k'}{m}} = \left(n + \frac{1}{2}\right) \hbar \omega \quad (n = 0, 1, 2, \dots) \quad (40.46)$$

Quantum number
Force constant
Oscillation angular frequency

Planck's constant divided by  $2\pi$ 
Particle's mass

**Figure 40.25** Energy levels for the harmonic oscillator. The spacing between any two adjacent levels is  $\Delta E = \hbar\omega$ . The energy of the ground level is  $E_0 = \frac{1}{2}\hbar\omega$ .



Note that the ground level of energy  $E_0 = \frac{1}{2}\hbar\omega$  is denoted by the quantum number  $n = 0$ , not  $n = 1$ .

Equation (40.46) confirms our guess [Eq. (40.43)] that adjacent energy levels are separated by a constant interval of  $\hbar\omega = hf$ , as Planck assumed in 1900. There are infinitely many levels; this shouldn't be surprising because we are dealing with an infinitely deep potential well. As  $|x|$  increases,  $U = \frac{1}{2}k'x^2$  increases without bound.

**Figure 40.25** shows the lowest six energy levels and the potential-energy function  $U(x)$ . For each level  $n$ , the value of  $|x|$  at which the horizontal line representing the total energy  $E_n$  intersects  $U(x)$  gives the amplitude  $A_n$  of the corresponding Newtonian oscillator.



**EXAMPLE 40.8** Vibration in a crystal

A sodium atom of mass  $3.82 \times 10^{-26}$  kg vibrates within a crystal. The potential energy increases by 0.0075 eV when the atom is displaced 0.014 nm from its equilibrium position. Treat the atom as a harmonic oscillator. (a) Find the angular frequency of the oscillations according to Newtonian mechanics. (b) Find the spacing (in electron volts) of adjacent vibrational energy levels according to quantum mechanics. (c) What is the wavelength of a photon emitted as the result of a transition from one level to the next lower level? In what region of the electromagnetic spectrum does this lie?

**IDENTIFY and SET UP** We'll find the force constant  $k'$  from the expression  $U = \frac{1}{2}k'x^2$  for potential energy. We'll then find the angular frequency  $\omega = (k'/m)^{1/2}$  and use this in Eq. (40.46) to find the spacing between adjacent energy levels. We'll calculate the wavelength of the emitted photon as in Example 40.6.

**EXECUTE** We are given that  $U = 0.0075$  eV  $= 1.2 \times 10^{-21}$  J when  $x = 0.014 \times 10^{-9}$  m, so we can solve  $U = \frac{1}{2}k'x^2$  for  $k'$ :

$$k' = \frac{2U}{x^2} = \frac{2(1.2 \times 10^{-21} \text{ J})}{(0.014 \times 10^{-9} \text{ m})^2} = 12.2 \text{ N/m}$$

(a) The Newtonian angular frequency is

$$\omega = \sqrt{\frac{k'}{m}} = \sqrt{\frac{12.2 \text{ N/m}}{3.82 \times 10^{-26} \text{ kg}}} = 1.79 \times 10^{13} \text{ rad/s}$$

(b) From Eq. (40.46) and Fig. 40.25, the spacing between adjacent energy levels is

$$\begin{aligned}\hbar\omega &= (1.055 \times 10^{-34} \text{ J}\cdot\text{s})(1.79 \times 10^{13} \text{ s}^{-1}) \\ &= 1.89 \times 10^{-21} \text{ J} \left( \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} \right) = 0.0118 \text{ eV}\end{aligned}$$

(c) The energy  $E$  of the emitted photon is equal to the energy lost by the oscillator in the transition, 0.0118 eV. Then

$$\begin{aligned}\lambda &= \frac{hc}{E} = \frac{(4.136 \times 10^{-15} \text{ eV}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{0.0118 \text{ eV}} \\ &= 1.05 \times 10^{-4} \text{ m} = 105 \mu\text{m}\end{aligned}$$

This photon wavelength is in the infrared region of the spectrum.

**EVALUATE** This example shows us that interatomic force constants are a few newtons per meter, about the same as those of household springs or spring-based toys such as the Slinky®. It also suggests that we can learn about the vibrations of molecules by measuring the radiation that they emit in transitioning to a lower vibrational state. We'll explore this idea further in Chapter 42.

**KEYCONCEPT** As in Newtonian physics, in a quantum-mechanical harmonic oscillator a particle of mass  $m$  moves under the influence of the potential-energy function of an ideal spring with force constant  $k'$ . The lowest-energy stationary state of the harmonic oscillator has energy  $\frac{1}{2}\hbar\omega$ , where  $\omega = \sqrt{k'/m}$  is the Newtonian angular frequency; each excited state has  $\hbar\omega$  more energy than the state below it.

**Comparing Quantum and Newtonian Oscillators**

The wave functions for the levels  $n = 0, 1, 2, \dots$  of the harmonic oscillator are called *Hermite functions*; they aren't encountered in elementary calculus courses but are well known to mathematicians. Each Hermite function is an exponential function multiplied by a polynomial in  $x$ . The harmonic-oscillator wave function corresponding to  $n = 0$  and  $E = E_0$  (the ground level) is

$$\psi(x) = Ce^{-\sqrt{mk'}x^2/2\hbar} \quad (40.47)$$

The constant  $C$  is chosen to normalize the function—that is, to make  $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$ . (We're using  $C$  rather than  $A$  as a normalization constant in this section, since we've already appropriated the symbol  $A$  to denote the Newtonian amplitude of a harmonic oscillator.) You can find  $C$  by using the following result from integral tables:

$$\int_{-\infty}^{\infty} e^{-a^2x^2} dx = \frac{\sqrt{\pi}}{a}$$

To confirm that  $\psi(x)$  as given by Eq. (40.47) really is a solution of the Schrödinger equation for the harmonic oscillator, you can calculate the second derivative of this wave function, substitute it into Eq. (40.44), and verify that the equation is satisfied if the energy  $E$  is equal to  $E_0 = \frac{1}{2}\hbar\omega$ . It's a little messy, but the result is satisfying and worth the effort.

**Figure 40.26** (next page) shows the the first four harmonic-oscillator wave functions. Each graph also shows the amplitude  $A$  of a Newtonian harmonic oscillator with the same energy—that is, the value of  $A$  determined from

$$\frac{1}{2}k'A^2 = \left(n + \frac{1}{2}\right)\hbar\omega \quad (40.48)$$

In each case there is some penetration of the wave function into the regions  $|x| > A$  that are forbidden by Newtonian mechanics. This is similar to the effect that we noted in Section 40.3 for a particle in a finite square well.

Figure 40.26 The first four wave functions for the harmonic oscillator. The amplitude  $A$  of a Newtonian oscillator with the same total energy is shown for each. Each wave function penetrates somewhat into the classically forbidden regions  $|x| > A$ . The total number of finite maxima and minima for each function is  $n + 1$ , one more than the quantum number.

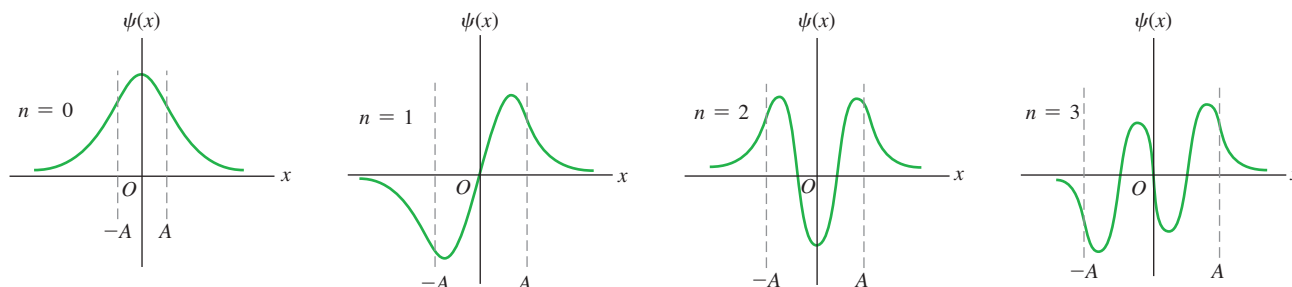


Figure 40.27 Probability distribution functions  $|\psi(x)|^2$  for the harmonic-oscillator wave functions shown in Fig. 40.26. The amplitude  $A$  of the Newtonian motion with the same energy is shown for each. The blue lines show the corresponding probability distributions for the Newtonian motion. As  $n$  increases, the averaged-out quantum-mechanical functions resemble the Newtonian curves more and more.

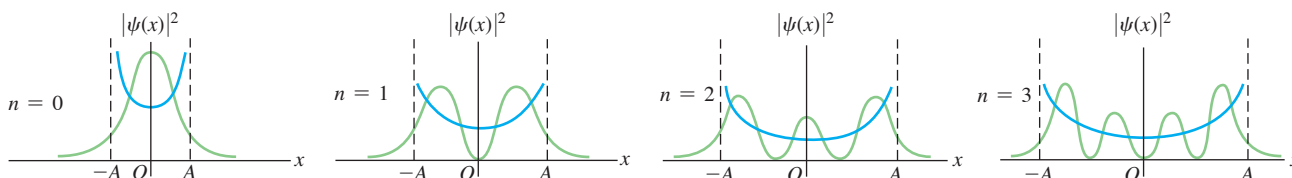


Figure 40.28 Newtonian and quantum-mechanical probability distribution functions for a harmonic oscillator for the state  $n = 10$ . The Newtonian amplitude  $A$  is also shown.

The larger the value of  $n$ , the more closely the quantum-mechanical probability distribution (green) matches the Newtonian probability distribution (blue).

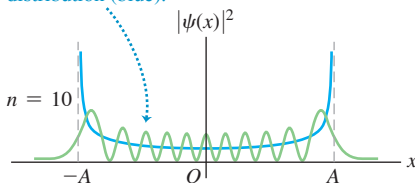


Figure 40.27 shows the probability distributions  $|\psi(x)|^2$  for these states. Each graph also shows the probability distribution determined from Newtonian physics, in which the probability of finding the particle near a randomly chosen point is inversely proportional to the particle's speed at that point. If we average out the wiggles in the quantum-mechanical probability curves, the results for  $n > 0$  resemble the Newtonian predictions. This agreement improves with increasing  $n$ ; Fig. 40.28 shows the classical and quantum-mechanical probability functions for  $n = 10$ . Notice that the spacing between zeros of  $|\psi(x)|^2$  in Fig. 40.28 increases with increasing distance from  $x = 0$ . This makes sense from the Newtonian perspective: As a particle moves away from  $x = 0$ , its kinetic energy  $K$  and the magnitude  $p$  of its momentum both decrease. Thinking quantum-mechanically, this means that the wavelength  $\lambda = h/p$  increases, so the spacing between zeros of  $\psi(x)$  (and hence of  $|\psi(x)|^2$ ) also increases.

In the Newtonian analysis of the harmonic oscillator the minimum energy is zero, with the particle at rest at its equilibrium position  $x = 0$ . This is not possible in quantum mechanics; no solution of the Schrödinger equation has  $E = 0$  and satisfies the boundary conditions. Furthermore, such a state would violate the Heisenberg uncertainty principle because there would be no uncertainty in either position or momentum. The energy must be at least  $\frac{1}{2}\hbar\omega$  for the system to conform to the uncertainty principle. To see qualitatively why this is so, consider a Newtonian oscillator with total energy  $\frac{1}{2}\hbar\omega$ . We can find the amplitude  $A$  and the maximum velocity just as we did in Section 14.3. When the particle is at its maximum displacement ( $x = \pm A$ ) and instantaneously at rest,  $K = 0$  and  $E = U = \frac{1}{2}k'A^2$ . When the particle is at equilibrium ( $x = 0$ ) and moving at its maximum speed,  $U = 0$  and  $E = K = \frac{1}{2}mv_{\max}^2$ . Setting  $E = \frac{1}{2}\hbar\omega$ , we find

$$E = \frac{1}{2}k'A^2 = \frac{1}{2}\hbar\omega = \frac{1}{2}\hbar\left(\frac{k'}{m}\right)^{1/2} \quad \text{so} \quad A = \frac{\hbar^{1/2}}{k'^{1/4}m^{1/4}}$$

$$E = \frac{1}{2}mv_{\max}^2 = \frac{1}{2}k'A^2 \quad \text{so} \quad v_{\max} = A\left(\frac{k'}{m}\right)^{1/2} = \frac{\hbar^{1/2}k'^{1/4}}{m^{3/4}}$$

The maximum *momentum* of the particle is

$$p_{\max} = mv_{\max} = \hbar^{1/2}k'^{1/4}m^{1/4}$$

Here's where the Heisenberg uncertainty principle comes in. It turns out that the uncertainties in the particle's position and momentum (calculated as standard deviations) are, respectively,  $\Delta x = A/\sqrt{2} = A/2^{1/2}$  and  $\Delta p_x = p_{\max}/\sqrt{2} = p_{\max}/2^{1/2}$ . Then the product of the two uncertainties is

$$\Delta x \Delta p_x = \left( \frac{\hbar^{1/2}}{2^{1/2} k^{1/4} m^{1/4}} \right) \left( \frac{\hbar^{1/2} k^{1/4} m^{1/4}}{2^{1/2}} \right) = \frac{\hbar}{2}$$

This product equals the minimum value allowed by Eq. (39.29),  $\Delta x \Delta p_x \geq \hbar/2$ , and thus satisfies the uncertainty principle. If the energy had been less than  $\frac{1}{2}\hbar\omega$ , the product  $\Delta x \Delta p_x$  would have been less than  $\hbar/2$ , and the uncertainty principle would have been violated.

Even when a potential-energy function isn't precisely parabolic in shape, we may be able to approximate it by the harmonic-oscillator potential for sufficiently small displacements from equilibrium. **Figure 40.29** shows a typical potential-energy function for an interatomic force in a molecule. At large separations the curve of  $U(r)$  versus  $r$  levels off, corresponding to the absence of force at great distances. But the curve is approximately parabolic near the minimum of  $U(r)$  (the equilibrium separation of the atoms). Near equilibrium the molecular vibration is approximately simple harmonic with energy levels given by Eq. (40.46), as we assumed in Example 40.8.

**TEST YOUR UNDERSTANDING OF SECTION 40.5** A quantum-mechanical system initially in its ground level absorbs a photon and ends up in the first excited state. The system then absorbs a second photon and ends up in the second excited state. For which of the following systems does the second photon have a longer wavelength than the first one? (i) A harmonic oscillator; (ii) a hydrogen atom; (iii) a particle in a box.

#### ANSWER

**(iii)** If the second photon has a longer wavelength and hence lower energy than the first photon, the difference in energy between the first and second excited levels must be less than the difference between the ground level and the first excited level. This is the case for the hydrogen atom, for which the energy difference between levels decreases as the energy increases (see Fig. 39.24). By contrast, the energy difference between successive levels increases for a particle in a box (see Fig. 40.11b) and is constant for a harmonic oscillator (see Fig. 40.25).

## 40.6 MEASUREMENT IN QUANTUM MECHANICS

We've seen how to use the Schrödinger equation to calculate the stationary-state wave functions and energy levels for various potential-energy functions  $U(x)$ . We've also seen how to interpret the wave function  $\Psi(x, t)$  of a particle in terms of the probability distribution function  $|\Psi(x, t)|^2$ . We'll conclude with a brief discussion of what happens when we try to *measure* the properties of a quantum-mechanical particle. As we'll see, the consequences of such a measurement can be startlingly different from what happens when we measure the properties of a familiar Newtonian particle, such as a marble or billiard ball.

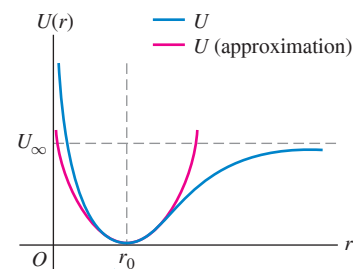
Let's consider a "particle in a box"—that is, a particle in an infinite square well of width  $L$ , as described in Section 40.2. This particle of mass  $m$  is free to move along the  $x$ -axis in the region  $0 \leq x \leq L$  but cannot move beyond this region. Let's suppose the particle is in a stationary state with definite energy  $E$ , equal to one of the energy levels  $E_n$  given by Eq. (40.31). If we measure the  $x$ -component of momentum of this particle, what is the result?

First let's consider the answer to that question for a Newtonian particle in a box (see Fig. 40.8). This could be a hockey puck sliding on frictionless ice and bouncing back and forth between two parallel walls. The energy  $E$  of the puck is equal to its kinetic energy  $p^2/2m$ , so the magnitude of its momentum is  $p = \sqrt{2mE}$ . The  $x$ -component of its momentum  $p_x$  is therefore

$$p_x = +\sqrt{2mE} \quad \text{or} \quad p_x = -\sqrt{2mE} \quad (40.49)$$

Whether  $p_x$  is positive or negative depends on whether the hockey puck is moving in the  $+x$ -direction (then  $p_x = +\sqrt{2mE}$ ) or the  $-x$ -direction (then  $p_x = -\sqrt{2mE}$ ). To

**Figure 40.29** A potential-energy function describing the interaction of two atoms in a diatomic molecule. The distance  $r$  is the separation between the centers of the atoms, and the equilibrium separation is  $r = r_0$ . The energy needed to dissociate the molecule is  $U_\infty$ .



When  $r$  is near  $r_0$ , the potential-energy curve is approximately parabolic (as shown by the red curve) and the system behaves approximately like a harmonic oscillator.

determine which value of  $p_x$  is correct at a given time, we need only look at the puck to see in which direction it's moving.

We can't make such an observation in the dark; we need to shine some light on the hockey puck. We know from Section 38.1 that light comes in the form of photons and that a photon of wavelength  $\lambda$  has momentum  $p = h/\lambda$ . When we shine light on the puck to observe it, the photons collide with the puck and *change* its momentum. The mere act of measuring the puck's momentum can affect the quantity that we're trying to measure! The good news is that this change is minuscule: A hockey puck of mass  $m = 0.165$  kg moving at speed  $v = 1.00$  m/s has momentum  $p = mv = 0.165$  kg · m/s, while a visible-light photon of wavelength 500 nm has momentum  $p = h/\lambda = 1.33 \times 10^{-27}$  kg · m/s. Even if we directed all of the photons from a 100 W light source onto the puck for a 1.00 s burst of light, the total momentum in this burst would be only  $3.33 \times 10^{-7}$  kg · m/s, and the resulting change in the momentum of the puck would be negligible. In general, we can measure any of the properties of a Newtonian particle—its momentum, position, energy, and so on—without appreciably changing the quantity that we are measuring.

The situation is very different for a quantum-mechanical particle in a box. From Eq. (40.21) the state of such a particle with energy  $E = E_n$  is described by the wave function

$$\Psi(x, t) = \psi_n(x)e^{-iE_nt/\hbar} = \psi_n(x)e^{-i\omega_nt} \quad (40.50)$$

In Eq. (40.50) the angular frequency is  $\omega_n = E_n/\hbar$  and the time-independent, stationary-state wave function  $\psi_n(x)$  is given by Eq. (40.35):

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad (n = 1, 2, 3, \dots) \quad (40.51)$$

This is a state of definite *energy*, but it is *not* a state of definite momentum: It represents a standing wave with equal amounts of momentum in the  $+x$ -direction and the  $-x$ -direction. To make this more explicit, recall from Eqs. (40.30) and (40.31) that the magnitude of momentum in a state of energy  $E_n$  is  $p_n = \sqrt{2mE_n} = nh/2L = n\pi\hbar/L$ , and the corresponding wave number is  $k_n = p_n/\hbar = n\pi/L$ . So we can replace  $n\pi/L$  in Eq. (40.51) with  $k_n$ :

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin k_n x$$

Recall also Euler's formula from Eq. (40.17):  $e^{i\theta} = \cos\theta + i\sin\theta$  and  $e^{-i\theta} = \cos\theta - i\sin\theta$ . Hence  $\sin\theta = (e^{i\theta} - e^{-i\theta})/2i$ , and we can write

$$\psi_n(x) = \sqrt{\frac{2}{L}} \left( \frac{e^{ik_n x} - e^{-ik_n x}}{2i} \right) = \frac{1}{i\sqrt{2L}} (e^{ik_n x} - e^{-ik_n x}) \quad (40.52)$$

Now we substitute Eq. (40.52) into Eq. (40.50) and distribute the factors  $1/i\sqrt{2L}$  and  $e^{-i\omega_nt}$ :

$$\begin{aligned} \Psi(x, t) &= \frac{1}{i\sqrt{2L}} (e^{ik_n x} - e^{-ik_n x}) e^{-i\omega_nt} \\ &= \frac{1}{i\sqrt{2L}} e^{ik_n x} e^{-i\omega_nt} - \frac{1}{i\sqrt{2L}} e^{-ik_n x} e^{-i\omega_nt} \end{aligned} \quad (40.53)$$

In Eq. (40.53) the  $e^{ik_n x} e^{-i\omega_nt}$  term is a wave function for a free particle with energy  $E_n = \hbar\omega_n$  and a *positive*  $x$ -component of momentum  $p_x = p_n = \hbar k_n$ . In the  $e^{-ik_n x} e^{-i\omega_nt}$  term,  $k_n$  is replaced by  $-k_n$ , so this term is a wave function for a free particle with the same energy  $E_n = \hbar\omega_n$  but a *negative*  $x$ -component of momentum  $p_x = -p_n = -\hbar k_n$ . These two possible values of  $p_x$  are the same as for a Newtonian particle in a box, Eq. (40.49). The difference is that as the Newtonian particle bounces back and forth between the walls of the box, it has positive  $p_x$  half of the time and negative  $p_x$  half of the time. Only its time-averaged value of  $p_x$  is zero. But because both terms for positive  $p_x$  and negative  $p_x$  are present in Eq. (40.53), the quantum-mechanical particle has *both* signs of the  $x$ -component of momentum present at *all* times. As we stated earlier, this stationary state for a quantum-mechanical particle in a box has a definite energy [both terms in Eq. (40.53) have the same value of  $\omega_n$



and hence the same value of  $E_n = \hbar\omega_n$ ] but does not have a definite momentum. Because the  $e^{ik_n x}e^{-i\omega_n t}$  and  $e^{-ik_n x}e^{-i\omega_n t}$  terms in Eq. (40.53) have coefficients of the same magnitude,  $1/\sqrt{2L}$ , the *instantaneous* average value of  $p_x$  for the quantum-mechanical particle is zero (the average of  $\hbar k_n$  and  $-\hbar k_n$ ) at *all* times.

What value do we get if we *measure* the momentum of the quantum-mechanical particle in a box? As for the Newtonian particle, we can measure the momentum by shining a light on it. Let's fire a single photon, moving in the  $-y$ -direction, at the particle and allow the photon and particle to collide (**Fig. 40.30**). Before the collision the total  $x$ -component of momentum of the system of photon and particle is zero. Momentum is conserved in the collision, so the same is true after the collision. After the collision, whichever sign of  $p_x$  the photon has, the  $x$ -component of momentum of the particle will have the opposite sign. If the photon is detected in detector A, we conclude that the particle has  $p_x = \hbar k_n$ ; if instead the photon is detected in detector B, we conclude that the particle has  $p_x = -\hbar k_n$ .

In this experiment, we need to be even more concerned about how the photon changes the momentum of the particle than in the Newtonian case. For an electron in a box of width  $L = 1.00 \times 10^{-6} \text{ m} = 1.00 \mu\text{m}$ , the electron momentum has a minimum magnitude of  $p = 3.31 \times 10^{-28} \text{ kg} \cdot \text{m/s}$  (corresponding to the  $n = 1$  energy level), which is only about one-quarter that of a visible-light photon of wavelength 500 nm. To minimize the change in the electron's magnitude of momentum due to the collision, we should use a photon of much longer wavelength (say, a radio-wave photon) and hence much smaller momentum.

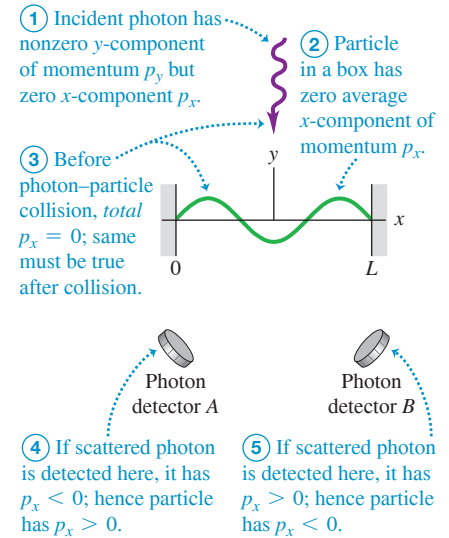
Even when we use a photon with the lowest possible momentum, however, we find that the state of the particle in the box *must* change as a result of the experiment. Here's a summary of the results:

1. If the measurement shows that the particle has positive  $p_x = \hbar k_n$ , the wave function *changes* from that given in Eq. (40.53) to one with an  $e^{ik_n x}e^{-i\omega_n t}$  term *only*. The other term, which corresponds to  $p_x = -\hbar k_n$ , disappears. We say that the wave function, which was a combination of two terms with different values of  $p_x$ , has undergone *wave-function collapse*—it has collapsed to one term with  $p_x = \hbar k_n$  as a consequence of measuring the value of  $p_x$ . To test this result, we fire a second photon immediately after the first. The second photon scatters from the particle as we would expect if the particle had the value  $p_x = \hbar k_n$ .
2. If the measurement shows that the particle has negative  $p_x = -\hbar k_n$ , the wave function collapses in the opposite way: It changes to one with an  $e^{-ik_n x}e^{-i\omega_n t}$  term only. The  $p_x = \hbar k_n$  term disappears.
3. If we repeat the experiment many times, each time starting with the particle described by the wave function in Eq. (40.53), 50% of the time we measure the particle to have  $p_x = \hbar k_n$  and 50% of the time we measure the particle to have  $p_x = -\hbar k_n$ . For any given time that we try the experiment, there is no way to predict which outcome will occur. We can state only that there is equal probability of either outcome.

These results reveal a fact of quantum-mechanical life: *Measuring a physical property of a system can change the wave function of that system.* By measuring the value of  $p_x$  for a particle in a box, we changed the wave function from one that was a combination of two wave functions, one for  $p_x = \hbar k_n$  and one for  $p_x = -\hbar k_n$ , to one with a definite value of  $p_x$ . This change in the wave function is not described by the time-dependent Schrödinger equation [Eq. (40.20)] but is a consequence of the measurement process. It is also independent of how the measurement is carried out: No matter how small the momentum of the incident photon shown in Fig. 40.30, the same collapse of the wave function takes place. Indeed, *any* experiment to measure  $p_x$  for a particle in a box in a steady state, no matter how the experiment is designed, will have the results that we described earlier.

(After the measurement, the wave function will undergo further change that is described by the Schrödinger equation. Neither  $e^{ik_n x}e^{-i\omega_n t}$  nor  $e^{-ik_n x}e^{-i\omega_n t}$  by itself satisfies the boundary conditions for a particle in a box—namely, that the wave function vanishes at  $x = 0$  and  $x = L$ . The wave function must evolve to satisfy these conditions.)

Figure 40.30 Using photon scattering to measure the  $x$ -component of momentum of a particle in a box.



**CAUTION Quantum measurement misconceptions** If we measure the particle to have  $p_x = \hbar k_n$ , does that mean it had  $p_x = \hbar k_n$  before the measurement? No; the particle acquired that value as a result of the measurement. If we measure the particle to have  $p_x = \hbar k_n$  instead of  $p_x = -\hbar k_n$ , does that mean there was some bias in the way we did the measurement? Again, no; the result of any given experiment is random. All quantum mechanics can do is predict the probability that this experiment will give us a certain result. ■

Note that not every measurement of a quantum-mechanical system causes a change in the wave function. If we perform an experiment that measures only the *energy* of a particle given by the wave function in Eq. (40.53), the wave function does *not* change. That's because the wave function already corresponds to a state of definite energy  $E_n = \hbar\omega_n$ , so there is a 100% probability that we'll measure that value of energy.

You may ask, Does the wave function really collapse? Many physicists would answer yes, but some theorists have devised alternative models of what happens in a quantum-mechanical measurement. One model, called the *many-worlds interpretation*, asserts that there is a *universal* wave function that describes all particles in the universe. Whenever a measurement of any sort takes place, whether of human origin (like our experiment) or natural origin (for example, a photon of sunlight scattering from an electron in an atom in the atmosphere), this universal wave function does not collapse. Instead, every measurement causes the universe to branch into alternative timelines. So, when we carry out the experiment depicted in Fig. 40.30, the universe splits into one timeline in which the photon goes into detector A and a second timeline in which the photon goes into detector B. These two timelines then no longer communicate.

As weird as these aspects of quantum mechanics are, others are far weirder. We'll investigate these in Chapter 41 after we have learned more about the nature of the electron.

**TEST YOUR UNDERSTANDING OF SECTION 40.6** A particle in a box is described by a wave function that is a combination of the  $n = 1$  and  $n = 2$  stationary states:  $\Psi(x, t) = C\psi_1(x)e^{-iE_1t/\hbar} + D\psi_2(x)e^{-iE_2t/\hbar}$ , where  $\psi_1(x)$  and  $\psi_2(x)$  are given by Eq. (40.35),  $E_1$  and  $E_2$  are given by Eq. (40.31), and  $C$  and  $D$  are nonzero constants. If you carry out an experiment to measure the energy of this particle, the result is *guaranteed* to be (i)  $E_1$ ; (ii)  $E_2$ ; (iii)  $(E_1 + E_2)/2$ ; (iv) intermediate between  $E_1$  and  $E_2$ , with a value that depends on the values of  $C$  and  $D$ ; (v) none of these.

**ANSWER** (v) The value of the energy of a particle in a box must be equal to one of the allowed energy levels, so the measured value will be either  $E_1$  or  $E_2$ . *Neither* of these results is guaranteed. If  $|C| = |D|$ , then  $E_1$  and  $E_2$  are of equal probability.  $E_1$  is the more likely result if  $|C| > |D|$ , and  $E_2$  is the more likely result if  $|C| < |D|$ .

## CHAPTER 40 SUMMARY

**Wave functions:** The wave function for a particle contains all of the information about that particle. If the particle moves in one dimension in the presence of a potential-energy function  $U(x)$ , the wave function  $\Psi(x, t)$  obeys the one-dimensional Schrödinger equation. (For a *free* particle on which no forces act,  $U(x) = 0$ .) The quantity  $|\Psi(x, t)|^2$ , called the probability distribution function, determines the relative probability of finding a particle near a given position at a given time. If the particle is in a state of definite energy, called a stationary state,  $\Psi(x, t)$  is a product of a function  $\psi(x)$  that depends on only spatial coordinates and a function  $e^{-iEt/\hbar}$  that depends on only time. For a stationary state, the probability distribution function is independent of time.

A spatial stationary-state wave function  $\psi(x)$  for a particle that moves in one dimension in the presence of a potential-energy function  $U(x)$  satisfies the time-independent Schrödinger equation. More complex wave functions can be constructed by superposing stationary-state wave functions. These can represent particles that are localized in a certain region, thus representing both particle and wave aspects. (See Examples 40.1 and 40.2.)

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + U(x)\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t} \quad (40.20)$$

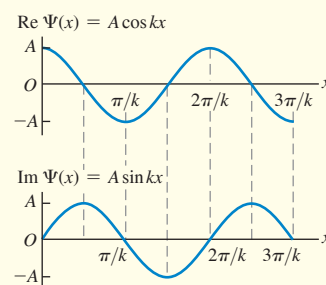
(general 1-D Schrödinger equation)

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar} \quad (40.21)$$

(time-dependent wave function for a state of definite energy)

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x) \quad (40.23)$$

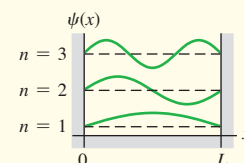
(time-independent 1-D Schrödinger equation)



**Particle in a box:** The energy levels for a particle of mass  $m$  in a box (an infinitely deep square potential well) with width  $L$  are given by Eq. (40.31). The corresponding normalized stationary-state wave functions of the particle are given by Eq. (40.35). (See Examples 40.3 and 40.4.)

$$E_n = \frac{p_n^2}{2m} = \frac{n^2 h^2}{8mL^2} = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad (n = 1, 2, 3, \dots) \quad (40.31)$$

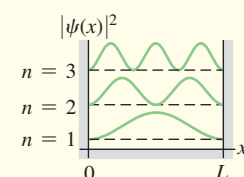
$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad (n = 1, 2, 3, \dots) \quad (40.35)$$



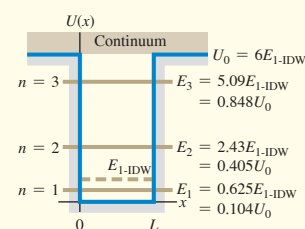
**Wave functions and normalization:** To be a solution of the Schrödinger equation, the wave function  $\psi(x)$  and its derivative  $d\psi(x)/dx$  must be continuous everywhere except where the potential-energy function  $U(x)$  has an infinite discontinuity. Wave functions are usually normalized so that the total probability of finding the particle somewhere is unity.

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1 \quad (40.33)$$

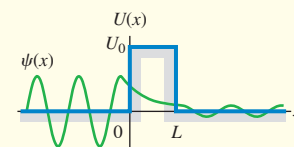
(normalization condition)



**Finite potential well:** In a potential well with finite depth  $U_0$ , the energy levels are lower than those for an infinitely deep well with the same width, and the number of energy levels corresponding to bound states is finite. The levels are obtained by matching wave functions at the well walls to satisfy the continuity of  $\psi(x)$  and  $d\psi(x)/dx$ . (See Examples 40.5 and 40.6.)

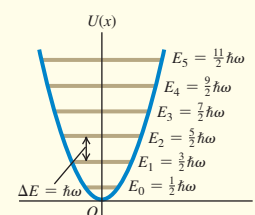


**Potential barriers and tunneling:** There is a certain probability that a particle will penetrate a potential-energy barrier even though its initial energy is less than the barrier height. This process is called tunneling. (See Example 40.7.)



**Quantum harmonic oscillator:** The energy levels for the harmonic oscillator (for which  $U(x) = \frac{1}{2}k'x^2$ ) are given by Eq. (40.46). The spacing between any two adjacent levels is  $\hbar\omega$ , where  $\omega = \sqrt{k'/m}$  is the oscillation angular frequency of the corresponding Newtonian harmonic oscillator. (See Example 40.8.)

$$E_n = \left(n + \frac{1}{2}\right) \hbar \sqrt{\frac{k'}{m}} = \left(n + \frac{1}{2}\right) \hbar \omega \quad (n = 0, 1, 2, 3, \dots) \quad (40.46)$$



**Measurement in quantum mechanics:** If the wave function of a particle does not correspond to a definite value of a certain physical property (such as momentum or energy), the wave function changes when we measure that property. This phenomenon is called wave-function collapse.

Chapter 40 Media Assets



## GUIDED PRACTICE

For assigned homework and other learning materials, go to Mastering Physics.

### KEY EXAMPLE VARIATION PROBLEMS

Be sure to review **EXAMPLES 40.3 and 40.4** (Section 40.2) before attempting these problems.

**VP40.4.1** The lowest energy level for an electron confined to a one-dimensional box is  $2.00 \times 10^{-19}$  J. Find (a) the width of the box and (b) the energies of the  $n = 2$  and  $n = 3$  energy levels.

**VP40.4.2** A proton (mass  $1.67 \times 10^{-27}$  kg) is confined to a one-dimensional box of width  $5.00 \times 10^{-15}$  m. Find the energy difference between (a) the  $n = 2$  and  $n = 1$  energy levels and (b) the  $n = 3$  and  $n = 2$  energy levels.

**VP40.4.3** A photon is emitted when an electron in a one-dimensional box transitions from the  $n = 2$  energy level to the  $n = 1$  energy level.

The wavelength of this photon is 655 nm. Find (a) the energy of this photon, (b) the width of the box, and (c) the wavelength of the photon emitted when the electron transitions from the  $n = 3$  level to the  $n = 2$  level.

**VP40.4.4** A wave function for a particle in a box with energy  $E$  is

$$\psi(x) = A \cos\left(\frac{x\sqrt{2mE}}{\hbar} + \phi\right)$$

(a) Find the second derivative of  $\psi(x)$  and show that this function satisfies the Schrödinger equation. (b) Use the boundary condition at  $x = 0$  to determine the value of  $\phi$ . (c) Use the boundary condition at  $x = L$  to determine the value of  $E$ .

**Be sure to review EXAMPLE 40.6** (Section 40.3) **before attempting these problems.**

**VP40.6.1** An electron is confined to a potential well of width 0.350 nm. (a) Find the ground-level energy  $E_{1-IDW}$  if the well is infinitely deep. If instead the depth  $U_0$  of the well is six times the value of  $E_{1-IDW}$ , find (b) the ground-level energy and (c) the minimum energy required to free the electron from the well.

**VP40.6.2** A finite potential well has a depth  $U_0$  that is six times greater than the ground-level energy  $E_{1-IDW}$  of an electron in an infinitely deep well of the same width. The photon emitted when an electron in the finite potential well transitions from the  $n = 3$  level to the  $n = 2$  level has energy  $2.50 \times 10^{-19}$  J. Find (a) the value of  $E_{1-IDW}$ , (b) the value of  $U_0$ , and (c) the width of the potential well.

**VP40.6.3** An electron in a finite potential well can emit a photon of only one of three different wavelengths when it makes a transition from one energy level to a lower energy level. The depth of this potential well

is six times greater than the ground-level energy  $E_{1-IDW}$  that the electron would have if the well had the same width but was infinitely deep. (a) If the shortest of the three wavelengths is 355 nm, find the quantum numbers  $n$  for the initial and final electron energy levels for this transition. (b) Find the other two wavelengths and the quantum numbers  $n$  of the initial and final energy levels for each transition.

**VP40.6.4** An electron is in a potential well that is 0.400 nm wide. (a) Find the ground-level energy of the electron  $E_{1-IDW}$ , in eV, if the potential well is infinitely deep. (b) If the depth of the potential is only 0.015 eV, much less than  $E_{1-IDW}$ , there is only one bound state. Find the energy, in eV, of this bound state.

**Be sure to review EXAMPLE 40.7** (Section 40.4) **before attempting these problems.**

**VP40.7.1** An electron of energy 3.75 eV encounters a potential barrier 6.10 eV high. Find the probability that the electron will tunnel through the barrier if the barrier width is (a) 0.750 nm and (b) 0.500 nm.

**VP40.7.2** A 3.50 eV electron encounters a barrier with height 4.00 eV. Find (a) the probability that the electron will tunnel through the barrier if its width is 0.800 nm and (b) the barrier width that gives twice the tunneling probability you found in part (a).

**VP40.7.3** A potential barrier is 5.00 eV high and 0.900 nm wide. Find the probability that an electron will tunnel through this barrier if its energy is (a) 4.00 eV, (b) 4.30 eV, and (c) 4.60 eV.

**VP40.7.4** There is a 1-in-417 probability that an electron with energy 3.00 eV will tunnel through a barrier with height 5.00 eV. Find the width of the barrier.

## BRIDGING PROBLEM A Packet in a Box

A particle of mass  $m$  in an infinitely deep well (see Fig. 40.9) has the following wave function in the region from  $x = 0$  to  $x = L$ :

$$\Psi(x, t) = \frac{1}{\sqrt{2}}\psi_1(x)e^{-iE_1t/\hbar} + \frac{1}{\sqrt{2}}\psi_2(x)e^{-iE_2t/\hbar}$$

Here  $\psi_1(x)$  and  $\psi_2(x)$  are the normalized stationary-state wave functions for the first two levels ( $n = 1$  and  $n = 2$ ), given by Eq. (40.35).  $E_1$  and  $E_2$ , given by Eq. (40.31), are the energies of these levels. The wave function is zero for  $x < 0$  and for  $x > L$ . (a) Find the probability distribution function for this wave function. (b) Does  $\Psi(x, t)$  represent a stationary state of definite energy? How can you tell? (c) Show that the wave function  $\Psi(x, t)$  is normalized. (d) Find the angular frequency of oscillation of the probability distribution function. What is the interpretation of this oscillation? (e) Suppose instead that  $\Psi(x, t)$  is a combination of the wave functions of the two lowest levels of a finite well of length  $L$  and height  $U_0$  equal to six times the energy of the lowest-energy bound state of an infinite well of length  $L$ . What would be the angular frequency of the probability distribution function in this case?

### SOLUTION GUIDE

#### IDENTIFY and SET UP

- In Section 40.1 we saw how to interpret a combination of two free-particle wave functions of different energies. In this problem you need to apply these same ideas to a combination of wave functions for the infinite well (Section 40.2) and the finite well (Section 40.3).

#### EXECUTE

- Write down the full time-dependent wave function  $\Psi(x, t)$  and its complex conjugate  $\Psi^*(x, t)$  by using the functions  $\psi_1(x)$  and  $\psi_2(x)$  from Eq. (40.35). Use these to calculate the probability

distribution function, and decide whether or not this function depends on time.

- To check for normalization, you'll need to verify that when you integrate the probability distribution function from step 2 over all values of  $x$ , the integral is equal to 1. [Hint: The trigonometric identities  $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$  and  $\sin\theta \sin\phi = \frac{1}{2}[\cos(\theta - \phi) - \cos(\theta + \phi)]$  may be helpful.]
- To find the answer to part (d) you'll need to identify the oscillation angular frequency  $\omega_{osc}$  in your expression from step 2 for the probability distribution function. To interpret the oscillations, draw graphs of the probability distribution functions at times  $t = 0$ ,  $t = T/4$ ,  $t = T/2$ , and  $t = 3T/4$ , where  $T = 2\pi/\omega_{osc}$  is the oscillation period of the probability distribution function.
- For the finite well you do not have simple expressions for the first two stationary-state wave functions  $\psi_1(x)$  and  $\psi_2(x)$ . However, you can still find the oscillation angular frequency  $\omega_{osc}$ , which is related to the energies  $E_1$  and  $E_2$  in the same way as for the infinite-well case. (Can you see why?)

#### EVALUATE

- Why are the factors of  $1/\sqrt{2}$  in the wave function  $\Psi(x, t)$  important?
- Why do you suppose the oscillation angular frequency for a finite well is lower than for an infinite well of the same width?



## PROBLEMS

•, ••, •••: Difficulty levels. **CP**: Cumulative problems incorporating material from earlier chapters. **CALC**: Problems requiring calculus. **DATA**: Problems involving real data, scientific evidence, experimental design, and/or statistical reasoning. **BIO**: Biosciences problems.

### DISCUSSION QUESTIONS

**Q40.1** If quantum mechanics replaces the language of Newtonian mechanics, why don't we have to use wave functions to describe the motion of macroscopic objects such as baseballs and cars?

**Q40.2** A student remarks that the relationship of ray optics to the more general wave picture is analogous to the relationship of Newtonian mechanics, with well-defined particle trajectories, to quantum mechanics. Comment on this remark.

**Q40.3** As Eq. (40.21) indicates, the time-dependent wave function for a stationary state is a complex number having a real part and an imaginary part. How can this function have any physical meaning, since part of it is *imaginary*?

**Q40.4** Why must the wave function of a particle be normalized?

**Q40.5** If a particle is in a stationary state, does that mean that the particle is not moving? If a particle moves in empty space with constant momentum  $\vec{p}$  and hence constant energy  $E = p^2/2m$ , is it in a stationary state? Explain your answers.

**Q40.6** For the particle in a box, we chose  $k = n\pi/L$  with  $n = 1, 2, 3, \dots$  to fit the boundary condition that  $\psi = 0$  at  $x = L$ . However,  $n = 0, -1, -2, -3, \dots$  also satisfy that boundary condition. Why didn't we also choose those values of  $n$ ?

**Q40.7** If  $\psi$  is normalized, what is the physical significance of the area under a graph of  $|\psi|^2$  versus  $x$  between  $x_1$  and  $x_2$ ? What is the total area under the graph of  $|\psi|^2$  when all  $x$  are included? Explain.

**Q40.8** For a particle in a box, what would the probability distribution function  $|\psi|^2$  look like if the particle behaved like a classical (Newtonian) particle? Do the actual probability distributions approach this classical form when  $n$  is very large? Explain.

**Q40.9** In Chapter 15 we represented a standing wave as a superposition of two waves traveling in opposite directions. Can the wave functions for a particle in a box also be thought of as a combination of two traveling waves? Why or why not? What physical interpretation does this representation have? Explain.

**Q40.10** A particle in a box is in the ground level. What is the probability of finding the particle in the right half of the box? (Refer to Fig. 40.12, but don't evaluate an integral.) Is the answer the same if the particle is in an excited level? Explain.

**Q40.11** The wave functions for a particle in a box (see Fig. 40.12a) are zero at certain points. Does this mean that the particle can't move past one of these points? Explain.

**Q40.12** For a particle confined to an infinite square well, is it correct to say that each state of definite energy is also a state of definite wavelength? Is it also a state of definite momentum? Explain. (*Hint*: Remember that momentum is a vector.)

**Q40.13** For a particle in a finite potential well, is it correct to say that each bound state of definite energy is also a state of definite wavelength? Is it a state of definite momentum? Explain.

**Q40.14** In Fig. 40.12b, the probability function is zero at the points  $x = 0$  and  $x = L$ , the "walls" of the box. Does this mean that the particle never strikes the walls? Explain.

**Q40.15** A particle is confined to a finite potential well in the region  $0 < x < L$ . How does the area under the graph of  $|\psi|^2$  in the region  $0 < x < L$  compare to the total area under the graph of  $|\psi|^2$  when including all possible  $x$ ?

**Q40.16** Compare the wave functions for the first three energy levels for a particle in a box of width  $L$  (see Fig. 40.12a) to the corresponding

wave functions for a finite potential well of the same width (see Fig. 40.15a). How does the wavelength in the interval  $0 \leq x \leq L$  for the  $n = 1$  level of the particle in a box compare to the corresponding wavelength for the  $n = 1$  level of the finite potential well? Use this to explain why  $E_1$  is less than  $E_{1-IDW}$  in the situation depicted in Fig. 40.15b.

**Q40.17** It is stated in Section 40.3 that a finite potential well always has at least one bound level, no matter how shallow the well. Does this mean that as  $U_0 \rightarrow 0$ ,  $E_1 \rightarrow 0$ ? Does this violate the Heisenberg uncertainty principle? Explain.

**Q40.18** Figure 40.15a shows that the higher the energy of a bound state for a finite potential well, the more the wave function extends outside the well (into the intervals  $x < 0$  and  $x > L$ ). Explain why this happens.

**Q40.19** In classical (Newtonian) mechanics, the total energy  $E$  of a particle can never be less than the potential energy  $U$  because the kinetic energy  $K$  cannot be negative. Yet in barrier tunneling (see Section 40.4) a particle passes through regions where  $E$  is less than  $U$ . Is this a contradiction? Explain.

**Q40.20** Figure 40.17 shows the scanning tunneling microscope image of 48 iron atoms placed on a copper surface, the pattern indicating the density of electrons on the copper surface. What can you infer about the potential-energy function inside the circle of iron atoms?

**Q40.21** Qualitatively, how would you expect the probability for a particle to tunnel through a potential barrier to depend on the height of the barrier? Explain.

**Q40.22** The wave function shown in Fig. 40.20 is nonzero for both  $x < 0$  and  $x > L$ . Does this mean that the particle splits into two parts when it strikes the barrier, with one part tunneling through the barrier and the other part bouncing off the barrier? Explain.

**Q40.23** The probability distributions for the harmonic-oscillator wave functions (see Figs. 40.27 and 40.28) begin to resemble the classical (Newtonian) probability distribution when the quantum number  $n$  becomes large. Would the distributions become the same as in the classical case in the limit of very large  $n$ ? Explain.

**Q40.24** In Fig. 40.28, how does the probability of finding a particle in the center half of the region  $-A < x < A$  compare to the probability of finding the particle in the outer half of the region? Is this consistent with the physical interpretation of the situation?

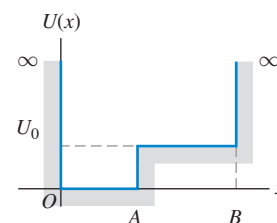
**Q40.25** Compare the allowed energy levels for the hydrogen atom, the particle in a box, and the harmonic oscillator. What are the values of the quantum number  $n$  for the ground level and the second excited level of each system?

**Q40.26** Sketch the wave function for Figure **Q40.26**

the potential-energy well shown in **Fig. Q40.26** when  $E_1$  is less than  $U_0$  and when  $E_3$  is greater than  $U_0$ .

**Q40.27** (a) A particle in a box has wave function  $\Psi(x, t) = \psi_2(x)e^{-iE_2t/\hbar}$ , where  $\psi_n$  and  $E_n$  are given by Eqs. (40.35) and (40.31), respectively. If the energy of the particle is measured, what is the result?

(b) If instead the particle has wave function  $\Psi(x, t) = (1/\sqrt{2})(\psi_1(x)e^{-iE_1t/\hbar} + \psi_2(x)e^{-iE_2t/\hbar})$  and the energy of the particle is measured, what is the result? (c) If we had many identical particles with the wave function of part (b) and measured the energy of each, what would be the average value of all of the measurements? Can we say that, before the measurement was made, each particle had this average energy? Explain.





## EXERCISES

## Section 40.1 Wave Functions and the One-Dimensional Schrödinger Equation

**40.1** • An electron is moving as a free particle in the  $-x$ -direction with momentum that has magnitude  $4.50 \times 10^{-24} \text{ kg} \cdot \text{m/s}$ . What is the one-dimensional time-dependent wave function of the electron?

**40.2** • A free particle moving in one dimension has wave function

$$\Psi(x, t) = A[e^{i(kx - \omega t)} - e^{i(2kx - 4\omega t)}]$$

where  $k$  and  $\omega$  are positive real constants. (a) At  $t = 0$  what are the two smallest positive values of  $x$  for which the probability function  $|\Psi(x, t)|^2$  is a maximum? (b) Repeat part (a) for time  $t = 2\pi/\omega$ . (c) Calculate  $v_{av}$  as the distance the maxima have moved divided by the elapsed time. Compare your result to the expression  $v_{av} = (\omega_2 - \omega_1)/(k_2 - k_1)$  from Example 40.1.

**40.3** • Consider the free-particle wave function of Example 40.1. Let  $k_2 = 3k_1 = 3k$ . At  $t = 0$  the probability distribution function  $|\Psi(x, t)|^2$  has a maximum at  $x = 0$ . (a) What is the smallest positive value of  $x$  for which the probability distribution function has a maximum at time  $t = 2\pi/\omega$ , where  $\omega = \hbar k^2/2m$ ? (b) From your result in part (a), what is the average speed with which the probability distribution is moving in the  $+x$ -direction? Compare your result to the expression  $v_{av} = (\omega_2 - \omega_1)/(k_2 - k_1)$  from Example 40.1.

**40.4** • A particle is described by a wave function  $\psi(x) = Ae^{-\alpha x^2}$ , where  $A$  and  $\alpha$  are real, positive constants. If the value of  $\alpha$  is increased, what effect does this have on (a) the particle's uncertainty in position and (b) the particle's uncertainty in momentum? Explain your answers.

**40.5** • Consider a wave function given by  $\psi(x) = A \sin kx$ , where  $k = 2\pi/\lambda$  and  $A$  is a real constant. (a) For what values of  $x$  is there the highest probability of finding the particle described by this wave function? Explain. (b) For which values of  $x$  is the probability zero? Explain.

**40.6** • **CALC** Let  $\psi_1$  and  $\psi_2$  be two solutions of Eq. (40.23) with energies  $E_1$  and  $E_2$ , respectively, where  $E_1 \neq E_2$ . Is  $\psi = A\psi_1 + B\psi_2$ , where  $A$  and  $B$  are nonzero constants, a solution to Eq. (40.23)? Explain your answer.

## Section 40.2 Particle in a Box

**40.7** • An electron is in a one-dimensional box. When the electron is in its ground state, the longest-wavelength photon it can absorb is 420 nm. What is the next longest-wavelength photon it can absorb, again starting in the ground state?

**40.8** • **CALC** A particle moving in one dimension (the  $x$ -axis) is described by the wave function

$$\psi(x) = \begin{cases} Ae^{-bx}, & \text{for } x \geq 0 \\ Ae^{bx}, & \text{for } x < 0 \end{cases}$$

where  $b = 2.00 \text{ m}^{-1}$ ,  $A > 0$ , and the  $+x$ -axis points toward the right. (a) Determine  $A$  so that the wave function is normalized. (b) Sketch the graph of the wave function. (c) Find the probability of finding this particle in each of the following regions: (i) within 50.0 cm of the origin, (ii) on the left side of the origin (can you first guess the answer by looking at the graph of the wave function?), (iii) between  $x = 0.500 \text{ m}$  and  $x = 1.00 \text{ m}$ .

**40.9** • **Ground-Level Billiards**. (a) Find the lowest energy level for a particle in a box if the particle is a billiard ball ( $m = 0.20 \text{ kg}$ ) and the box has a width of 1.3 m, the size of a billiard table. (Assume that the billiard ball slides without friction rather than rolls; that is, ignore the rotational kinetic energy.) (b) Since the energy in part (a) is all kinetic, to what speed does this correspond? How much time would it take at this speed for the ball to move from one side of the table to the other? (c) What is the difference in energy between the  $n = 2$  and  $n = 1$  levels? (d) Are quantum-mechanical effects important for the game of billiards?

**40.10** • A proton is in a box of width  $L$ . What must the width of the box be for the ground-level energy to be 5.0 MeV, a typical value for the energy with which the particles in a nucleus are bound? Compare your result to the size of a nucleus—that is, on the order of  $10^{-14} \text{ m}$ .

**40.11** • Find the width  $L$  of a one-dimensional box for which the ground-state energy of an electron in the box equals the absolute value of the ground state of a hydrogen atom.

**40.12** • When a hydrogen atom undergoes a transition from the  $n = 2$  to the  $n = 1$  level, a photon with  $\lambda = 122 \text{ nm}$  is emitted. (a) If the atom is modeled as an electron in a one-dimensional box, what is the width of the box in order for the  $n = 2$  to  $n = 1$  transition to correspond to emission of a photon of this energy? (b) For a box with the width calculated in part (a), what is the ground-state energy? How does this correspond to the ground-state energy of a hydrogen atom? (c) Do you think a one-dimensional box is a good model for a hydrogen atom? Explain. (*Hint*: Compare the spacing between adjacent energy levels as a function of  $n$ .)

**40.13** • A certain atom requires 3.0 eV of energy to excite an electron from the ground level to the first excited level. Model the atom as an electron in a box and find the width  $L$  of the box.

**40.14** • An electron in a one-dimensional box has ground-state energy 2.00 eV. What is the wavelength of the photon absorbed when the electron makes a transition to the second excited state?

**40.15** • A particle with mass  $m$  is in a one-dimensional box with width  $L$ . If the energy of the particle is  $9\pi^2\hbar^2/2mL^2$ , (a) what is the linear momentum of the particle and (b) what is the ratio of the width of the box to the de Broglie wavelength  $\lambda$  of the particle?

**40.16** • Recall that  $|\psi|^2 dx$  is the probability of finding the particle that has normalized wave function  $\psi(x)$  in the interval  $x$  to  $x + dx$ . Consider a particle in a box with rigid walls at  $x = 0$  and  $x = L$ . Let the particle be in the ground level and use  $\psi_n$  as given in Eq. (40.35). (a) For which values of  $x$ , if any, in the range from 0 to  $L$  is the probability of finding the particle zero? (b) For which values of  $x$  is the probability highest? (c) In parts (a) and (b) are your answers consistent with Fig. 40.12? Explain.

**40.17** • Consider two different particles in two different boxes. Particle  $A$  has nine times the mass of particle  $B$ , while particle  $B$ 's box has twice the width of particle  $A$ 's box. What are the two lowest quantum numbers for the two systems for which particles  $A$  and  $B$  have equal energies?

**40.18** • (a) Find the excitation energy from the ground level to the third excited level for an electron confined to a box of width 0.360 nm. (b) The electron makes a transition from the  $n = 1$  to  $n = 4$  level by absorbing a photon. Calculate the wavelength of this photon.

**40.19** • An electron is in a box of width  $3.0 \times 10^{-10} \text{ m}$ . What are the de Broglie wavelength and the magnitude of the momentum of the electron if it is in (a) the  $n = 1$  level; (b) the  $n = 2$  level; (c) the  $n = 3$  level? In each case how does the wavelength compare to the width of the box?

**40.20** • When an electron in a one-dimensional box makes a transition from the  $n = 1$  energy level to the  $n = 2$  level, it absorbs a photon of wavelength 426 nm. What is the wavelength of that photon when the electron undergoes a transition (a) from the  $n = 2$  to the  $n = 3$  energy level and (b) from the  $n = 1$  to the  $n = 3$  energy level? (c) What is the width  $L$  of the box?

**40.21** • A particle is in a box with infinitely rigid walls. The walls are at  $x = -L/2$  and  $x = +L/2$ . (a) Show that  $\psi_n = A \cos k_n x$  is a possible solution. What must  $k_n$  equal? (b) Show that  $\psi_n = A \sin k_n x$  is a possible solution. What must  $k_n$  equal? (c) What are the allowed energy levels for  $\psi_n = A \sin k_n x$  and for  $\psi_n = A \cos k_n x$ ? (d) How does the set of energy levels you found in part (c) compare to the energy levels given by Eq. (40.31)?

## Section 40.3 Potential Wells

**40.22 ••** An electron is moving past the square well shown in Fig. 40.13. The electron has energy  $E = 3U_0$ . What is the ratio of the de Broglie wavelength of the electron in the region  $x > L$  to the wavelength for  $0 < x < L$ ?

**40.23 •** An electron is bound in a square well of depth  $U_0 = 6E_{1-IDW}$ . What is the width of the well if its ground-state energy is 2.00 eV?

**40.24 ••** An electron is in the ground state of a square well of width  $L = 4.00 \times 10^{-10}$  m. The depth of the well is six times the ground-state energy of an electron in an infinite well of the same width. What is the kinetic energy of this electron after it has absorbed a photon of wavelength 72 nm and moved away from the well?

**40.25 ••** An electron is bound in a square well of width 1.50 nm and depth  $U_0 = 6E_{1-IDW}$ . If the electron is initially in the ground level and absorbs a photon, what maximum wavelength can the photon have and still liberate the electron from the well?

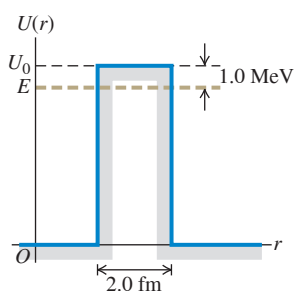
**40.26 ••** An electron is bound in a square well that has a depth equal to six times the ground-level energy  $E_{1-IDW}$  of an infinite well of the same width. The longest-wavelength photon that is absorbed by this electron has a wavelength of 582 nm. Determine the width of the well.

**40.27 ••** A proton is bound in a square well of width 4.0 fm  $= 4.0 \times 10^{-15}$  m. The depth of the well is six times the ground-level energy  $E_{1-IDW}$  of the corresponding infinite well. If the proton makes a transition from the level with energy  $E_1$  to the level with energy  $E_3$  by absorbing a photon, find the wavelength of the photon.

## Section 40.4 Potential Barriers and Tunneling

**40.28 •• Alpha Decay.** In a simple model for a radioactive nucleus, an alpha particle ( $m = 6.64 \times 10^{-27}$  kg) is trapped by a square barrier that has width 2.0 fm and height 30.0 MeV. (a) What is the tunneling probability when the alpha particle encounters the barrier if its kinetic energy is 1.0 MeV below the top of the barrier (Fig. E40.28)? (b) What is the tunneling probability if the energy of the alpha particle is 10.0 MeV below the top of the barrier?

Figure E40.28



**40.29 ••** (a) An electron with initial kinetic energy 32 eV encounters a square barrier with height 41 eV and width 0.25 nm. What is the probability that the electron will tunnel through the barrier? (b) A proton with the same kinetic energy encounters the same barrier. What is the probability that the proton will tunnel through the barrier?

**40.30 •** An electron with initial kinetic energy 5.0 eV encounters a barrier with height  $U_0$  and width 0.60 nm. What is the transmission coefficient if (a)  $U_0 = 7.0$  eV; (b)  $U_0 = 9.0$  eV; (c)  $U_0 = 13.0$  eV?

**40.31 •** An electron with initial kinetic energy 6.0 eV encounters a barrier with height 11.0 eV. What is the probability of tunneling if the width of the barrier is (a) 0.80 nm and (b) 0.40 nm?

**40.32 ••** An electron is moving past the square barrier shown in Fig. 40.19, but the energy of the electron is *greater* than the barrier height. If  $E = 2U_0$ , what is the ratio of the de Broglie wavelength of the electron in the region  $x > L$  to the wavelength for  $0 < x < L$ ?

## Section 40.5 The Harmonic Oscillator

**40.33 •** A wooden block with mass 0.250 kg is oscillating on the end of a spring that has force constant 110 N/m. Calculate the ground-level energy and the energy separation between adjacent levels. Express your results in joules and in electron volts. Are quantum effects important?

**40.34 ••** A harmonic oscillator with mass  $m$  and force constant  $k'$  is in an excited state that has quantum number  $n$ . (a) Let  $p_{\max} = mv_{\max}$ , where  $v_{\max}$  is the maximum speed calculated in the Newtonian analysis of the oscillator. Derive an expression for  $p_{\max}$  in terms of  $n$ ,  $\hbar$ ,  $k'$ , and  $m$ . (b) Derive an expression for the classical amplitude  $A$  in terms of  $n$ ,  $\hbar$ ,  $k'$ , and  $m$ . (c) If  $\Delta x = A/\sqrt{2}$  and  $\Delta p_x = p_{\max}/\sqrt{2}$ , what is the uncertainty product  $\Delta x \Delta p_x$ ? How does the uncertainty product depend on  $n$ ?

**40.35 •** Chemists use infrared absorption spectra to identify chemicals in a sample. In one sample, a chemist finds that light of wavelength 5.8  $\mu\text{m}$  is absorbed when a molecule makes a transition from its ground harmonic oscillator level to its first excited level. (a) Find the energy of this transition. (b) If the molecule can be treated as a harmonic oscillator with mass  $5.6 \times 10^{-26}$  kg, find the force constant.

**40.36 •** A harmonic oscillator absorbs a photon of wavelength 6.35  $\mu\text{m}$  when it undergoes a transition from the ground state to the first excited state. What is the ground-state energy, in electron volts, of the oscillator?

**40.37 ••** The ground-state energy of a harmonic oscillator is 5.60 eV. If the oscillator undergoes a transition from its  $n = 3$  to  $n = 2$  level by emitting a photon, what is the wavelength of the photon?

**40.38 ••** While undergoing a transition from the  $n = 1$  to the  $n = 2$  energy level, a harmonic oscillator absorbs a photon of wavelength 6.50  $\mu\text{m}$ . What is the wavelength of the absorbed photon when this oscillator undergoes a transition (a) from the  $n = 2$  to the  $n = 3$  energy level and (b) from the  $n = 1$  to the  $n = 3$  energy level? (c) What is the value of  $\sqrt{k'/m}$ , the angular oscillation frequency of the corresponding Newtonian oscillator?

**40.39 ••** For the sodium atom of Example 40.8, find (a) the ground-state energy; (b) the wavelength of a photon emitted when the  $n = 4$  to  $n = 3$  transition occurs; (c) the energy difference for any  $\Delta n = 1$  transition.

**40.40 ••** For the ground-level harmonic oscillator wave function  $\psi(x)$  given in Eq. (40.47),  $|\psi|^2$  has a maximum at  $x = 0$ . (a) Compute the ratio of  $|\psi|^2$  at  $x = +A$  to  $|\psi|^2$  at  $x = 0$ , where  $A$  is given by Eq. (40.48) with  $n = 0$  for the ground level. (b) Compute the ratio of  $|\psi|^2$  at  $x = +2A$  to  $|\psi|^2$  at  $x = 0$ . In each case is your result consistent with what is shown in Fig. 40.27?

## PROBLEMS

**40.41 ••** A particle of mass  $m$  in a one-dimensional box has the following wave function in the region  $x = 0$  to  $x = L$ :

$$\Psi(x, t) = \frac{1}{\sqrt{2}}\psi_1(x)e^{-iE_1t/\hbar} + \frac{1}{\sqrt{2}}\psi_3(x)e^{-iE_3t/\hbar}$$

Here  $\psi_1(x)$  and  $\psi_3(x)$  are the normalized stationary-state wave functions for the  $n = 1$  and  $n = 3$  levels, and  $E_1$  and  $E_3$  are the energies of these levels. The wave function is zero for  $x < 0$  and for  $x > L$ . (a) Find the value of the probability distribution function at  $x = L/2$  as a function of time. (b) Find the angular frequency at which the probability distribution function oscillates.

**40.42 ••** Hydrogen emits radiation with four prominent visible wavelengths—one red, one cyan, one blue, and one violet. The respective frequencies are 656 nm, 486 nm, 434 nm, and 410 nm. We can model the hydrogen atom as an electron in a one-dimensional box, and attempt to match four adjacent emission lines in the predicted spectrum to the visible part of the hydrogen spectrum. (a) Determine the photon energies associated with the visible part of the hydrogen spectrum. (b) The electron-in-a-box emission spectrum is  $E_{n_i \rightarrow n_f} = (n_i^2 - n_f^2)\epsilon$ , where  $n_i$  and  $n_f$  are the initial and final quantum numbers of the electron when it drops to a lower energy level and  $\epsilon$  is the energy determined

by the Schrödinger equation. What is the smallest possible value of  $n_i$  that can accommodate four emission lines? (c) Using the value from part (b) for  $n_i$ , estimate the order of magnitude of  $\epsilon$  by dividing the four photon energies by the relevant differences  $n_i^2 - n_f^2$  for transitions in the possible sets of  $(n_i, n_f)$  pairings. (d) Using Eq. (40.31) to identify  $\epsilon$ , and using the mass of the electron, use your result from part (c) to estimate the length  $L$  of the box. (e) What is the ratio of your estimate of  $L$  to twice the Bohr radius? (Note: The hydrogen atom is better modeled using the Coulomb potential rather than as a particle in a box.)

**40.43 •• CALC** Consider a beam of free particles that move with velocity  $v = p/m$  in the  $x$ -direction and are incident on a potential-energy step  $U(x) = 0$ , for  $x < 0$ , and  $U(x) = U_0 < E$ , for  $x > 0$ . The wave function for  $x < 0$  is  $\psi(x) = Ae^{ik_1x} + Be^{-ik_1x}$ , representing incident and reflected particles, and for  $x > 0$  is  $\psi(x) = Ce^{ik_2x}$ , representing transmitted particles. Use the conditions that both  $\psi$  and its first derivative must be continuous at  $x = 0$  to find the constants  $B$  and  $C$  in terms of  $k_1$ ,  $k_2$ , and  $A$ .

**40.44 • CALC** A particle is in the ground level of a box that extends from  $x = 0$  to  $x = L$ . (a) What is the probability of finding the particle in the region between 0 and  $L/4$ ? Calculate this by integrating  $|\psi(x)|^2 dx$ , where  $\psi$  is normalized, from  $x = 0$  to  $x = L/4$ . (b) What is the probability of finding the particle in the region  $x = L/4$  to  $x = L/2$ ? (c) How do the results of parts (a) and (b) compare? Explain. (d) Add the probabilities calculated in parts (a) and (b). (e) Are your results in parts (a), (b), and (d) consistent with Fig. 40.12b? Explain.

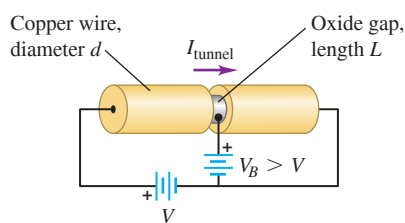
**40.45 • Photon in a Dye Laser.** An electron in a long, organic molecule used in a dye laser behaves approximately like a particle in a box with width 4.18 nm. What is the wavelength of the photon emitted when the electron undergoes a transition (a) from the first excited level to the ground level and (b) from the second excited level to the first excited level?

**40.46 ••** Consider a particle in a box with rigid walls at  $x = 0$  and  $x = L$ . Let the particle be in the ground level. Calculate the probability  $|\psi|^2 dx$  that the particle will be found in the interval  $x$  to  $x + dx$  for (a)  $x = L/4$ ; (b)  $x = L/2$ ; (c)  $x = 3L/4$ .

**40.47 ••** Repeat Problem 40.46 for a particle in the first excited level.

**40.48 ••** Suppose we have two copper wires that meet on either side of an oxide gap with

Figure P40.48



length  $L = 1$  nm, as shown in **Fig. P40.48**. If the left side is at a potential  $V$  relative to the right side, then we can estimate the tunneling current as follows: The wires have diameter  $d = 1$  mm, and copper has  $n = 8.5 \times 10^{28}$  free electrons per  $\text{m}^3$ . (a) Assume that the oxide gap provides a rectangular potential barrier of height 12 eV and that the energy of the free electrons incident on this barrier is 5.0 eV. Assume the gap has length  $L = 1$  nm. What is the probability  $T$  that an electron will tunnel through the barrier? (b) A length  $x$  of wire on the left of the barrier will have  $nAx$  free electrons, where  $A = \pi(d/2)^2$  is the cross-sectional area of the wire. In a similar length of wire on the right side of the barrier, the number of tunneled electrons will be  $T$  times that number. If these electrons move with effective velocity  $v = dx/dt$ , then what will be the tunneling current, expressed symbolically in terms of  $T$ ,  $n$ ,  $A$ ,  $e$ , and  $v$ ? (c) Define their effective speed  $v$  by  $\frac{1}{2}mv^2 = eV$ . The tunneled electrons have energy  $eV$ . What is their effective speed  $v$ , expressed symbolically in terms of  $e$ ,  $V$ , and  $m$ , where  $m$  is the mass of an electron? (f) Put these elements together to estimate the tunneling current.

**40.49 •• CALC** What is the probability of finding a particle in a box of length  $L$  in the region between  $x = L/4$  and  $x = 3L/4$  when the particle is in (a) the ground level and (b) the first excited level? (Hint: Integrate  $|\psi(x)|^2 dx$ , where  $\psi$  is normalized, between  $L/4$  and  $3L/4$ .) (c) Are your results in parts (a) and (b) consistent with Fig. 40.12b? Explain.

**40.50 ••** The penetration distance  $\eta$  in a finite potential well is the distance at which the wave function has decreased to  $1/e$  of the (b) wave function at the classical turning point:

$$\psi(x = L + \eta) = \frac{1}{e}\psi(L)$$

The penetration distance can be shown to be

$$\eta = \frac{\hbar}{\sqrt{2m(U_0 - E)}}$$

The probability of finding the particle beyond the penetration distance is nearly zero. (a) Find  $\eta$  for an electron having a kinetic energy of 13 eV in a potential well with  $U_0 = 20$  eV. (b) Find  $\eta$  for a 20.0 MeV proton trapped in a 30.0-MeV-deep potential well.

**40.51 •• CALC** A fellow student proposes that a possible wave function for a free particle with mass  $m$  (one for which the potential-energy function  $U(x)$  is zero) is

$$\psi(x) = \begin{cases} e^{+\kappa x}, & x < 0 \\ e^{-\kappa x}, & x \geq 0 \end{cases}$$

where  $\kappa$  is a positive constant. (a) Graph this proposed wave function. (b) Show that the proposed wave function satisfies the Schrödinger equation for  $x < 0$  if the energy is  $E = -\hbar^2\kappa^2/2m$ —that is, if the energy of the particle is *negative*. (c) Show that the proposed wave function also satisfies the Schrödinger equation for  $x \geq 0$  with the same energy as in part (b). (d) Explain why the proposed wave function is nonetheless *not* an acceptable solution of the Schrödinger equation for a free particle. (Hint: What is the behavior of the function at  $x = 0$ ?) It is in fact impossible for a free particle (one for which  $U(x) = 0$ ) to have an energy less than zero.

**40.52 •** An electron with initial kinetic energy 5.5 eV encounters a square potential barrier of height 10.0 eV. What is the width of the barrier if the electron has a 0.50% probability of tunneling through the barrier?

**40.53 ••• CP** Consider a one-dimensional lattice of carbon nuclei with interatomic spacing  $d = 0.500$  nm. The potential energy of one nucleus due to electrostatic interaction with its two nearest neighbors is

$$V(x) = \frac{q^2}{4\pi\epsilon_0} \left( \frac{1}{d-x} + \frac{1}{d+x} \right)$$

where  $q = 6e$  is the charge of each carbon nucleus and  $x$  is its position relative to its equilibrium position. (a) Sketch the potential  $V(x)$  between  $x = -d$  and  $x = d$ . (b) At low energy, the nucleus remains near its equilibrium position at  $x = 0$  and the potential energy is well approximated as a harmonic oscillator. Use the power series in Appendix B to write  $V(x)$  as a quadratic function in  $x$ , dropping contributions at higher order in  $x/d$ . (c) What is the spring constant  $k'$ ? (d) What is the energy of the classical ground state, in eV? (e) What is the energy of the lowest-energy photons emitted when this system transitions between energy levels? (f) What is the wavelength of the corresponding radiation?

**40.54 • CP** A harmonic oscillator consists of a 0.020 kg mass on a spring. The oscillation frequency is 1.50 Hz, and the mass has a speed



of 0.480 m/s as it passes the equilibrium position. (a) What is the value of the quantum number  $n$  for its energy level? (b) What is the difference in energy between the levels  $E_n$  and  $E_{n+1}$ ? Is this difference detectable?

**40.55 •** For small amplitudes of oscillation the motion of a pendulum is simple harmonic. For a pendulum with a period of 0.500 s, find the ground-level energy and the energy difference between adjacent energy levels. Express your results in joules and in electron volts. Are these values detectable?

**40.56 •• CALC** (a) Show by direct substitution in the Schrödinger equation for the one-dimensional harmonic oscillator that the wave function  $\psi_1(x) = A_1 x e^{-\alpha^2 x^2/2}$ , where  $\alpha^2 = m\omega/\hbar$ , is a solution with energy corresponding to  $n = 1$  in Eq. (40.46). (b) Find the normalization constant  $A_1$ . (c) Show that the probability density has a minimum at  $x = 0$  and maxima at  $x = \pm 1/\alpha$ , corresponding to the classical turning points for the ground state  $n = 0$ .

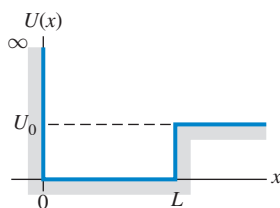
**40.57 •• CP** (a) The wave nature of particles results in the quantum-mechanical situation that a particle confined in a box can assume only wavelengths that result in standing waves in the box, with nodes at the box walls. Use this to show that an electron confined in a one-dimensional box of length  $L$  will have energy levels given by

$$E_n = \frac{n^2 h^2}{8mL^2}$$

(Hint: Recall that the relationship between the de Broglie wavelength and the speed of a nonrelativistic particle is  $mv = h/\lambda$ . The energy of the particle is  $\frac{1}{2}mv^2$ .) (b) If a hydrogen atom is modeled as a one-dimensional box with length equal to the Bohr radius, what is the energy (in electron volts) of the lowest energy level of the electron?

**40.58 •••** Consider a potential Figure P40.58

well defined as  $U(x) = \infty$  for  $x < 0$ ,  $U(x) = 0$  for  $0 < x < L$ , and  $U(x) = U_0 > 0$  for  $x > L$  (Fig. P40.58). Consider a particle with mass  $m$  and kinetic energy  $E < U_0$  that is trapped in the well. (a) The boundary condition at the infinite wall ( $x = 0$ ) is  $\psi(0) = 0$ .



What must the form of the function  $\psi(x)$  for  $0 < x < L$  be in order to satisfy both the Schrödinger equation and this boundary condition? (b) The wave function must remain finite as  $x \rightarrow \infty$ . What must the form of the function  $\psi(x)$  for  $x > L$  be in order to satisfy both the Schrödinger equation and this boundary condition at infinity? (c) Impose the boundary conditions that  $\psi$  and  $d\psi/dx$  are continuous at  $x = L$ . Show that the energies of the allowed levels are obtained from solutions of the equation  $k \cot kL = -\kappa$ , where  $k = \sqrt{2mE}/\hbar$  and  $\kappa = \sqrt{2m(U_0 - E)}/\hbar$ .

**40.59 •• DATA** In your research on new solid-state devices, you are studying a solid-state structure that can be modeled accurately as an electron in a one-dimensional infinite potential well (box) of width  $L$ . In one of your experiments, electromagnetic radiation is absorbed in transitions in which the initial state is the  $n = 1$  ground state. You measure that light of frequency  $f = 9.0 \times 10^{14}$  Hz is absorbed and that the next higher absorbed frequency is  $16.9 \times 10^{14}$  Hz. (a) What is quantum number  $n$  for the final state in each of the transitions that leads to the absorption of photons of these frequencies? (b) What is the width  $L$  of the potential well? (c) What is the longest wavelength in air of light that can be absorbed by an electron if it is initially in the  $n = 1$  state?

**40.60 •• DATA** As an intern at a research lab, you study the transmission of electrons through a potential barrier. You know the height of the barrier, 8.0 eV, but must measure the width  $L$  of the barrier. When you

measure the tunneling probability  $T$  as a function of the energy  $E$  of the electron, you get the results shown in the table.

$E$ (eV)	4.0	5.0	6.0	7.0	7.6
$T$	$2.4 \times 10^{-6}$	$1.5 \times 10^{-5}$	$1.2 \times 10^{-4}$	$1.3 \times 10^{-3}$	$8.1 \times 10^{-3}$

(a) For each value of  $E$ , calculate the quantities  $G$  and  $\kappa$  that appear in Eq. (40.42). Graph  $\ln(T/G)$  versus  $\kappa$ . Explain why your data points, when plotted this way, fall close to a straight line. (b) Use the slope of the best-fit straight line to the data in part (a) to calculate  $L$ .

**40.61 •• DATA** When low-energy electrons pass through an ionized gas, electrons of certain energies pass through the gas as if the gas atoms weren't there and thus have transmission coefficients (tunneling probabilities)  $T$  equal to unity. The gas ions can be modeled approximately as a rectangular barrier. The value of  $T = 1$  occurs when an integral or half-integral number of de Broglie wavelengths of the electron as it passes over the barrier equal the width  $L$  of the barrier. You are planning an experiment to measure this effect. To assist you in designing the necessary apparatus, you estimate the electron energies  $E$  that will result in  $T = 1$ . You assume a barrier height of 10 eV and a width of  $1.8 \times 10^{-10}$  m. Calculate the three lowest values of  $E$  for which  $T = 1$ .

**40.62 ••• CP** A particle is confined to move on a circle with radius  $R$  but is otherwise free. We can parameterize points on this circle by using the distance  $x$  from a reference point or by using the angle  $\theta = x/R$ . Since  $x = 0$  and  $x = 2\pi R$  describe the same point, the wave function must satisfy  $\psi(x) = \psi(x + 2\pi R)$  and  $\psi'(x) = \psi'(x + 2\pi R)$ .

(a) Solve the free-particle time-independent Schrödinger equation subject to these boundary conditions. You should find solutions  $\psi_n^\pm$ , where  $n$  is a positive integer and where lower  $n$  corresponds to lower energy. Express your solutions in terms of  $\theta$  using unspecified normalization constants  $A_n^+$  and  $A_n^-$  corresponding, respectively, to modes that move "counterclockwise" toward higher  $x$  and "clockwise" toward lower  $x$ . (b) Normalize these functions to determine  $A_n^\pm$ . (c) What are the energy levels  $E_n$ ? (d) Write the time-dependent wave functions  $\Psi_n^\pm(x, t)$  corresponding to  $\Psi_n^\pm(x)$ . Use the symbol  $\omega$  for  $E_1/\hbar$ . (e) Consider the nonstationary state defined at  $t = 0$  by  $\Psi(x, 0) = \frac{1}{\sqrt{2}}[\Psi_1^+(x) + \Psi_2^+(x)]$ . Determine the probability density  $|\Psi(x, t)|^2$  in terms of  $R$ ,  $\omega$ , and  $t$ . Simplify your result using the identity  $1 + \cos \alpha = 2\cos^2(\alpha/2)$ . (f) With what angular speed does the density peak move around the circle? (g) If the particle is an electron and the radius is the Bohr radius, then with what speed does its probability peak move?

## CHALLENGE PROBLEMS

**40.63 ••• CALC** The Schrödinger equation for the quantum-mechanical harmonic oscillator in Eq. (40.44) may be written as

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

where  $\omega = \sqrt{k'/m}$  is the angular frequency for classical oscillations. Its solutions may be cleverly addressed using the following observations: The difference in applying two operations  $A$  and  $B$ , in opposite order, called a commutator, is denoted by  $[A, B] = AB - BA$ .

For example, if  $A$  represents differentiation, so that  $Af = \frac{df}{dx}$ , where  $f = f(x)$  is a function, and  $B$  represents multiplication by  $x$ , then  $[A, B] = \left[\frac{d}{dx}, x\right]f = \frac{d}{dx}(xf) - x\frac{df}{dx}$ . Applying the product rule for differentiation on the first term, we determine  $\left[\frac{d}{dx}, x\right]f = f$ , which

we summarize by writing  $\left[\frac{d}{dx}, x\right] = 1$ . Similarly, consider the two operators  $a_+$  and  $a_-$  defined by  $a_{\pm} = 1/\sqrt{2m\hbar\omega} \left(\mp \hbar \frac{d}{dx} + m\omega x\right)$ .

(a) Determine the commutator  $[a_-, a_+]$ . (b) Compute  $a_+ a_- \psi$  in terms of  $\psi$  and  $\psi''$ , where  $\psi = \psi(x)$  is a wave function. Be mindful that  $\frac{d}{dx}(x\psi) = \psi + x\psi'$ . (c) The Schrödinger equation above may be written as  $H\psi = E\psi$ , where  $H$  is a differential operator. Use your previous result to write  $H$  in terms of  $a_+$  and  $a_-$ . (d) Determine the commutators  $[H, a_{\pm}]$ . (e) Consider a wave function  $\psi_n$  with definite energy  $E_n$ , whereby  $H\psi_n = E_n\psi_n$ . If we define a new function  $\psi_{n+1} = a_+\psi_n$ , then we can readily determine its energy by computing  $H\psi_{n+1} = Ha_+\psi_n = (a_+H + [H, a_+])\psi_n$  and comparing the result with  $E_{n+1}\psi_{n+1}$ . Finish this calculation by inserting what we have determined to find  $E_{n+1}$  in terms of  $E_n$  and  $n$ . (f) We can prove that the lowest-energy wave function  $\psi_0$  is annihilated by  $a_-$ , meaning that  $a_-\psi_0 = 0$ . Using your expression for  $H$  in terms of  $a_{\pm}$ , determine the ground-state energy  $E_0$ . (g) By applying  $a_+$  repeatedly, we can generate all higher states. The energy of the  $n$ th excited state can be determined by considering  $Ha_+^n\psi_0 = E_0\psi_0$ . Using the above results, determine  $E_n$ . (Note: We did not have to solve any differential equations or take any derivatives to determine the spectrum of this theory.)

**40.64 ••• CALC The WKB Approximation.** It can be a challenge to solve the Schrödinger equation for the bound-state energy levels of an arbitrary potential well. An alternative approach that can yield good approximate results for the energy levels is the *WKB approximation* (named for the physicists Gregor Wentzel, Hendrik Kramers, and Léon Brillouin, who pioneered its application to quantum mechanics). The WKB approximation begins from three physical statements: (i) According to de Broglie, the magnitude of momentum  $p$  of a quantum-mechanical particle is  $p = h/\lambda$ . (ii) The magnitude of momentum is related to the kinetic energy  $K$  by the relationship  $K = p^2/2m$ . (iii) If there are no nonconservative forces, then in Newtonian mechanics the energy  $E$  for a particle is constant and equal at each point to the sum of the kinetic and potential energies at that point:  $E = K + U(x)$ , where  $x$  is the coordinate. (a) Combine these three relationships to show that the wavelength of the particle at a coordinate  $x$  can be written as

$$\lambda(x) = \frac{h}{\sqrt{2m[E - U(x)]}}$$

Thus we envision a quantum-mechanical particle in a potential well  $U(x)$  as being like a free particle, but with a wavelength  $\lambda(x)$  that is a function of position. (b) When the particle moves into a region of increasing potential energy, what happens to its wavelength? (c) At a point where  $E = U(x)$ , Newtonian mechanics says that the particle has zero kinetic energy and must be instantaneously at rest. Such a point is called a *classical turning point*, since this is where a Newtonian particle must stop its motion and reverse direction. As an example, an object oscillating in simple harmonic motion with amplitude  $A$  moves back and forth between the points  $x = -A$  and  $x = +A$ ; each of these is a classical turning point, since there the potential energy  $\frac{1}{2}k'x^2$  equals the total energy  $\frac{1}{2}k'A^2$ . In the WKB expression for  $\lambda(x)$ , what is the wavelength at a classical turning point? (d) For a particle in a box with length  $L$ , the walls of the box are classical turning points (see Fig. 40.8). Furthermore, the number of wavelengths that fit within the box must be a half-integer (see Fig. 40.10), so that  $L = (n/2)\lambda$  and hence  $L/\lambda = n/2$ , where  $n = 1, 2, 3, \dots$  [Note that this is a restatement of Eq. (40.29).] The WKB scheme for finding the allowed bound-state energy levels of an *arbitrary* potential well is an extension of these

observations. It demands that for an allowed energy  $E$ , there must be a half-integer number of wavelengths between the classical turning points for that energy. Since the wavelength in the WKB approximation is not a constant but depends on  $x$ , the number of wavelengths between the classical turning points  $a$  and  $b$  for a given value of the energy is the integral of  $1/\lambda(x)$  between those points:

$$\int_a^b \frac{dx}{\lambda(x)} = \frac{n}{2} \quad (n = 1, 2, 3, \dots)$$

Using the expression for  $\lambda(x)$  you found in part (a), show that the *WKB condition for an allowed bound-state energy* can be written as

$$\int_a^b \sqrt{2m[E - U(x)]} dx = \frac{nh}{2} \quad (n = 1, 2, 3, \dots)$$

(e) As a check on the expression in part (d), apply it to a particle in a box with walls at  $x = 0$  and  $x = L$ . Evaluate the integral and show that the allowed energy levels according to the WKB approximation are the same as those given by Eq. (40.31). (Hint: Since the walls of the box are infinitely high, the points  $x = 0$  and  $x = L$  are classical turning points for *any* energy  $E$ . Inside the box, the potential energy is zero.) (f) For the finite square well shown in Fig. 40.13, show that the WKB expression given in part (d) predicts the *same* bound-state energies as for an infinite square well of the same width. (Hint: Assume  $E < U_0$ . Then the classical turning points are at  $x = 0$  and  $x = L$ .) This shows that the WKB approximation does a poor job when the potential-energy function changes discontinuously, as for a finite potential well. In the next two problems we consider situations in which the potential-energy function changes gradually and the WKB approximation is much more useful.

**40.65 ••• CALC** The WKB approximation (see Challenge Problem 40.64) can be used to calculate the energy levels for a harmonic oscillator. In this approximation, the energy levels are the solutions to the equation

$$\int_a^b \sqrt{2m[E - U(x)]} dx = \frac{nh}{2} \quad n = 1, 2, 3, \dots$$

Here  $E$  is the energy,  $U(x)$  is the potential-energy function, and  $x = a$  and  $x = b$  are the classical turning points (the points at which  $E$  is equal to the potential energy, so the Newtonian kinetic energy would be zero). (a) Determine the classical turning points for a harmonic oscillator with energy  $E$  and force constant  $k'$ . (b) Carry out the integral in the WKB approximation and show that the energy levels in this approximation are  $E_n = \hbar\omega$ , where  $\omega = \sqrt{k'/m}$  and  $n = 1, 2, 3, \dots$  (Hint: Recall that  $\hbar = h/2\pi$ . A useful standard integral is

$$\int \sqrt{A^2 - x^2} dx = \frac{1}{2} \left[ x\sqrt{A^2 - x^2} + A^2 \arcsin\left(\frac{x}{A}\right) \right]$$

where arcsin denotes the inverse sine function. Note that the integrand is even, so the integral from  $-x$  to  $x$  is equal to twice the integral from 0 to  $x$ .) (c) How do the approximate energy levels found in part (b) compare with the true energy levels given by Eq. (40.46)? Does the WKB approximation give an underestimate or an overestimate of the energy levels?

**40.66 ••• CALC** Protons, neutrons, and many other particles are made of more fundamental particles called *quarks* and *antiquarks* (the antimatter equivalent of quarks). A quark and an antiquark can form a bound state with a variety of different energy levels, each of which corresponds to a different particle observed in the laboratory. As an example, the  $\psi$  particle is a low-energy bound state of a so-called charm quark and its antiquark, with a rest energy of 3097 MeV; the  $\psi(2S)$  particle is



an excited state of this same quark–antiquark combination, with a rest energy of 3686 MeV. A simplified representation of the potential energy of interaction between a quark and an antiquark is  $U(x) = A|x|$ , where  $A$  is a positive constant and  $x$  represents the distance between the quark and the antiquark. You can use the WKB approximation (see Challenge Problem 40.64) to determine the bound-state energy levels for this potential-energy function. In the WKB approximation, the energy levels are the solutions to the equation

$$\int_a^b \sqrt{2m[E - U(x)]} dx = \frac{n\hbar}{2} \quad (n = 1, 2, 3, \dots)$$

Here  $E$  is the energy,  $U(x)$  is the potential-energy function, and  $x = a$  and  $x = b$  are the classical turning points (the points at which  $E$  is equal to the potential energy, so the Newtonian kinetic energy would be zero). (a) Determine the classical turning points for the potential  $U(x) = A|x|$  and for an energy  $E$ . (b) Carry out the above integral and show that the allowed energy levels in the WKB approximation are given by

$$E_n = \frac{1}{2m} \left( \frac{3mA\hbar}{4} \right)^{2/3} n^{2/3} \quad (n = 1, 2, 3, \dots)$$

(Hint: The integrand is even, so the integral from  $-x$  to  $x$  is equal to twice the integral from 0 to  $x$ .) (c) Does the difference in energy between successive levels increase, decrease, or remain the same as  $n$  increases? How does this compare to the behavior of the energy levels for the harmonic oscillator? For the particle in a box? Can you suggest a simple rule that relates the difference in energy between successive levels to the shape of the potential-energy function?

## MCAT-STYLE PASSAGE PROBLEMS

**Quantum Dots.** A *quantum dot* is a type of crystal so small that quantum effects are significant. One application of quantum dots is in fluorescence imaging, in which a quantum dot is bound to a molecule or structure of interest. When the quantum dot is illuminated with light, it absorbs photons and then re-emits photons at a different wavelength. This phenomenon is called *fluorescence*. The wavelength that a quantum dot emits when

stimulated with light depends on the dot's size, so the synthesis of quantum dots with different photon absorption and emission properties may be possible. We can understand many quantum-dot properties via a model in which a particle of mass  $M$  (roughly the mass of the electron) is confined to a two-dimensional rigid square box of sides  $L$ . In this model, the quantum-dot energy levels are given by  $E_{m,n} = (m^2 + n^2)(\pi^2\hbar^2)/2ML^2$ , where  $m$  and  $n$  are integers 1, 2, 3, . . .

**40.67** According to this model, which statement is true about the energy-level spacing of dots of different sizes? (a) Smaller dots have equally spaced levels, but larger dots have energy levels that get farther apart as the energy increases. (b) Larger dots have greater spacing between energy levels than do smaller dots. (c) Smaller dots have greater spacing between energy levels than do larger dots. (d) The spacing between energy levels is independent of the dot size.

**40.68** When a given dot with side length  $L$  makes a transition from its first excited state to its ground state, the dot emits green (550 nm) light. If a dot with side length  $1.1L$  is used instead, what wavelength is emitted in the same transition, according to this model? (a) 600 nm; (b) 670 nm; (c) 500 nm; (d) 460 nm.

**40.69** Dots that are the same size but made from different materials are compared. In the same transition, a dot of material 1 emits a photon of longer wavelength than the dot of material 2 does. Based on this model, what is a possible explanation? (a) The mass of the confined particle in material 1 is greater. (b) The mass of the confined particle in material 2 is greater. (c) The confined particles make more transitions per second in material 1. (d) The confined particles make more transitions per second in material 2.

**40.70** One advantage of the quantum dot is that, compared to many other fluorescent materials, excited states have relatively long lifetimes (10 ns). What does this mean for the spread in the energy of the photons emitted by quantum dots? (a) Quantum dots emit photons of more well-defined energies than do other fluorescent materials. (b) Quantum dots emit photons of less well-defined energies than do other fluorescent materials. (c) The spread in the energy is affected by the size of the dot, not by the lifetime. (d) There is no spread in the energy of the emitted photons, regardless of the lifetime.

## ANSWERS

### Chapter Opening Question ?

(i) When an electron in one of these particles—called *quantum dots*—makes a transition from an excited level to a lower level, it emits a photon whose energy is equal to the difference in energy between the levels. The smaller the quantum dot, the larger the energy spacing between levels and hence the shorter (bluer) the wavelength of the emitted photons. See Example 40.6 (Section 40.3) for more details.

### Key Example VARIATION Problems

**VP40.4.1** (a) 0.549 nm (b)  $E_2 = 8.00 \times 10^{-19}$  J,  $E_3 = 1.80 \times 10^{-18}$  J

**VP40.4.2** (a)  $3.94 \times 10^{-12}$  J (b)  $6.57 \times 10^{-12}$  J

**VP40.4.3** (a)  $3.03 \times 10^{-19}$  J (b) 0.772 nm (c) 393 nm

**VP40.4.4** (a)  $\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2} \text{Acos}\left(\frac{x\sqrt{2mE}}{\hbar} + \phi\right) = -\frac{2mE}{\hbar^2} \psi(x)$ ,

so  $-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x)$  (b)  $\phi = \pm\pi/2$  (c)  $\frac{L\sqrt{2mE}}{\hbar} = n\pi$ , so

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2}, \text{ where } n = 1, 2, 3, \dots$$

**VP40.6.1** (a)  $4.92 \times 10^{-19}$  J (b)  $3.07 \times 10^{-19}$  J (c)  $2.64 \times 10^{-18}$  J

**VP40.6.2** (a)  $9.40 \times 10^{-20}$  J (b)  $5.64 \times 10^{-19}$  J (c) 0.800 nm

**VP40.6.3** (a) initial  $n = 3$ , final  $n = 1$  (b) 596 nm for initial  $n = 3$ , final  $n = 2$ ; 878 nm for initial  $n = 2$ , final  $n = 1$

**VP40.6.4** (a) 2.35 eV (b) 0.010 eV

**VP40.7.1** (a)  $2.90 \times 10^{-5}$  (b)  $1.47 \times 10^{-3}$

**VP40.7.2** (a)  $5.33 \times 10^{-3}$  (b) 0.704 nm

**VP40.7.3** (a)  $2.54 \times 10^{-4}$  (b)  $8.59 \times 10^{-4}$  (c)  $3.46 \times 10^{-3}$

**VP40.7.4** 0.509 nm

### Bridging Problem

$$(a) |\Psi(x, t)|^2 = \frac{1}{L} \left[ \sin^2 \frac{\pi x}{L} + \sin^2 \frac{2\pi x}{L} + 2 \sin \frac{\pi x}{L} \sin \frac{2\pi x}{L} \cos \left( \frac{(E_2 - E_1)t}{\hbar} \right) \right]$$

(b) no

$$(d) \frac{3\pi^2\hbar}{2mL^2}$$

$$(e) \frac{0.903\pi^2\hbar}{mL^2}$$