QUANTUM MECHANICS

40

?Each of these containers holds a solution of microscopic semiconductor particles, each of which acts like a nanometer-sized "atom." The particles glow when exposed to ultraviolet light. Why do the smallest particles (on the left) glow blue, while the largest particles (on the right) glow red?

LEARNING GOALS

By studying this chapter, you will learn:

- How to calculate the wave functions and energy levels for a particle confined to a box.
- How to analyze the quantum-mechanical behavior of a particle in a potential well.
- How quantum mechanics makes it possible for particles to go where Newtonian mechanics says they cannot.
- How to use quantum mechanics to analyze a harmonic oscillator.
- How to extend quantum-mechanical calculations to three-dimensional problems.

In Chapter 39 we found that particles sometimes behave like waves and that they can be described by wave functions. Now we're ready for a systematic analysis of particles that are trapped in *bound states* (such as electrons in atoms), including finding their possible wave functions and energy levels.

Our analysis involves finding solutions of the Schrödinger equation, which we introduced in Chapter 39. For any quantum-mechanical system, the wave functions for any state of definite energy must be solutions of the Schrödinger equation for that system. As we will see, solving the Schrödinger equation automatically gives the possible energy levels for the system. We'll discuss several simple one-dimensional applications of the Schrödinger equation.

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.

Finally, we'll generalize the Schrödinger equation to three dimensions. This will pave the way for describing the wave functions for the hydrogen atom in Chapter 41. The hydrogen-atom wave functions 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 Particle in a Box

In this chapter we want to learn how to use the Schrödinger equation to determine the possible energy levels and the corresponding wave functions for various systems. As in Chapter 39, we refer to the states of definite energy as *stationary states.* For simplicity, we begin with problems in which the particle can move

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20.2 Particle in a Box

only along the x-axis. From Section 39.5, the Schrödinger equation for such one-dimensional problems is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x) \qquad \text{(one-dimensional Schrödinger equation)} \qquad (40.1)$$

This equation is really a statement that the kinetic energy [represented by the term $-(\hbar^2/2m)d^2\psi(x)/dx^2$] plus the potential energy [represented by the term $U(x)\psi(x)$] is equal to the total energy [represented by the term $E\psi(x)$]. The fundamental problem is then the following: 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 39.5 we solved this problem for the case $U(x) = 0$, corresponding to a *free* particle. The allowed wave functions and corresponding energies are

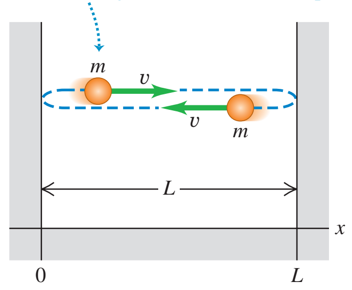
$$\psi(x) = Ae^{ikx} \qquad E = \frac{\hbar^2k^2}{2m} \qquad \text{(free particle)} \qquad (40.2)$$

The wave number k is equal to $2\pi/\lambda$, where λ 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. 40.1). 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. 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. The potential-energy function is graphed in Fig. 40.2.

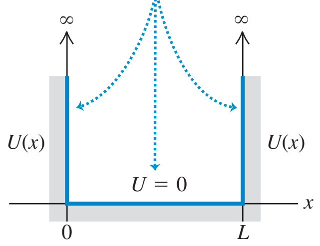
40.1 The Newtonian view of a particle in a box.

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



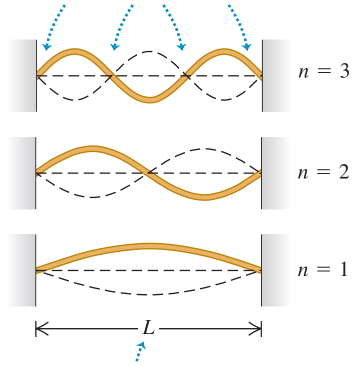
40.2 The potential-energy function for a particle in a box.

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



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

Each end is a node, and there are $n - 1$ additional nodes between the ends.



The length is an integral number of half-wavelengths: $L = n\lambda_n/2$.

Wave Function for a Particle in a Box

To solve the Schrödinger equation for this system, we begin with some restrictions on the particle's wave function $\psi(x)$. Because the particle is confined to the region $0 \le x \le L$, we expect $\psi(x)$ to be zero outside that region. This agrees with the Schrödinger equation: If the term $U(x)\psi(x)$ in Eq. (40.1) 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. If it is, then $\psi(x)$ must be zero at the region's boundary, $x = 0$ and $x = L$. These two conditions serve as *boundary conditions* for the 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. 40.3); you should review that discussion.

An additional condition is that to calculate the second derivative $d^2\psi(x)/dx^2$ in Eq. (40.1), 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. 40.3, cannot have a kink 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 $0 \le x \le L$ subject to the above conditions. In this region $U(x) = 0$, so the wave function in this region must satisfy

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \qquad \text{(particle in a box)} \qquad (40.3)$$

Equation (40.3) 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. (40.2). 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. (40.2) 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 39.6 (Section 39.5), in which we found that a more general stationary-state solution to the Schrödinger equation with $U(x) = 0$ is

$$\psi(x) = A_1e^{ikx} + A_2e^{-ikx} \qquad (40.4)$$

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 the situation for standing waves on a string (Fig. 40.3), 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. (40.4) is $E = \hbar^2k^2/2m$, just as for a single wave.

To see whether the wave function given by Eq. (40.4) can satisfy the boundary conditions, let's first rewrite it in terms of sines and cosines using Euler's formula, Eq. (39.15):

$$\begin{aligned}\psi(x) &= A_1(\cos kx + i\sin kx) + A_2[\cos(-kx) + i\sin(-kx)]\\ &= A_1(\cos kx + i\sin kx) + A_2(\cos kx - i\sin kx) \qquad (40.5)\\ &= (A_1 + A_2)\cos kx + i(A_1 - A_2)\sin kx\end{aligned}$$

At $x = 0$ this is equal to $\psi(0) = A_1 + A_2$, which must equal zero if we are to satisfy the boundary condition at that point. Hence $A_2 = -A_1$, and Eq. (40.5) becomes

$$\psi(x) = 2iA_1\sin kx = C\sin kx \qquad (40.6)$$

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. (40.6) does give the stationary-state wave functions for a particle in a box in the region $0 \le x \le L$. (Outside this region, $\psi(x) = 0$.) The possible values of k and the wavelength $\lambda = 2\pi/k$ are

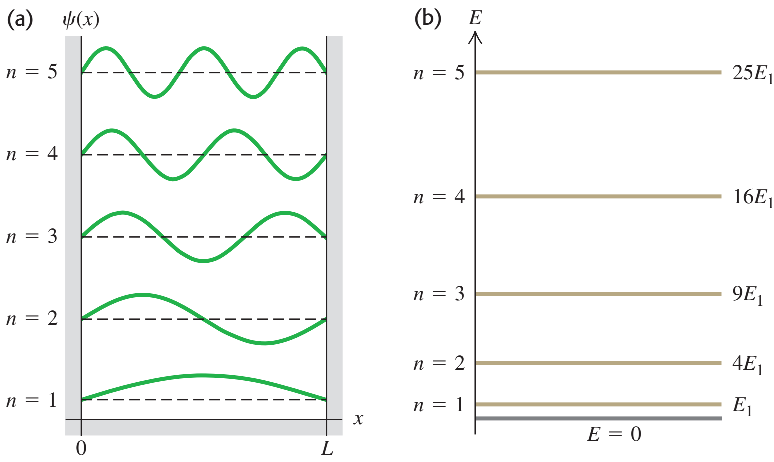
$$k = \frac{n\pi}{L} \quad \text{and} \quad \lambda = \frac{2\pi}{k} = \frac{2L}{n} \qquad (n = 1, 2, 3, \dots) \qquad (40.7)$$

Just as for the string in Fig. 40.3, 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 are given by $E = \hbar^2k^2/2m = p^2/2m$, 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 λ. This makes sense, since inside the region $0 \le x \le L$ the potential energy is zero and the energy is all kinetic. For each value of n there are corresponding values of p, λ, and E; let's call them p_n, λ_n, and E_n. Putting the pieces together, we get

$$p_n = \frac{h}{\lambda_n} = \frac{nh}{2L} \qquad (40.8)$$



40.4 (a) Wave functions for a particle in a box, with $n = 1, 2, 3, 4$, and 5. Each of the horizontal dashed lines represents $\psi = 0$ for the respective wave function. The five graphs have been displaced vertically for clarity, as in Fig. 40.3. (b) Energy-level diagram for a particle in a box. Each energy is n^2E_1, where E_1 is the ground-level energy.

and

$$E_n = \frac{p_n^2}{2m} = \frac{n^2h^2}{8mL^2} = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad (n = 1, 2, 3 \ldots) \qquad \text{(energy levels, particle in a box)} \qquad (40.9)$$

These are the possible energy levels for a particle in a box. Each energy level has its own value of the quantum number n and a corresponding wave function, which we denote by ψ_n. When we replace k in Eq. (40.6) by $n\pi/L$ from Eq. (40.7), we find

$$\psi_n(x) = C\sin\frac{n\pi x}{L} \qquad (n = 1, 2, 3 \ldots) \qquad (40.10)$$

Figure 40.4a 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 (Fig. 40.3). Figure 40.4b shows the energy-level diagram for this system. The levels of successively higher energies, proportional to n^2, 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.

CAUTION **Zero energy is not permitted** Note that the energy of a particle in a box *cannot* be zero. Equation (40.9) shows that $E = 0$ would require $n = 0$, but substituting $n = 0$ into Eq. (40.10) gives a zero wave function. Since a particle is described by a nonzero wave function, this means that there cannot be a particle with $E = 0$.

Example 40.1 Electron in an atom-size box

Find the lowest energy level for a particle in a box if the particle is an electron in a box 5.0×10^{-10} m across, or a little bigger than an atom.

SOLUTION

IDENTIFY: This problem uses what we have learned in this section about a particle in a box.

SET UP: The lowest energy level (that is, the ground level) corresponds to $n = 1$ in Eq. (40.9).

EXECUTE: From Eq. (40.9),

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

EVALUATE: A particle trapped in a box is rather different from an electron bound in an atom, but it is reassuring that this energy is of the same order of magnitude as actual atomic energy levels.

You should be able to show that replacing the electron with a proton or a neutron $(m = 1.67 \times 10^{-27}\ \text{kg})$ in a box the width of a medium-sized nucleus $(L = 1.1 \times 10^{-14}\ \text{m})$ gives $E_1 = 1.7$ MeV. This shows us that the energies for particles in the nucleus are about a million times greater than the energies of electrons in atoms, giving us a clue as to why each nuclear fission and fusion reaction provides so much more energy than each chemical reaction.

If you repeat this calculation for a billiard ball $(m = 0.2\ \text{kg})$ bouncing back and forth between the cushions of a frictionless, perfectly elastic billiard table $(L = 1.5\ \text{m})$, you'll find the separation between energy levels to be as small as 4×10^{-67} J (See Exercise 40.1). This negligible value shows that quantum effects won't have much effect on your billiard game.

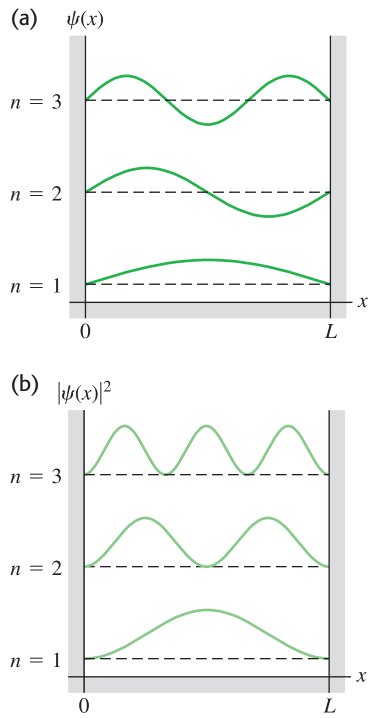
Probability and Normalization

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 ψ that we discussed in Section 39.5. 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,

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

Both $\psi(x)$ and $|\psi(x)|^2$ are plotted in Fig. 40.5 for $n = 1, 2$, and 3. We note that not all positions are equally likely. This is in contrast to the situation in classical mechanics, in which all positions between $x = 0$ and $x = L$ are equally likely. We see in Fig. 40.5b that $|\psi(x)|^2 = 0$ at some points, so the probability is zero of finding the particle exactly at 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 $x = L$, not to be exactly at some particular value of x.

40.5 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.



We know that the particle must be *somewhere* in the universe—that is, 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 is,

$$\int_{-\infty}^{\infty} |\psi(x)|^2\,dx = 1 \qquad \text{(normalization condition)} \qquad (40.11)$$

A wave function is said to be *normalized* if it has a constant such as C in Eq. (40.10) that is calculated to make the total probability equal 1 in Eq. (40.11). The process of determining the constant is called **normalization,** as we mentioned in Section 39.5. Why bother with normalization? Because for a normalized wave function, $|\psi(x)|^2\,dx$ is not merely proportional to, but *equals,* the probability of finding the particle in dx. Recall from Section 39.5 that we call $|\psi(x)|^2$ the *probability distribution function.*

Now let's normalize the wave function $\psi(x)$ given by Eq. (40.10) for the particle in a box. Since $\psi(x)$ is zero except between $x = 0$ and $x = L$, Eq. (40.11) becomes

$$\int_0^L C^2\sin^2\frac{n\pi x}{L}\,dx = 1 \qquad (40.12)$$

You can evaluate this integral using the trigonometric identity $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$; the result is $C^2L/2$. Thus our probability interpretation of the wave function demands that $C^2L/2 = 1$, 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

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \qquad (n = 1, 2, 3, \ldots) \qquad \text{(particle in a box)} \qquad (40.13)$$

Next, let's check whether our results for the particle in a box are consistent with the uncertainty principle. We can write the position of the particle as $x = L/2 \pm L/2$, so we can estimate the uncertainty in position as $\Delta x \approx L/2$. From Eq. (40.8) the magnitude of momentum in state n is $p_n = nh/2L$. A reasonable estimate of the momentum uncertainty is the difference in momentum of two levels that differ by 1 in their n values, that is, $\Delta p_x \approx h/2L$. Then the product $\Delta x\,\Delta p_x$ is

$$\Delta x\,\Delta p_x = \frac{h}{4}$$

This is consistent with the uncertainty principle, Eq. (39.11), $\Delta x\,\Delta p_x \geq \hbar = h/2\pi$, in which the uncertainties were more precisely defined as standard deviations.

Example 40.2 A nonsinusoidal wave function?

(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?

SOLUTION

IDENTIFY: This problem uses the idea that any physically reasonable wave function must satisfy both the Schrödinger equation and the appropriate boundary conditions.

SET UP: In part (a) we substitute $\psi(x)$ into the Schrödinger equation for a particle in a box, Eq. (40.3), to determine whether it is a solution. In part (b) we demand that $\psi(x)$ be equal to zero at $x = 0$ and at $x = L$.

EXECUTE: (a) From Eq. (40.3), the Schrödinger equation for this situation is $-(\hbar^2/2m)\,d^2\psi(x)/dx^2 = E\psi(x)$. 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. Since we assume $E = 0$, the right side of the equation is also zero. Since $0 = 0$, $\psi(x) = Ax + B$ 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 $\psi(0) = B$, so the constant B must be zero and $\psi(x) = Ax$. Applying the boundary condition at $x = L$ gives $\psi(L) = AL = 0$, so the constant A must also be zero. Thus the wave function equals zero inside the box as well as outside the box, and there is *zero* probability of finding the particle anywhere with this wave function. Hence $\psi(x) = Ax + B$ is not a physically valid wave function.

EVALUATE: The moral of this story 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 boundary conditions.

Time Dependence

Finally, we note that the wave functions $\psi_n(x)$ in Eq. (40.13) depend only on the *spatial* coordinate x. From Section 39.5, the full wave function also depends on *time*. Equation (39.14) shows that if $\psi(x)$ is the wave function for a state of definite energy E, the full time-dependent wave function $\Psi(x, t)$ is

$$\Psi(x, t) = \psi(x)\, e^{-iEt/\hbar} \qquad \text{(time-dependent wave function for a stationary state)} \qquad (40.14)$$

From Eq. (40.12), it follows that the time-dependent wave functions for a particle in a box are

$$\Psi(x, t) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)e^{-iE_n t/\hbar} \qquad (n = 1, 2, 3, \dots) \qquad (40.15)$$

In this expression the energies E_n are given by Eq. (40.9).

The absolute value of $e^{-iEt/\hbar}$ is unity: $|e^{-iEt/\hbar}|^2 = e^{+iEt/\hbar}e^{-iEt/\hbar} = e^0 = 1$. Hence $|\Psi(x, t)|^2$ is equal to $|\psi(x)|^2$, and the probability distribution function does not depend on time. We saw in Section 39.5 that this is the origin of the term *stationary state* for a state of definite energy. So in calculations with states that have definite energy, we are justified in omitting the time factor. We'll be concerned mostly with stationary states in our applications of quantum mechanics.

Test Your Understanding of Section 40.1 If a particle in a box is in the nth 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.

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20.1 Potential Energy Diagrams
20.2 Potential Wells

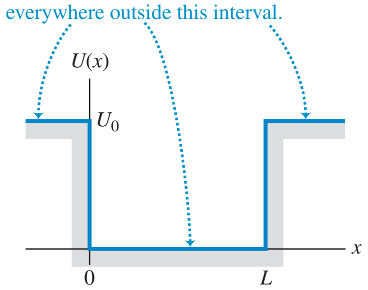
40.2 Potential Wells

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 13. 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. This function corresponds to a few situations found in nature, as mentioned in Section 40.1, but the correspondence is only approximate.

A potential well that serves as a better approximation to several actual physical situations is a well with straight sides but *finite* height. Figure 40.6 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 38.2 in connection with the photoelectric effect. In a three-dimensional application a spherical version of a potential well can be used to approximately describe the motions of protons and neutrons within a nucleus.

40.6 A square-well potential.

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



Bound States of a Square-Well Potential

In Newtonian mechanics, the particle is trapped (localized) in a well if the total 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, but if E is greater than U_0 for a finite well, the particle is *not* bound.

For a finite square well, let's consider bound-state solutions of the Schrödinger equation, corresponding to $E < U_0$. The easiest approach is to consider separately the regions where $U = 0$ and where $U = U_0$. Where $U = 0$, the Schrödinger equation reduces to Eq. (40.3). Rearranging this equation, we find

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) \qquad (40.16)$$

From Eq. (40.5), we can express the solutions of this equation as combinations of $\cos kx$ and $\sin kx$, where $E = \hbar^2k^2/2m$ and so $k = \sqrt{2mE}/\hbar$. Hence inside the square well $(0 \leq x \leq L)$ we have

$$\psi(x) = A\cos\frac{\sqrt{2mE}}{\hbar}x + B\sin\frac{\sqrt{2mE}}{\hbar}x \qquad \text{(inside the well)} \qquad (40.17)$$

where A and B are constants. So far, this looks a lot like the particle-in-a-box analysis in Section 40.1.

In the regions $x < 0$ and $x > L$ we use Eq. (40.1)with $U = U_0$. Rearranging, we get

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m(U_0 - E)}{\hbar^2}\psi(x) \qquad (40.18)$$

The quantity $U_0 - E$ is positive, so the solutions of this equation are exponential. Using κ (the Greek letter kappa) as positive in the abbreviation $\kappa = [2m(U_0 - E)]^{1/2}/\hbar$, we can write the solutions as

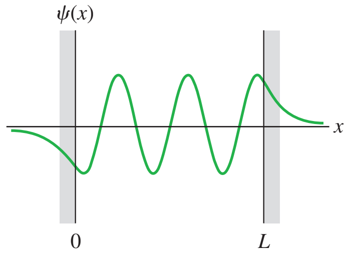
$$\psi(x) = Ce^{\kappa x} + De^{-\kappa x} \qquad \text{(outside the well)} \qquad (40.19)$$

where C and D are constants with different values in the $x < 0$ and $x > L$ regions.

We see that the bound-state wave functions for this system are sinusoidal inside the well and exponential outside it. We have to use the positive exponent in the $x < 0$ region and the negative exponent in the $x > L$ region. That is, $D = 0$ for $x < 0$ and $C = 0$ for $x > L$. Without this choice of constants, ψ would approach infinity as $|x|$ approached infinity, and the normalization condition, Eq. (40.11), could not be satisfied. We also have to match the wave functions so that they satisfy the boundary conditions that we mentioned in Section 40.1: $\psi(x)$ 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. But that would violate the Schrödinger equation, which says that at every point, $d^2\psi(x)/dx^2$ is proportional to $U - E$. In our situation, $U - E$ 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 40.7 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, despite the fact that in classical mechanics this is impossible. This penetration into classically forbidden regions is a quantum effect that has no classical analog for particles. We will discuss an amazing result of this effect in Section 40.3.

40.7 A possible wave function for a particle in a finite potential well. The function is sinusoidal inside the well ($0 \le x \le L$) 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 40.3 Well versus box

Show that Eq. (40.19), $\psi(x) = Ce^{\kappa x} + De^{-\kappa x}$, is consistent with the corresponding particle-in-a-box wave function.

SOLUTION

IDENTIFY: Equation (40.19) gives the possible wave functions outside the potential well. Since the wave function outside the box (an infinite potential well) equals zero, we must show that $\psi(x) = Ce^{\kappa x} + De^{-\kappa x}$ approaches zero for both $x < 0$ and $x > L$ as the depth of the potential well (U_0) approaches infinity.

SET UP: We use our knowledge of the exponential function and the definition of the quantity κ in Eq. (40.19): $\kappa = [2m(U_0 - E)]^{1/2}/\hbar$.

EXECUTE: As U_0 approaches infinity, κ also approaches infinity. In the region $x < 0$, the wave function is $\psi(x) = Ce^{\kappa x}$; as $\kappa \to \infty$, $\kappa x \to -\infty$ and $e^{\kappa x} \to 0$, so the wave function approaches zero for all $x < 0$. In the region $x > L$, the wave function is $\psi(x) = De^{-\kappa x}$; as $\kappa \to \infty$, $-\kappa x \to -\infty$ and $e^{-\kappa x} \to 0$, so the wave function also approaches zero for all $x > L$.

EVALUATE: In Section 40.1 we *assumed* $\psi(x) = 0$ outside the box. This analysis validates our assumption.

In our study of mechanics, we often considered limiting cases to check our results (see Examples 5.11 and 5.13 in Section 5.2). This example shows that this technique is also useful for problems in quantum mechanics, as it is for problems in all branches of physics.

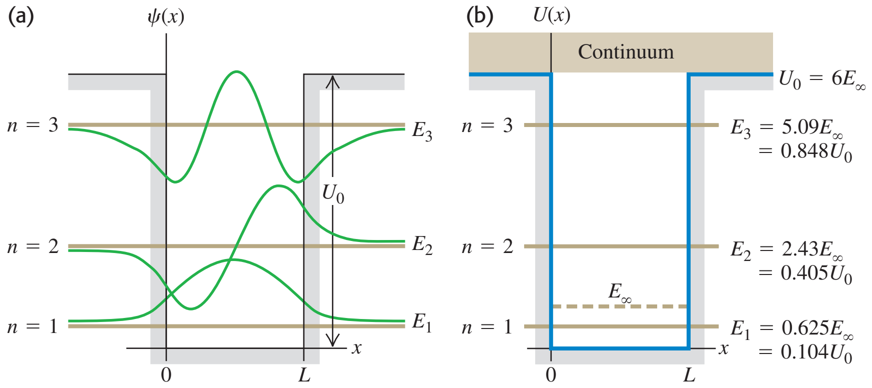
Comparing Finite and Infinite Square Wells

Let's continue the comparison of the finite-depth potential well with the infinitely deep well that we began in Example 40.3. First, because the wave functions for the finite well aren't 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. From $p = h/\lambda$ this increase in λ corresponds to a reduced magnitude of momentum 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.

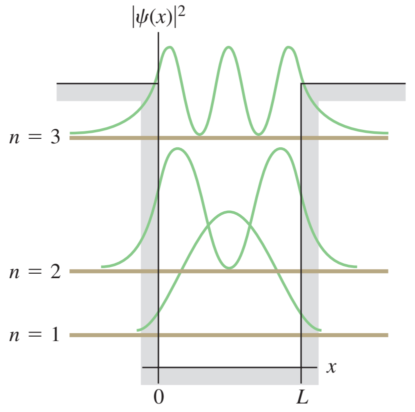
Second, a well with finite depth U_0 has only a *finite* number of bound states and corresponding energy levels, compared to the *infinite* number for an infinitely deep well. How many levels there are depends on the magnitude of U_0 in comparison with the ground-level energy for the infinite well, which we call E_∞. From Eq. (40.9),

$$E_\infty = \frac{\pi^2\hbar^2}{2mL^2} \tag{40.20}$$

40.8 (a) Wave functions for the three bound states for a particle in a finite potential well with depth U_0, for the case $U_0 = 6E_\infty$. 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. (b) Energy-level diagram for this system. The energies are expressed both as multiples of E_∞ and as fractions of U_0. All energies greater than U_0 are possible; states with $E > U_0$ form a continuum.



40.9 Probability distribution functions $|\psi(x)|^2$ for the square-well wave functions shown in Fig. 40.8. The horizontal brown line for each wave function corresponds to $|\psi|^2 = 0$.



When U_0 is *much larger* than E_∞ (a very deep well), 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_∞, there are only a few bound states. (But 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 40.8 shows the particular case in which $U_0 = 6E_\infty$; for this case there are three bound states. The energy levels are expressed both as fractions of the well depth U_0 and as multiples of E_∞. Note that if the well were infinitely deep, the lowest three levels, as given by Eq. (40.9), would be E_∞, $4E_\infty$, and $9E_\infty$. The wave functions for the three bound states are also shown.

It turns out that when U_0 is less than E_∞, there is only one bound state. In the limit when U_0 is *much smaller* than E_∞ (a very shallow or very narrow well), the energy of this single state is approximately $E = 0.68U_0$.

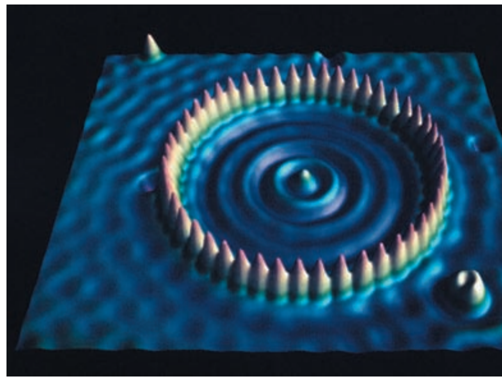
Figure 40.9 shows graphs of the probability distributions—that is, the values of $|\psi|^2$,—for the wave functions shown in Fig. 40.8a. As with the infinite well, not all positions are equally likely. We have already commented on the possibility of finding the particle outside the well, in the classically forbidden regions.

There are also states for which E is *greater than* U_0. In this case the particle is not bound but is free to move through all values of x. Thus *any* energy E greater than U_0 is possible. These free-particle states thus 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 in the well than outside it.

The square-well potential described in this section has a number of practical applications. We mentioned earlier the example of an electron inside a metallic sheet. A three-dimensional version, in which U is zero inside a spherical region with radius R and has the value U_0 outside, provides a simple model to represent the interaction of a neutron with a nucleus in neutron-scattering experiments. In this context the model is called the *crystal-ball model* of the nucleus, because neutrons interacting with such a potential are scattered in a way that's analogous to scattering of light by a crystal ball.

Figure 40.10 shows a graphic demonstration of particles in a *two*-dimensional finite potential well, and Example 40.4 describes another application of the square-well potential.

40.10 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, to be discussed in Section 40.3.)



Example 40.4 Electron in a square well

An electron is trapped in a square well with a width of 0.50 nm (comparable to a few atomic diameters). (a) Find the ground-level energy if the well is infinitely deep. (b) If the actual well depth is six times the ground-level energy found in part (a), find the energy levels. (c) If the atom makes a transition from a state with energy E_2 to a state with energy E_1 by emitting a photon, find the wavelength of the photon. In what region of the electromagnetic spectrum does the photon lie? (d) If the electron is initially in its ground level and absorbs a photon, what is the minimum energy the photon must have to liberate the electron from the well? In what region of the spectrum does the photon lie?

SOLUTION

IDENTIFY: We use the ideas of a particle in a box and a square well. 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.

SET UP: We use Eq. (40.20) to find the ground-level energy E_∞ for an infinitely deep well. The energies for a square well with $U_0 = 6E_\infty$. are shown in Fig. 40.8b. The photon wavelength is given by the relationship $E = hf = hc/\lambda$ [Eq. (38.8)].

EXECUTE: (a) From Eq. (40.20),

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

(b) We are given $U_0 = 6E_\infty$, so $U_0 = 6(1.5\ \text{eV}) = 9.0\ \text{eV}$. We can simply read off the energy levels from Fig. 40.8b. Our answers are

$$E_1 = 0.104U_0 = 0.104(9.0\ \text{eV}) = 0.94\ \text{eV}$$
$$E_2 = 0.405U_0 = 0.405(9.0\ \text{eV}) = 3.6\ \text{eV}$$
$$E_3 = 0.848U_0 = 0.848(9.0\ \text{eV}) = 7.6\ \text{eV}$$

Alternatively,

$$E_1 = 0.625E_\infty = 0.625(1.5\ \text{eV}) = 0.94\ \text{eV}$$
$$E_2 = 2.43E_\infty = 2.43(1.5\ \text{eV}) = 3.6\ \text{eV}$$
$$E_3 = 5.09E_\infty = 5.09(1.5\ \text{eV}) = 7.6\ \text{eV}$$

(c) The photon energy is

$$E_2 - E_1 = 3.6\ \text{eV} - 0.94\ \text{eV} = 2.7\ \text{eV}$$

We determine the wavelength from $E = hf = hc/\lambda$:

$$\lambda = \frac{hc}{E} = \frac{(4.136 \times 10^{-15}\ \text{eV}\cdot\text{s})(3.00 \times 10^{8}\ \text{m/s})}{2.7\ \text{eV}} = 460\ \text{nm}$$

This photon is in the blue region of the visible spectrum.

(d) We see from Fig. 40.8b that the minimum energy needed to lift the electron out of the well from its $n = 1$ ground level is the well depth $(U_0 = 9.0\ \text{eV})$ minus the electron's initial energy $(E_1 = 0.94\ \text{eV})$, or 8.1 eV. Since 8.1 eV is three times the 2.7-eV photon energy of part (c), the corresponding photon wavelength is one-third of 460 nm, or 150 nm, which is in the ultraviolet region of the spectrum.

EVALUATE: To check our results for the energies of the three bound states, note that if the well had been infinitely deep, the energies would have been

$$E_1 = E_\infty = 1.5\ \text{eV}$$
$$E_2 = 4E_\infty = 6.0\ \text{eV}$$
$$E_3 = 9E_\infty = 13.5\ \text{eV}$$

The energies we found in part (b) are less than these values. This makes sense: 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 to *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 with a 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 like 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, from $n = 3$ to $n = 2$ and from $n = 2$ to $n = 1$), one of the steps will involve emitting a visible-light photon as we have calculated here. (We described this process of *fluorescence* in Section 38.3.) Increasing the value of L decreases the energies of the levels and hence the spacing between them, and hence 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 of which emits a characteristic wavelength depending 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.

Test Your Understanding of Section 40.2 Suppose that the width of the finite potential well shown in Fig. 40.8 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. 40.8b? (i) U_0 must increase by a factor of 4; (ii) U_0 must increase by a factor of 2; (iii) U_0 must remain the same; (iv) U_0 must decrease by a factor of $\frac{1}{2}$; (v) U_0 must decrease by a factor of $\frac{1}{4}$.

40.3 Potential Barriers and Tunneling

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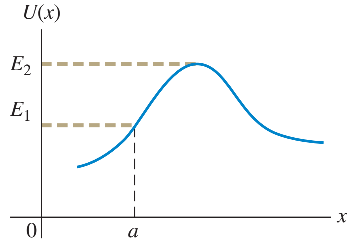
20.4 Potential Barriers

A **potential barrier** is the opposite of a potential well; it is a potential-energy function with a *maximum.* Figure 40.11 shows an example. In Newtonian mechanics, if the total energy is E_1, a particle that is initially to the left of the barrier must remain to the left of the point $x = a$. If it were to move to the right of this point, the potential energy U would be greater than the total energy E. Because $K = E - U$, the kinetic energy would be negative, and this is impossible since a negative value of $K = \frac{1}{2}mv^2$ would require negative mass or imaginary speed.

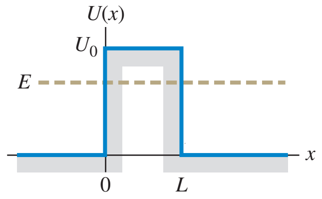


40.11 A potential-energy barrier. According to Newtonian mechanics, if the total energy is E_1, a particle that is on the left side of the barrier can go no farther than $x = a$. If the total energy is greater than E_2, the particle can pass the barrier.

If the total energy is greater than E_2, the particle can get past the barrier. A roller-coaster car can surmount a hill if it has enough kinetic energy at the bottom. If it doesn't, it stops partway up and then rolls back down.

Quantum mechanics supplies us with a peculiar and very interesting phenomenon in connection with potential barriers. A particle that encounters such a barrier is not necessarily turned back; there is some probability for it to emerge on the other side, even when it doesn't have enough kinetic energy to surmount the barrier according to Newtonian mechanics. This penetration of a barrier is called **tunneling.** It's a natural name; if you dig a tunnel through a hill, you don't have to go over the top. However, in quantum-mechanical tunneling, the particle does not actually bore a hole through the barrier and it loses no energy in the tunneling process.

Tunneling Through a Rectangular Barrier



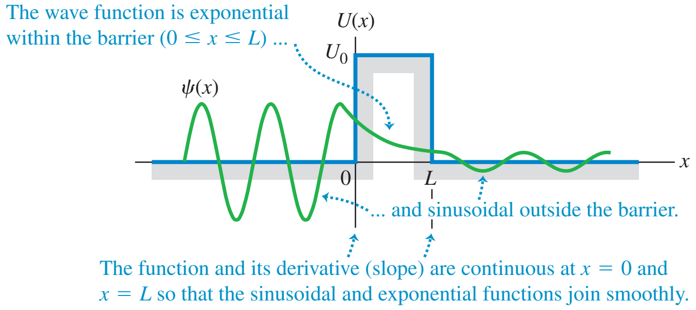
40.12 A rectangular potential-energy barrier with width L and height U_0. According to Newtonian mechanics, if the total energy E is less than U_0, a particle cannot pass over this barrier but is confined to the side where it starts.

To understand how tunneling can occur, let's look at the potential-energy function $U(x)$ shown in Fig. 40.12. It's like Fig. 40.6 turned upside-down; the potential energy is zero everywhere except in the range $0 \le x \le L$, where it has the value U_0. This might represent a simple model for an electron and two slabs of metal separated by an air gap of thickness L. We let the potential energy be zero within either slab but equal to U_0 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 40.2. In the regions $x < 0$ and $x > L$ the solution is sinusoidal and given by Eq. (40.17). Within the barrier $(0 \le x \le L)$ the solution is exponential, as in Eq. (40.19). Just as with the finite potential well, the functions have to join smoothly at the boundary points $x = 0$ and $x = L$. That is, the function and its derivative have to be continuous at these points.

These requirements lead to a wave function like the one shown in Fig. 40.13. 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 a probability? That depends on the width L of the barrier and the particle's energy E (all kinetic) in comparison with the barrier height U_0. The probability T that the particle gets through the barrier is proportional to the square of the ratio of the amplitudes of 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

$$T = Ge^{-2\kappa L} \quad \text{where} \quad G = 16\frac{E}{U_0}\left(1 - \frac{E}{U_0}\right) \quad \text{and} \quad \kappa = \frac{\sqrt{2m(U_0 - E)}}{\hbar}$$
$$\text{(probability of tunneling)} \qquad (40.21)$$



40.13 A possible wave function for a particle tunneling through the potential-energy barrier shown in Fig. 40.12.

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

Example 40.5 Tunneling through a barrier

A 2.0-eV electron encounters a barrier with height 5.0 eV. 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 (roughly ten and five atomic diameters, respectively)?

SOLUTION

IDENTIFY: This problem uses the ideas of tunneling through a rectangular barrier like that shown in Figs. 40.12 and 40.13.

SET UP: Our target variable is the tunneling probability T in Eq. (40.21), which we evaluate for the given values $E = 2.0\ \text{eV}$ (electron energy), $U = 5.0\ \text{eV}$ (barrier height), $m = 9.11 \times 10^{-31}\ \text{kg}$ (mass of the electron), and $L = 1.00\ \text{nm}$ or $0.50\ \text{nm}$ (barrier width).

EXECUTE: First we evaluate G and κ in Eq. (40.21), using $E = K = 2.0\ \text{eV}$:

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

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

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

(Note that the eV energy units canceled in calculating G, but we had to convert eV to $\text{J} = \text{kg}\cdot\text{m}^2/\text{s}^2$ to find κ in m^{-1}.)

(a) When $L = 1.00\ \text{nm} = 1.00 \times 10^{-9}\ \text{m}$, $2\kappa L = 2(8.9 \times 10^{9}\ \text{m}^{-1}) \times (1.00 \times 10^{-9}\ \text{m}) = 17.8$, and

$$T = Ge^{-2\kappa L} = 3.8e^{-17.8} = 7.1 \times 10^{-8}$$

(b) When $L = 0.50\ \text{nm}$, half of 1.00 nm, $2\kappa L$ is half of 17.8, or 8.9, and

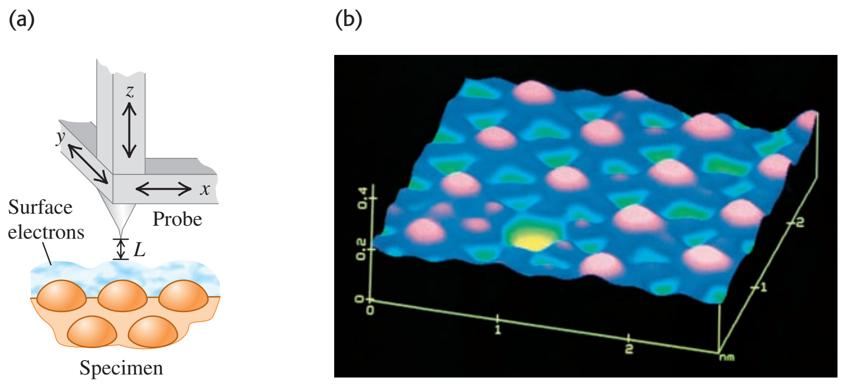
$$T = 3.8e^{-8.9} = 5.2 \times 10^{-4}$$

EVALUATE: Halving the width of this barrier increases the tunneling probability by a factor of nearly ten thousand.

Applications of Tunneling

Tunneling is significant in many areas of physics, including some with considerable practical importance. For example, 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. The *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. The *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.

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. 40.14a).

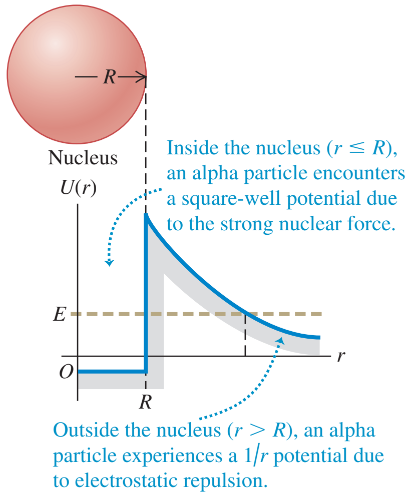


40.14 (a) Schematic diagram of the probe of a scanning tunneling microscope (STM). As the sharp conducting probe is scanned across the surface in the x- and y-directions, it is also moved in the z-direction to maintain a constant tunneling current. The changing position of the probe is recorded and used to construct an image of the surface. (b) This colored STM image shows sodium atoms (pink) adsorbed on a platinum surface. The yellow spot indicates a missing atom.

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 40.5 shows, the tunneling probability and hence the tunneling current depend strongly on 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 and at the same time is moved perpendicular to the surface to maintain a constant tunneling current. The needle motion is recorded, and 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 40.14b shows an image of sodium atoms on the surface of a platinum crystal. (Figure 40.10 is also an STM image.)

Tunneling is 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 also involves tunneling. An alpha particle at the surface of 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. 40.15). The alpha particle tunnels through this barrier. Because the tunneling probability depends so critically on the barrier height and width, the lifetimes of alpha-emitting nuclei vary over an extremely wide range. We'll return to alpha decay in Chapter 43.

40.15 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.



Inside the nucleus ($r \leq R$), an alpha particle encounters a square-well potential due to the strong nuclear force.

Outside the nucleus ($r > R$), an alpha particle experiences a $1/r$ potential due to electrostatic repulsion.

Test Your Understanding of Section 40.3 Is it possible for a particle undergoing tunneling to be found *within* the barrier rather than on either side of it?

40.4 The Harmonic Oscillator

In Newtonian mechanics a **harmonic oscillator** is a particle with mass m acted on by a conservative force component $F_x = -k'x$. (In this discussion we will use k' for the *force constant* to minimize confusion with the wave number $k = 2\pi/\lambda$.) This force component 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. 40.16). When the particle is displaced from equilibrium, it undergoes sinusoidal motion with angular frequency $\omega = (k'/m)^{1/2}$. We studied this system in detail in Chapter 13; you should review that discussion.

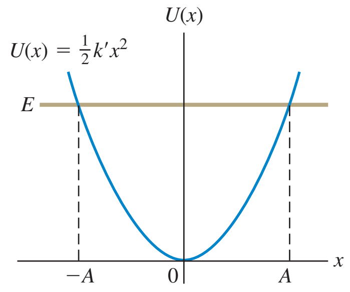
A quantum-mechanical analysis of the harmonic oscillator using the Schrödinger equation is an interesting and useful study. The solutions provide insight into vibrations of molecules, the quantum theory of heat capacities, atomic vibrations in crystalline solids, and many other situations.

Before we get into the details, let's make an enlightened guess about the energy levels. The energy E of a *photon* is related to its angular frequency ω by $E = hf = (h/2\pi)(\omega/2\pi) = \hbar\omega$. The harmonic oscillator has a characteristic angular frequency ω, at least in Newtonian mechanics. So a reasonable guess would be that in the quantum-mechanical analysis the energy levels of a harmonic oscillator would be multiples of the quantity

$$\hbar\omega = \hbar\sqrt{\frac{k'}{m}}$$

These are the energy levels that Planck assumed in deriving his radiation law (see Section 38.8). It was a good assumption; the energy levels are in fact half-integer $\left(\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots\right)$ multiples of $\hbar\omega$.

40.16 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 $x = A$.



For the harmonic oscillator we write $\frac{1}{2}k'x^2$ in place of U in the one-dimensional Schrödinger equation, Eq. (40.1):

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}k'x^2\psi = E\psi \qquad \text{(Schrödinger equation for the harmonic oscillator)} \qquad (40.22)$$

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

Wave Functions, Boundary Conditions, and Energy Levels

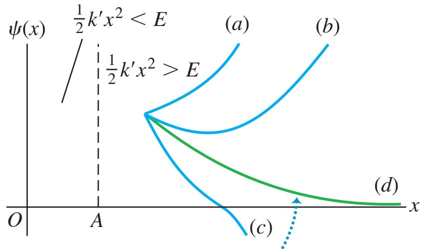
In the discussion of square-well potentials in Section 40.2 we found that the energy levels are determined by boundary conditions at the walls of the well. However, the harmonic-oscillator potential has no walls as such; what, then, are the appropriate boundary conditions? Classically, $|x|$ cannot be greater than the amplitude A, which is the maximum displacement from equilibrium. 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.

Satisfying the requirement that $\psi(x) \to 0$ as $|x| \to \infty$ is not as trivial as it may seem. Suppose we compute solutions of Eq. (40.22) *numerically.* We start at some point x, choosing values of $\psi(x)$ and $d\psi(x)/dx$ at that point. Using the Schrödinger equation to evaluate $d^2\psi(x)/dx^2$ at the point, we can compute $\psi(x)$ and $d\psi(x)/dx$ at a neighboring point $x + \Delta x$, and so on. By using a computer to iterate this process many times with sufficiently small steps Δx, we can compute the wave function with great precision. There is no guarantee, however, that a function obtained in this way will approach zero at large x. To see what kinds of trouble we can get into, let's rewrite Eq. (40.22) in the form

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2}\left(\frac{1}{2}k'x^2 - E\right)\psi(x) \qquad (40.23)$$

In this form, the equation shows that when x is large enough (either positive or negative) to make the quantity $\left(\frac{1}{2}k'x^2 - E\right)$ positive, the function $\psi(x)$ and its second derivative $d^2\psi(x)/dx^2$ have the same sign.

40.17 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.

The second derivative of $\psi(x)$ is the rate of change of the *slope* of $\psi(x)$. Consider a point with $x > A$ for which $\frac{1}{2}k'x^2 - E > 0$. If $\psi(x)$ is positive, so is $d^2\psi(x)/dx^2$ and the function is *concave upward.* Figure 40.17 shows four possible kinds of behavior beginning at a point $x > A$. If the slope is initially positive, the function curves upward more and more steeply (curve a) and goes to infinity. If the slope is initially negative at the point, there are three possibilities. If the slope changes too quickly (curve b), the curve bends up and again goes to infinity. If the slope doesn't change quickly enough, the curve bends down and crosses the x-axis. After it has crossed, $\psi(x)$ and $d^2\psi(x)/dx^2$ are both negative (curve c) and the concave-downward curve heads for *negative* infinity. Between these infinities is the chance that the curve may bend just enough to glide in asymptotically to the x-axis (curve d). In this case, $\psi(x)$, $d\psi(x)/dx$, and $d^2\psi(x)/dx^2$ all approach zero at large x; in this possibility lies the only hope of satisfying the boundary condition that $\psi(x) \to 0$ as $|x| \to \infty$, and it occurs only for certain very special values of the constant E.

This qualitative discussion offers some insight into how the boundary conditions for this problem determine the possible energy levels. Equation (40.22) can also be solved exactly. The solutions, although not encountered in elementary calculus courses, are well known to mathematicians; they are called *Hermite functions.* Each one is an exponential function multiplied by a polynomial in x. The state with lowest energy (the ground level) has the wave function

$$\psi(x) = Ce^{-\sqrt{mk'}\,x^2/2\hbar} \qquad (40.24)$$

The constant C is chosen to normalize the function—that is, to make $\int_{-\infty}^{\infty}|\psi|^2\,dx = 1$. You can find C using, from integral tables,

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

The corresponding energy, which we'll call E_0, is the ground-state energy; it is

$$E_0 = \frac{1}{2}\hbar\omega = \frac{1}{2}\hbar\sqrt{\frac{k'}{m}} \qquad (40.25)$$

You may not believe that Eq. (40.24) really *is* a solution of Eq. (40.22) (the Schrödinger equation for the harmonic oscillator) with the energy given by Eq. (40.25). We invite you to calculate the second derivative of Eq. (40.24), substitute it into Eq. (40.22), and verify that it really is a solution if Eq. (40.25) gives E_0 (see exercise 40.28). It's a little messy, but the result is satisfying and worth the effort.

Further analysis of the Schrödinger equation for the harmonic oscillator shows that it can be written in the form

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2}\left[\frac{1}{2}k'x^2 - \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{m}}\right]\psi(x)$$

Comparing this complicated expression to Eq. (40.23) gives us a pleasant surprise: The energy levels, which we'll call E_n, are given by the simple formula

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

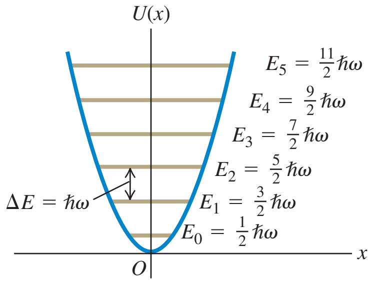
$$\text{(energy levels, harmonic oscillator)} \qquad (40.26)$$

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

Equation (40.26) confirms our guess that the energy levels are multiples of $\hbar\omega$. 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 40.18 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.

40.18 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 $E_0 = \frac{1}{2}\hbar\omega$.



Example 40.6 Vibration in a sodium crystal

A sodium atom of mass 3.82×10^{-26} kg vibrates with simple harmonic motion in a crystal. The potential energy increases by 0.0075 eV when the atom is displaced 0.014 nm from its equilibrium position. (a) Find the angular frequency, according to Newtonian mechanics. (b) Find the spacing of adjacent energy levels in electron volts. (c) If an atom emits a photon during a transition from one vibrational level to the next lower level, what is the wavelength of the emitted photon? In what region of the electromagnetic spectrum does it lie?

SOLUTION

IDENTIFY: This problem uses both the Newtonian and quantum-mechanical descriptions of a harmonic oscillator.

SET UP: To find the angular frequency $\omega = (k'/m)^{1/2}$, we use the information given and the expression $U(x) = \frac{1}{2}k'x^2$ for the potential energy. The spacing between adjacent energy levels is given by Eq. (40.26). We calculate the wavelength of the emitted photon using the same ideas as in Example 40.4 (Section 40.2).

Continued

EXECUTE: We don't know k', but we can find it from the fact that $U = 0.0075\ \text{eV} = 1.2 \times 10^{-21}\ \text{J}$ when $x = 0.014 \times 10^{-9}\ \text{m}$. We have

$$U = \frac{1}{2}k'x^2$$

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

(a) The 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. (40.26) and Fig. 40.18 the spacing between adjacent energy levels is

$$\hbar\omega = (1.054 \times 10^{-34}\ \text{J}\cdot\text{s})(1.79 \times 10^{13}\ \text{s}^{-1})$$
$$= 1.88 \times 10^{-21}\ \text{J} = 0.0118\ \text{eV}$$

(c) From $E = hc/\lambda$ the corresponding wavelength is

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

This photon is in the infrared region of the spectrum.

EVALUATE: This example shows us that the force constants for interatomic forces are on the order of a few N/m, not very different from the values for household springs or spring-based toys such as a Slinky.™ It also suggests that physicists can learn about the vibrations of atoms by measuring the radiation that they emit as they transition from one vibrational state to a lower state. We will explore this idea further in Chapter 42.

Comparing Quantum and Newtonian Oscillators

20.1.6 Potential Energy Diagrams, Question 6

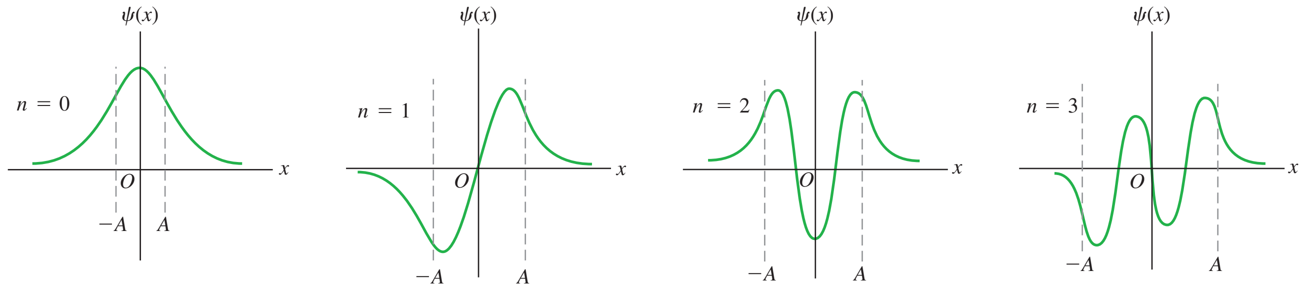
Figure 40.19 shows the first four harmonic-oscillator wave functions. Each graph also shows the amplitude A of a Newtonian harmonic oscillator with the same energy—that is, the value of A determined from

$$\frac{1}{2}k'A^2 = \left(n + \frac{1}{2}\right)\hbar\omega \qquad (40.27)$$

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 with the particle in a finite square well.

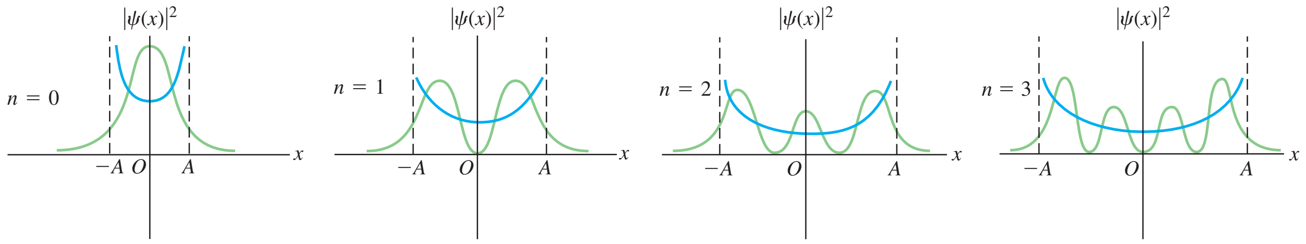
CAUTION **Be very careful with your algebraic symbols** This Newtonian amplitude A (in units of m) is *not* the same as the quantum-mechanical normalizing constant A (in $\text{m}^{-1/2}$) that is used in several wave functions in this chapter. Also the angular frequency ω (in rad/s) of the harmonic oscillator is *not* the same as the angular frequency ω (also in rad/s) obtained from the de Broglie relationship $E = \hbar\omega$ (which is why we expressed Eq. (40.14) in terms of $2\pi E/h = E/\hbar$ rather than in terms of ω). Finally, we have distinguished the force constant k' (in N/m or kg/s^2) from the wave number k (in rad/m). Neither of these is the same as κ (in m^{-1}) used in Eqs. (40.19) and (40.21) or the kinetic energy K (in J or eV). ▮

Figure 40.20 shows the probability distributions $|\psi(x)|^2$ for these same states. Each graph also shows the probability distribution determined from Newtonian analysis, in which the probability of finding the particle near a randomly chosen point is inversely proportional to its 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. 40.21 shows the classical and quantum-mechanical probability functions for $n = 10$. Notice that the spacing between zeros of $|\psi(x)|^2$ in Fig. 40.21 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.



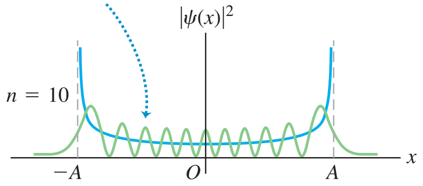
40.19 The first four wave functions for the harmonic oscillator. The amplitude A of a Newtonian oscillator with the same total energy is shown for each. Each wave function penetrates somewhat into the classically forbidden regions $|x| > A$. The total number of finite maxima and minima for each function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

40.20 Probability distribution functions $|\psi|^2$ for the harmonic-oscillator wave functions shown in Fig. 40.19. 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.



40.21 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).



In the Newtonian analysis of the harmonic oscillator the minimum energy is zero, with the particle at rest at its equilibrium position. This is not possible in quantum mechanics; no solution of the Schrödinger equation has $E = 0$ and satisfies the boundary conditions. Furthermore, if there were such a state, it would violate the uncertainty principle because there would be no uncertainty in either position or momentum. Indeed, 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 13.3. The appropriate relationships are Eqs. (13.21) for the total energy and (13.23) for the maximum speed. Setting $E = \frac{1}{2}\hbar\omega$, we find

$$E = \frac{1}{2}k'A^2 = \frac{1}{2}\hbar\omega = \frac{1}{2}\hbar\sqrt{\frac{k'}{m}} \qquad A = \sqrt{\frac{\hbar}{\sqrt{k'm}}}$$

$$p_{\text{max}} = mv_{\text{max}} = m\sqrt{\frac{k'}{m}}A = m\sqrt{\frac{k'}{m}}\sqrt{\frac{\hbar}{\sqrt{k'm}}} = \sqrt{\hbar\sqrt{k'm}}$$

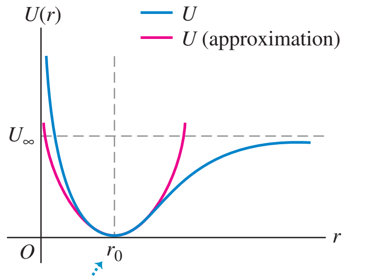
Finally, if we assume that A represents the uncertainty Δx in position and p_{max} is the corresponding uncertainty Δp_x in momentum, then the product of the two uncertainties is

$$\Delta x\, \Delta p_x = \sqrt{\frac{\hbar}{\sqrt{k'm}}}\sqrt{\hbar\sqrt{k'm}} = \hbar$$

So the product equals the minimum value allowed by Eq. (39.11), $\Delta x\, \Delta p_x \geq \hbar$, 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 $\hbar$, 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 40.22 shows a typical potential-energy function for an interatomic force in a molecule. At large separations it levels off, corresponding to the absence of force at great distances. But it is approximately parabolic near the minimum point (the equilibrium position of the

40.22 A potential-energy function describing the interaction of two atoms in a diatomic molecule. The equilibrium position is at $r = r_0$. The potential energy needed to dissociate the molecule is U_∞.



When r is near r_0, the potential-energy curve is approximately parabolic (as shown by the red curve) and the motion is approximately simple harmonic.

atoms). Near equilibrium the molecular vibration is approximately simple harmonic with energy levels given by Eq. (40.26), as we assumed in Example 40.6.

Test Your Understanding of Section 40.4 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.

40.5 Three-Dimensional Problems

We have discussed the Schrödinger equation and its applications only for *one-dimensional* problems, the analog of a Newtonian particle moving along a straight line. The straight-line model is adequate for some applications, but to understand atomic structure, we need a three-dimensional generalization.

It's not difficult to guess what the three-dimensional Schrödinger equation should look like. First, the wave function ψ is a function of all three space coordinates (x, y, z). In general, the potential-energy function also depends on all three coordinates and can be written as $U(x, y, z)$. Next, note that the term $-(\hbar^2/2m)d^2\psi/dx^2$ in the one-dimensional Schrödinger equation, Eq. (40.1), is related to the kinetic energy of the particle in the state described by the wave function ψ. For example, if we insert into this term the wave function $\psi(x) = Ae^{ikx}$ for a free particle with magnitude of momentum $p = \hbar k$ and kinetic energy $K = p^2/2m$, we obtain $-(\hbar^2/2m)(ik)^2Ae^{ikx} = (\hbar^2k^2/2m)Ae^{ikx} = (p^2/2m)\psi(x) = K\psi(x)$. If the particle's momentum has three components (p_x, p_y, p_z), then the kinetic energy is

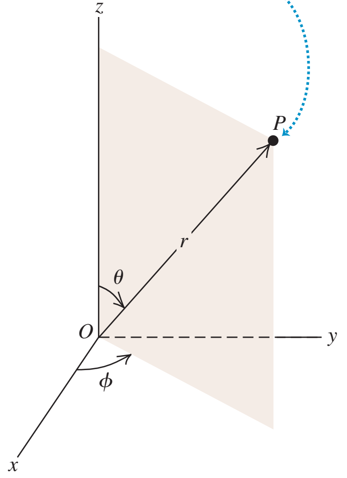
$$K = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \tag{40.28}$$

These observations, taken together, suggest that the correct generalization of the Schrödinger equation to three dimensions is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi(x, y, z)}{\partial x^2} + \frac{\partial^2\psi(x, y, z)}{\partial y^2} + \frac{\partial^2\psi(x, y, z)}{\partial z^2}\right) + U(x, y, z)\psi(x, y, z)$$
$$= E\psi(x, y, z) \qquad \text{(three-dimensional Schrödinger equation)} \tag{40.29}$$

40.23 In quantum mechanics, spherical coordinates are particularly useful in problems in which the potential energy depends only on r, the distance from the origin.

The position of a point P can be described by the rectangular coordinates (x, y, z) or by the spherical coordinates (r, θ, ϕ).



We use partial derivatives, since ψ is a function of x, y, and z. As in one dimension, E is constant for a state of particular energy.

We won't pretend that we have *derived* Eq. (40.29). Like the one-dimensional version, this equation has to be tested by comparison of its predictions with experimental results. As we will see in later chapters, Eq. (40.29) passes this test with flying colors, so we are confident that it *is* the correct equation.

In many practical problems, in atomic structure and elsewhere, the potential-energy function is *spherically symmetric;* it depends only on the distance $r = (x^2 + y^2 + z^2)^{1/2}$ from the origin of coordinates. To take advantage of this symmetry, we use *spherical coordinates* (r, θ, ϕ) (Fig. 40.23) instead of Cartesian coordinates (x, y, z). Then a spherically symmetric potential-energy function is a function only of r, not of θ or ϕ, so $U = U(r)$. This fact turns out to simplify greatly the problem of finding solutions of the Schrödinger equation, even though the derivatives in Eq. (40.29) are considerably more complex when expressed in terms of spherical coordinates. Be careful; many math texts exchange the angles θ and ϕ shown in Fig. 40.23.

For the hydrogen atom the potential-energy function $U(r)$ is the familiar Coulomb's-law function:

$$U(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r} \tag{40.30}$$

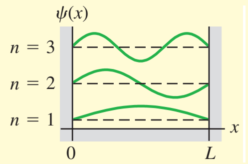
We will find that for *all* spherically symmetric potential-energy functions $U(r)$, each possible wave function can be expressed as a product of three functions: one a function only of r, one only of θ, and one only of ϕ. Furthermore, the functions of θ and ϕ are *the same* for *every* spherically symmetric potential-energy function. This result is directly related to the problem of finding the possible values of *angular momentum* for the various states. We'll discuss these matters more in the next chapter.

CHAPTER 40 SUMMARY

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. (40.9). The corresponding normalized wave functions of the particle are given by Eq. (40.13). (See Examples 40.1 and 40.2.)

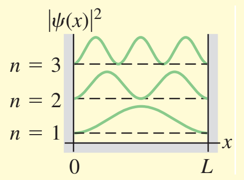
$$E_n = \frac{p_n^2}{2m} = \frac{n^2h^2}{8mL^2} = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad (40.9)$$
$$(n = 1, 2, 3, \ldots)$$

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \qquad (40.13)$$
$$(n = 1, 2, 3, \ldots)$$

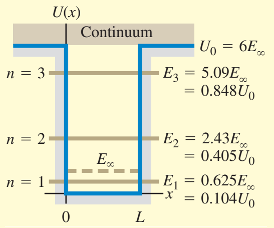


Wave functions and normalization: To be a solution of the Schrödinger equation, the wave function $\psi(x)$ and its derivative $d\psi(x)/dx$ must be continuous everywhere, except where the potential-energy function $U(x)$ has an infinite discontinuity. Wave functions are usually normalized so that the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

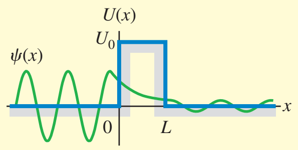
$$\int_{-\infty}^{\infty} |\psi(x)|^2\,dx = 1 \qquad (40.11)$$
(normalization condition)



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 40.3 and 40.4.)

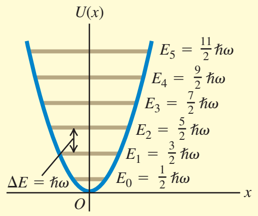


Potential barriers and tunneling: There is a certain probability that a particle will penetrate a potential-energy barrier even though its initial kinetic energy is less than the barrier height. This process is called tunneling. (See Example 40.5.)



Quantum harmonic oscillator: The energy levels for the harmonic oscillator, for which $U(x) = \frac{1}{2}k'x^2$, are given by Eq. (40.26). 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 40.6.)

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{m}} \qquad (40.26)$$
$$(n = 0, 1, 2, 3, \ldots)$$



Three-dimensional problems: The Schrödinger equation for three-dimensional problems is given by Eq. (40.29).

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi(x,y,z)}{\partial x^2} + \frac{\partial^2\psi(x,y,z)}{\partial y^2} + \frac{\partial^2\psi(x,y,z)}{\partial z^2}\right) + U(x,y,z)\psi(x,y,z) = E\psi(x,y,z) \qquad (40.29)$$

Key Terms

particle in a box, *1376*
normalization, *1379*
potential well, *1380*
square-well potential, *1381*
bound state, *1381*
potential barrier, *1384*
tunneling, *1385*
harmonic oscillator, *1387*

Answer to Chapter Opening Question

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 40.4 (Section 40.2) for more details.

Answers to Test Your Understanding Questions

40.1 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.

40.2 Answer (i) The energy levels are arranged as shown in Fig. 40.8b if $U_0 = 6E_\infty$, where $E_\infty = \pi^2\hbar^2/2mL^2$ is the ground-level energy of an infinite well. If the well width L is reduced to $\frac{1}{2}$ of its initial value, E_∞ increases by a factor of 4 and so U_0 must also increase by a factor of 4. The energies E_1, E_2, and E_3 shown in Fig. 40.8b are all specific fractions of U_0, so they will also increase by a factor of 4.

40.3 Answer: yes Figure 40.13 shows a possible wave function $\psi(x)$ for tunneling; since $\psi(x)$ is not zero within the barrier $(0 \le x \le L)$, there is some probability that the particle can be found there.

40.4 Answer: (ii) 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. 38.9). By contrast, the energy difference between successive levels increases for a particle in a box (see Fig. 40.4b) and is constant for a harmonic oscillator (see Fig. 40.18).

PROBLEMS

For instructor-assigned homework, go to **www.masteringphysics.com**

Discussion Questions

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

Q40.2. If ψ 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.

Q40.3. 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.

Q40.4. 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.

Q40.5. 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. 40.5, but don't evaluate an integral.) Is the answer the same if the particle is in an excited level? Explain.

Q40.6. The wave functions for a particle in a box (see Fig. 40.5a) are zero at certain points. Does this mean that the particle can't move past one of these points? Explain.

Q40.7. 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.)

Q40.8. 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.

Q40.9. Equation 40.15 gives the time-dependent wave functions for a particle in a box. How can a wave function that has both a real part and an imaginary part describe the position (a real number) of a particle?

Q40.10. In Fig. 40.5b, 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.

Q40.11. 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?

Q40.12. Compare the wave functions for the first three energy levels for a particle in a box of width L (see Fig. 40.5a) to the corresponding wave functions for a finite potential well of the same width (see Fig. 40.8a). How does the wavelength in the interval $0 \le x \le L$ 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_∞ in the situation depicted in Fig. 40.8b.

Q40.13. It is stated in Section 40.2 that a finite potential well always has at least one bound level, no matter how shallow the well. Does this mean that as $U_0 \to 0$, $E_1 \to 0$? Does this violate the Heisenberg uncertainty principle? Explain.

Q40.14. Figure 40.8a 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.

Q40.15. 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 40.3) a particle passes through regions where E is less than U. Is this a contradiction? Explain.

Q40.16. Figure 40.10 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?

Q40.17. 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.

Q40.18. The wave function shown in Fig. 40.13 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.

Q40.19. The probability distributions for the harmonic oscillator wave functions (see Figs. 40.20 and 40.21) 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.

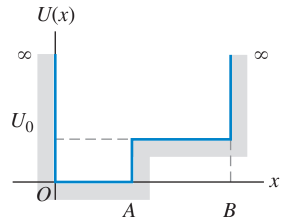
Q40.20. In Fig. 40.21, how does the probability of finding a particle in the center half of the region $-A < x < A$ compare to the probability of finding the particle in the outer half of the region? Is this consistent with the physical interpretation of the situation?

Q40.21. 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?

Q40.22. In the hydrogen atom the potential-energy function depends only on distance r from the nucleus, not on direction; that is, it is spherically symmetric. Would you expect all the corresponding wave functions for the electron in the hydrogen atom to be spherically symmetric? Explain.

Q40.23. Sketch the wave function for the potential-energy well shown in Fig. 40.24 when E_1 is less than U_0 and when E_3 is greater than U_0.

Figure 40.24 Question Q40.23.



Exercises

Section 40.1 Particle in a Box

40.1. 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 1.5 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?

40.2. 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} m.

40.3. Find the width L of a one-dimensional box that would correspond to the absolute value of the ground state of a hydrogen atom.

40.4. When a hydrogen atom undergoes a transition from the $n = 2$ to the $n = 1$ level, a photon with $\lambda = 122$ 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.)

40.5. 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.

40.6. 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 ψ_n as given in Eq. (40.13). (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. 40.8? Explain.

40.7. Repeat Exercise 40.6 for the particle in the first excited level.

40.8. (a) Show that $\psi = A\sin kx$ is a solution to Eq. (40.3) if $k = \sqrt{2mE}/\hbar$. (b) Explain why this is an acceptable wave function for a particle in a box with rigid walls at $x = 0$ and $x = L$ only if k is an integer multiple of π/L.

40.9. (a) Repeat Exercise 40.8 for $\psi = A\cos kx$. (b) Explain why this cannot be an acceptable wave function for a particle in a box with rigid walls at $x = 0$ and $x = L$ no matter what the value of k.

40.10. (a) Find the excitation energy from the ground level to the third excited level for an electron confined to a box that has a width of 0.125 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.

40.11. An electron is in a box of width 3.0×10^{-10} 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?

40.12. Show that the time-dependent wave function given by Eq. (40.15) is a solution to the one-dimensional Schrödinger equation, Eq. (40.1).

Section 40.2 Potential Wells

40.13. (a) Show that $\psi = A\sin kx$, where k is a constant, is *not* a solution of Eq. (40.1) for $U = U_0$ and $E < U_0$. 9 (b) Is this ψ a solution for $E > U_0$?

40.14. An electron is moving past the square well shown in Fig. 40.6. 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 $0 < x < L$?

40.15. An electron is bound in a square well of depth $U_0 = 6E_\infty$. What is the width of the well if its ground-state energy is 2.00 eV?

40.16. An electron is bound in a square well of width 1.50 nm and depth $U_0 = 6E_\infty$. 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?

40.17. Calculate $d^2\psi/dx^2$ for the wave function of Eq. (40.17), and show that the function is a solution of Eq. (40.16).

40.18. Calculate $d^2\psi/dx^2$ for the wave function of Eq. (40.19), and show that for any values of C and D it is a solution of Eq. (40.1) for $x \le 0$ and $x \ge L$ when $U = U_0$ and $E < U_0$.

40.19. A proton is bound in a square well of width 4.0 fm $=$ 4.0×10^{-15} m. The depth of the well is six times the ground-level energy E_∞ 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.

40.20. An electron is bound in a square well with a depth equal to six times the ground-level energy E_∞ of an infinite well of the same width. The longest-wavelength photon that is absorbed by the electron has a wavelength of 400.0 nm. Determine the width of the well.

Section 40.3 Potential Barriers and Tunneling

40.21. 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?

40.22. An electron with initial kinetic energy 5.0 eV encounters a barrier with height U_0 and width .060 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?

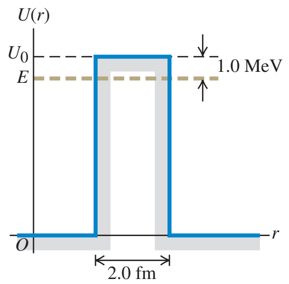
40.23. An electron is moving past the square barrier shown in Fig. 40.12, but the energy of the electron is *greater* than the barrier height. If $E = 2U_0$, what is the ratio of the de Broglie wavelength of the electron in the region $x > L$ to the wavelength for $0 < x < L$?

40.24. A proton with initial kinetic energy 50.0 eV encounters a barrier of height 70.0 eV. What is the width of the barrier if the probability of tunneling is 3.0×10^{-3}? How does this compare with the barrier width for an electron with the same energy tunneling through a barrier of the same height with the same probability?

40.25. (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?

40.26. Alpha Decay. In a simple model for a radioactive nucleus, an alpha particle $(m = 6.64 \times 10^{-27}\ \text{kg})$ 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. 40.25)? (b) What is the tunneling probability if the energy of the alpha particle is 10.0 MeV below the top of the barrier?

Figure 40.25 Exercise 40.26.



Section 40.4 The Harmonic Oscillator

40.27. 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?

40.28. Show that $\psi(x)$ given by Eq. (40.24) is a solution to Eq. (40.22) with energy $E_0 = \hbar\omega/2$.

40.29. Chemists use infrared absorption spectra to identify chemicals in a sample. In one sample, a chemist finds that light of wavelength 5.8 μm is absorbed. (a) Find the energy of this transition. (b) If the molecule has mass 5.6×10^{-26} kg, find the force constant.

40.30. 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?

40.31. In Section 40.4 it is shown that for the ground level of a harmonic oscillator, $\Delta x \Delta p_x = \hbar$. Do a similar analysis for an excited level that has quantum number n. How does the uncertainty product $\Delta x \Delta p_x$ depend on n?

40.32. For the ground-level harmonic oscillator wave function $\psi(x)$ given in Eq. (40.24), $|\psi|^2$ 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. (40.27) 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. 40.20?

40.33. For the sodium atom of Example 40.6, 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.

Problems

40.34. Show that the wave function $\psi(x) = Ae^{ikx}$ is a solution of Eq. 40.1 for a particle of mass m, in a region where the potential energy is a constant $U_0 < E$. Find an expression for k, and relate it to the particle's momentum and to its de Broglie wavelength.

40.35. Wave functions like the one in Problem 40.34 can represent free particles moving with velocity $v = p/m$ in the x-direction. Consider a beam of such particles 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 ψ 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.

40.36. Let ΔE_n be the energy difference between the adjacent energy levels E_n and E_{n+1} for a particle in a box. The ratio $R_n = \Delta E_n/E_n$ compares the energy of a level to the energy separation of the next higher energy level. a) For what value of n is R_n largest, and what is this largest R_n? (b) What does R_n approach as n becomes very large? How does this result compare to the classical value for this quantity?

40.37. 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?

40.38. 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 ψ 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. 40.5b? Explain.

40.39. 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 ψ is normalized, between $L/4$ and $3L/4$.) (c) Are your results in parts (a) and (b) consistent with Fig. 40.5b? Explain.

40.40. 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) $x = 3L/4$.

40.41. Repeat Problem 40.40 for a particle in the first excited level.

40.42. A particle is confined within a box with perfectly rigid walls at $x = 0$ and $x = L$. Although the magnitude of the instantaneous force exerted on the particle by the walls is infinite and the time over which it acts is zero, the impulse (that involves a product of force and time) is both finite and quantized. Show that the impulse exerted by the wall at $x = 0$ is $(nh/L)\hat{\imath}$ and that the impulse exerted by the wall at $x = L$ is $-(nh/L)\hat{\imath}$. (*Hint:* You may wish to review Section 8.1.)

40.43. 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 κ 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.

40.44. The penetration distance η in a finite potential well is the distance at which the wave function has decreased to $1/e$ of the 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 η for an electron having a kinetic energy of 13 eV in a potential well with $U_0 = 20$ ev. (b) Find η for a 20.0-MeV proton trapped in a 30.0-MeV-deep potential well.

40.45. (a) For the finite potential well of Fig. 40.6, what relationships among the constants A and B of Eq. (40.17) and C and D of Eq. (40.19) are obtained by applying the boundary condition that ψ be continuous at $x = 0$ and at $x = L$? (b) What relationships among A, B, C, and D are obtained by applying the boundary condition that $d\psi/dx$ be continuous at $x = 0$ and at $x = L$?

40.46. An electron with initial kinetic energy 5.5 eV encounters a square potential barrier with height 10.0 eV. What is the width of the barrier if the electron has a 0.10% probability of tunneling through the barrier?

40.47. A particle with mass m and total energy E tunnels through a square barrier of height U_0 and width L. When the transmission coefficient is *not* much less than unity, it is given by

$$T = \left[1 + \frac{(U_0 \sinh \kappa L)^2}{4E(U_0 - E)}\right]^{-1}$$

where $\sinh \kappa L = (e^{\kappa L} - e^{-\kappa L})/2$ is the hyperbolic sine of κL. (a) Show that if $\kappa L \gg 1$, this expression for T approaches Eq. (40.21). (b) Explain why the restriction $\kappa L \gg 1$ in part (a) implies either that the barrier is relatively wide or that the energy E is relatively low compared to U_0. (c) Show that as the particle's incident kinetic energy E approaches the barrier height U_0, T approaches $[1 + (kL/2)^2]^{-1}$, where $k = \sqrt{2mE}/\hbar$ is the wave number of the incident particle. (*Hint:* If $|z| \ll 1$, then $\sinh z \approx z$.)

40.48. A harmonic oscillator consists of a 0.020-kg mass on a spring. Its frequency is 1.50 Hz, and the mass has a speed of 0.360 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?

40.49. 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?

40.50. Some 164.9-nm photons are emitted in a $\Delta n = 1$ transition within a solid-state lattice. The lattice is modeled as electrons in a box having length 0.500 nm. What transition corresponds to the emitted light?

40.51. (a) Show by direct substitution in the Schrödinger equation for the one-dimensional harmonic oscillator that the wave function $\psi_0(x) = A_0 e^{-\alpha^2 x^2/2}$, where $\alpha^2 = m\omega/\hbar$, is a solution with energy corresponding to $n = 0$ in Eq. (40.22). (b) Find the normalization constant A_0. (c) Find the classical turning points and show, in contrast, that the probability density has a maximum at $x = 0$.

40.52. (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. (40.22). (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 $n = 0$.

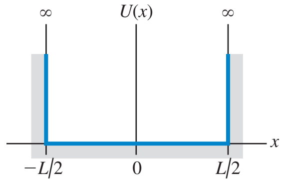
40.53. A Three-Dimensional Isotropic Harmonic Oscillator. An isotropic harmonic oscillator has the potential-energy function $U(x, y, z) = \frac{1}{2}k'(x^2 + y^2 + z^2)$. (*Isotropic* means that the force constant k' is the same in all three coordinate directions.) (a) Show that for this potential, a solution to Eq. (40.29) is given by $\psi = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$. In this expression, $\psi_{n_x}(x)$ is a solution to the one-dimensional harmonic oscillator Schrödinger equation, Eq. (40.22), with energy $E_{n_x} = (n_x + \frac{1}{2})\hbar\omega$. The functions $\psi_{n_y}(y)$ and $\psi_{n_z}(z)$ are analogous one-dimensional wave functions for oscillations in the y- and z-directions. Find the energy associated with this ψ. (b) From your results in part (a) what are the ground-level and first-excited-level energies of the three-dimensional isotropic oscillator? (c) Show that there is only one state (one set of quantum numbers n_x, n_y, and n_z) for the ground level but three states for the first excited level.

40.54. Three-Dimensional Anisotropic Harmonic Oscillator. An oscillator has the potential-energy function $U(x, y, z) = \frac{1}{2}k_1'(x^2 + y^2) + \frac{1}{2}k_2'z^2$, where $k_1' > k_2'$. This oscillator is called *anisotropic* because the force constant is not the same in all three coordinate directions. (a) Find a general expression for the energy levels of the oscillator (see Problem 40.53). (b) From your results in part (a), what are the ground-level and first-excited-level energies of this oscillator? (c) How many states (different sets of quantum numbers n_x, n_y, and n_z) are there for the ground level and for the first excited level? Compare to part (c) of Problem 40.53.

Challenge Problems

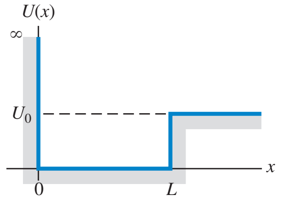
40.55. Section 40.1 considered a box with walls at $x = 0$ and $x = L$. Now consider a box with width L but centered at $x = 0$, so that it extends from $x = -L/2$ to $x = +L/2$ (Fig. 40.26). Note that this box is symmetrical about $x = 0$. (a) Consider possible wave functions of the form $\psi(x) = A \sin kx$. Apply the boundary conditions at the wall to obtain the allowed energy levels. (b) Another set of possible wave functions are functions of the form $\psi(x) = A \cos kx$. Apply the boundary conditions at the wall to obtain the allowed energy levels. (c) Compare the energies obtained in parts (a) and (b) to the set of energies given in Eq. (40.9). (d) An odd function f satisfies the condition $f(x) = -f(-x)$, and an even function g satisfies $g(x) = g(-x)$. Of the wave functions from parts (a) and (b), which are even and which are odd?

Figure 40.26 Challenge Problem 40.55.



40.56. Consider a potential 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. 40.27). 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 ψ 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 $\kappa = \sqrt{2m(U_0 - E)}/\hbar$.

Figure 40.27 Challenge Problem 40.56.



40.57. 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. 40.1). Furthermore, the number of wavelengths that fit within the box must be a half-integer (see Fig. 40.3), so that $L = (n/2)\lambda$ and hence $L/\lambda = n/2$, where $n = 1, 2, 3, \ldots$. [Note that this is a restatement of Eq. (40.7).] 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:

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

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

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

(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. (40.9). (*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. 40.6, 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.

40.58. The WKB approximation (see Challenge Problem 40.57) can be used to calculate the energy levels for a harmonic oscillator. In this approximation, the energy levels are the solutions to the equation

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

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 $n = 1, 2, 3, \ldots$. (*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. (40.26)? Does the WKB approximation give an underestimate or an overestimate of the energy levels?

40.59. 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 ψ 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 40.57) 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

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

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

$$E_n = \frac{1}{2m}\left(\frac{3mAh}{4}\right)^{2/3} n^{2/3} \qquad (n = 1, 2, 3, \ldots)$$

(*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?