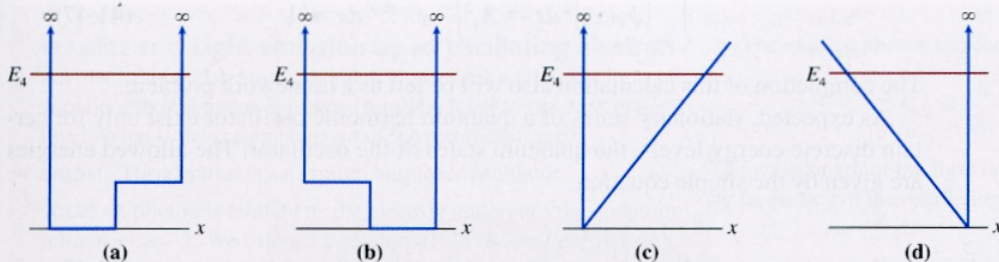
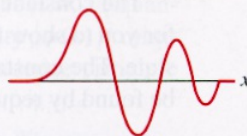


STOP TO THINK 41.4

For which potential energy is this an appropriate

 $n = 4$ wave function?

41.8 The Quantum Harmonic Oscillator

Simple harmonic motion is exceptionally important in classical physics, where it serves as a prototype for more complex oscillations. As you might expect, a microscopic oscillator—the **quantum harmonic oscillator**—is equally important as a model of oscillations at the atomic level.

The defining characteristic of simple harmonic motion is a linear restoring force: $F = -kx$, where k is the spring constant. The corresponding potential-energy function, as you learned in Chapter 10, is

$$U(x) = \frac{1}{2}kx^2 \quad (41.42)$$

where we'll assume that the equilibrium position is $x_e = 0$. The potential energy of a harmonic oscillator is shown in **FIGURE 41.20**. It is a potential-energy well with curved sides.

A classical particle of mass m oscillates with angular frequency

$$\omega = \sqrt{\frac{k}{m}} \quad (41.43)$$

between the two turning points where the energy line crosses the parabolic potential-energy curve. As you've learned, this classical description fails if m represents an atomic particle, such as an electron or an atom. In that case, we need to solve the Schrödinger equation to find the wave functions.

The Schrödinger equation for a quantum harmonic oscillator is

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi(x) \quad (41.44)$$

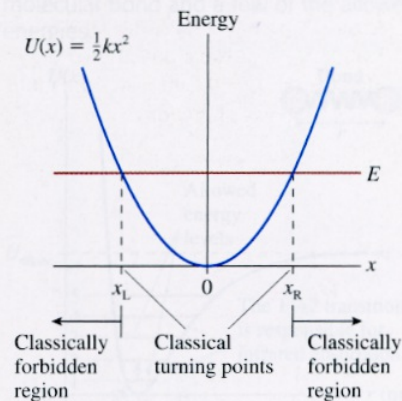
where we used $U(x) = \frac{1}{2}kx^2$. We will assert, without deriving them, that the wave functions of the first three states are

$$\begin{aligned} \psi_1(x) &= A_1 e^{-x^2/2b^2} \\ \psi_2(x) &= A_2 \frac{x}{b} e^{-x^2/2b^2} \\ \psi_3(x) &= A_3 \left(1 - \frac{2x^2}{b^2}\right) e^{-x^2/2b^2} \end{aligned} \quad (41.45)$$

where

$$b = \sqrt{\frac{\hbar}{m\omega}} \quad (41.46)$$

FIGURE 41.20 The potential energy of a harmonic oscillator.



The constant b has dimensions of length. We will leave it as a homework problem for you to show that b is the classical turning point of an oscillator in the $n = 1$ ground state. The constants A_1 , A_2 , and A_3 are normalization constants. For example, A_1 can be found by requiring

$$\int_{-\infty}^{\infty} |\psi_1(x)|^2 dx = A_1^2 \int_{-\infty}^{\infty} e^{-x^2/b^2} dx = 1 \quad (41.47)$$

The completion of this calculation also will be left as a homework problem.

As expected, stationary states of a quantum harmonic oscillator exist only for certain discrete energy levels, the quantum states of the oscillator. The allowed energies are given by the simple equation

$$E_n = \left(n - \frac{1}{2}\right)\hbar\omega \quad n = 1, 2, 3, \dots \quad (41.48)$$

where ω is the classical angular frequency, Equation 41.43, and n is the quantum number.

NOTE ▶ The ground-state energy of the quantum harmonic oscillator is $E_1 = \frac{1}{2}\hbar\omega$. An atomic mass on a spring can *not* be brought to rest. This is a consequence of the uncertainty principle. ◀

FIGURE 41.21 shows the first three energy levels and wave functions of a quantum harmonic oscillator. Notice that the energy levels are equally spaced by $\Delta E = \hbar\omega$. This result differs from the particle in a box, where the energy levels get increasingly farther apart. Also notice that the wave functions, like those of the finite potential well, extend beyond the turning points into the classically forbidden region.

FIGURE 41.21 The first three energy levels and wave functions of a quantum harmonic oscillator.

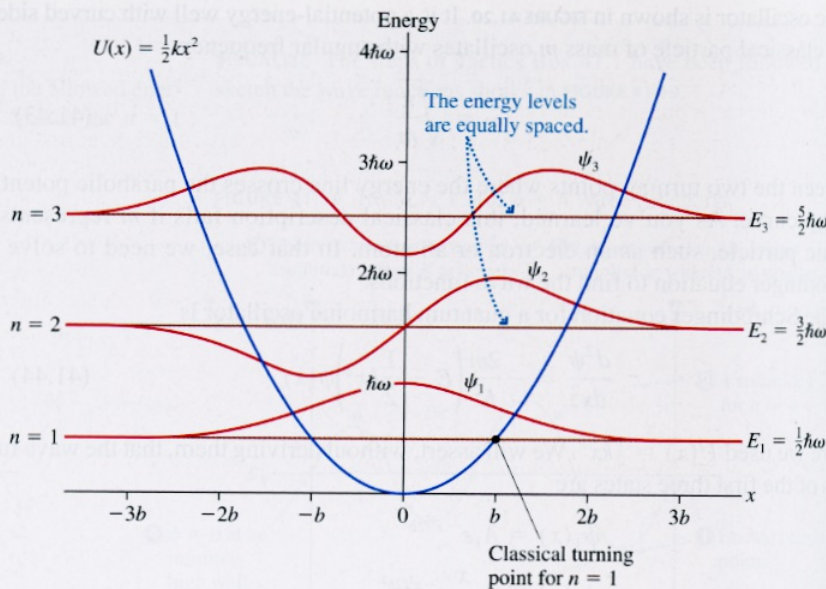


FIGURE 41.22 The quantum and classical probability densities for the $n = 11$ state of a quantum harmonic oscillator.

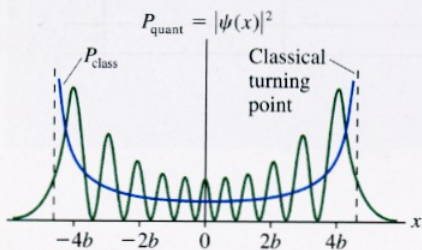


FIGURE 41.22 shows the probability density $|\psi(x)|^2$ for the $n = 11$ state of a quantum harmonic oscillator. Notice how the node spacing and the amplitude both increase as the particle moves away from the equilibrium position at $x = 0$. This is consistent with item 3 of Tactics Box 41.1. The particle slows down as it moves away from the origin, causing its de Broglie wavelength *and* the probability of finding it to increase.

Section 41.5 introduced the classical probability density $P_{\text{class}}(x)$ and noted that a classical particle is most likely to be found where it is moving the slowest. Figure 41.22

shows $P_{\text{class}}(x)$ for a classical particle with the same total energy as the $n = 11$ quantum state. You can see that *on average* the quantum probability density $|\psi(x)|^2$ mimics the classical probability density. This is just what the correspondence principle leads us to expect.

EXAMPLE 41.9 Light emission by an oscillating electron

An electron in a harmonic-oscillator potential well emits light of wavelength 600 nm as it jumps from one level to the next lowest level. What is the spring constant of the restoring force?

MODEL The electron is a quantum harmonic oscillator.

SOLVE A photon is emitted as the electron undergoes the quantum jump $n \rightarrow n - 1$. We can use Equation 41.48 for the energy levels to find that the electron loses energy

$$\Delta E = E_n - E_{n-1} = \left(n - \frac{1}{2}\right)\hbar\omega_e - \left(n - 1 - \frac{1}{2}\right)\hbar\omega_e = \hbar\omega_e$$

$\Delta E = \hbar\omega_e$ for *all* transitions, independent of n , because the energy levels of the quantum harmonic oscillator are equally spaced. We need to distinguish the harmonic oscillations of the electron from the oscillations of the light wave, hence the subscript e on ω_e .

The emitted photon has energy $E_{\text{photon}} = hf_{\text{ph}} = \Delta E$. Thus

$$\hbar\omega_e = \frac{h}{2\pi}\omega_e = hf_{\text{ph}} = \frac{hc}{\lambda}$$

The wavelength of the light is $\lambda = 600$ nm, so the classical angular frequency of the oscillating electron is

$$\omega_e = 2\pi\frac{c}{\lambda} = 3.14 \times 10^{15} \text{ rad/s}$$

The electron's angular frequency is related to the spring constant of the restoring force by

$$\omega_e = \sqrt{\frac{k}{m}}$$

Thus $k = m\omega_e^2 = 9.0$ N/m.

Molecular Vibrations

We've made many uses of the idea that atoms are held together by spring-like molecular bonds. We've always assumed that the bonds could be modeled as classical springs. The classical model is acceptable for some purposes, but it fails to explain some important features of molecular vibrations. Not surprisingly, the quantum harmonic oscillator is a better model of a molecular bond.

FIGURE 41.23 shows the potential energy of two atoms connected by a molecular bond. Nearby atoms attract each other through a polarization force, much as a charged rod picks up small pieces of paper. If the atoms get too close, a *repulsive* force between the negative electrons pushes them away. The equilibrium separation at which the attractive and repulsive forces are balanced is r_0 , and two classical atoms would be at rest at this separation. But quantum particles, even in their lowest energy state, have $E > 0$. Consequently, the molecule *vibrates* as the two atoms oscillate back and forth along the bond.

U_{dissoc} is the energy at which the molecule will *dissociate* and the two atoms will fly apart. Dissociation can occur at very high temperatures or after the molecule has absorbed a high-energy (ultraviolet) photon, but under typical conditions a molecule has energy $E \ll U_{\text{dissoc}}$. In other words, the molecule is in an energy level near the bottom of the potential well.

You can see that the lower portion of the potential well is very nearly a parabola. Consequently, we can model a molecular bond as a quantum harmonic oscillator. The energy associated with the molecular vibration is quantized and can have *only* the values

$$E_{\text{vib}} \approx \left(n - \frac{1}{2}\right)\hbar\omega \quad n = 1, 2, 3, \dots \quad (41.49)$$

where ω is the angular frequency with which the atoms would vibrate if the bond were a classical spring. The molecular potential-energy curve is not exactly that of a harmonic oscillator, hence the \approx sign, but the model is very good for low values of the quantum number n . The energy levels calculated by Equation 41.49 are called the **vibrational energy levels** of the molecule. The first few vibrational energy levels are shown in Figure 41.23.

At room temperature, most molecules are in the $n = 1$ vibrational ground state. Their vibrational motion can be excited by absorbing photons of frequency $f = \Delta E/h$.

FIGURE 41.23 The potential energy of a molecular bond and a few of the allowed energies.

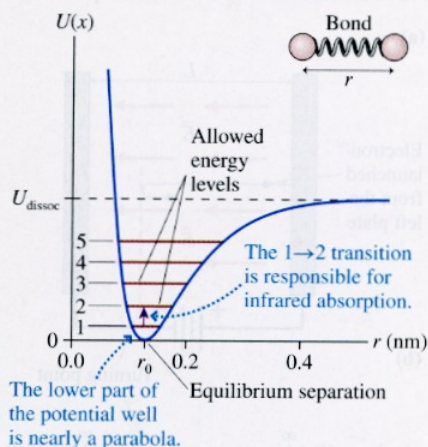
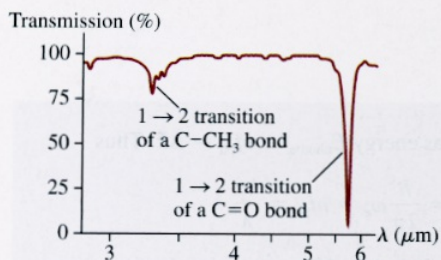


FIGURE 41.24 The absorption spectrum of acetone.



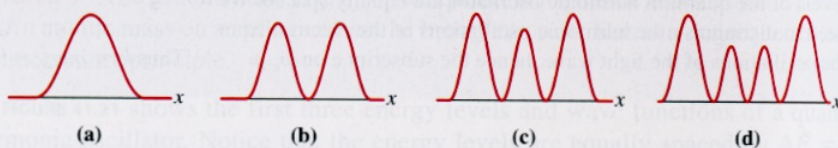
This frequency is usually in the infrared region of the spectrum, and these *vibrational transitions* give each molecule a unique and distinctive infrared absorption spectrum.

As an example, **FIGURE 41.24** shows the infrared absorption spectrum of acetone. The vertical axis is the percentage of the light intensity passing all the way through the sample. The sample is essentially transparent at most wavelengths (transmission $\approx 100\%$), but there are two prominent absorption features. The transmission drops to $\approx 75\%$ at $\lambda = 3.3 \mu\text{m}$ and to a mere 7% at $\lambda = 5.8 \mu\text{m}$. The $3.3 \mu\text{m}$ absorption is due to the $n = 1$ to $n = 2$ transition in the vibration of a $\text{C}-\text{CH}_3$ carbon-methyl bond. The $5.8 \mu\text{m}$ absorption is the $1 \rightarrow 2$ transition of a vibrating $\text{C}=\text{O}$ carbon-oxygen double bond.

Absorption spectra such as this are known for thousands of molecules, and chemists routinely use absorption spectroscopy to identify the chemicals in a sample. A specific bond has the same absorption wavelength regardless of the larger molecule in which it is embedded; thus the presence of that absorption wavelength is a “signature” that the bond is present within a molecule.

STOP TO THINK 41.5

Which probability density represents a quantum harmonic oscillator with $E = \frac{5}{2}\hbar\omega$?



41.9 More Quantum Models

In this section we’ll look at two more examples of quantum-mechanical models.

A Particle in a Capacitor

Many semiconductor devices are designed to confine electrons within a layer only a few nanometers thick. If a potential difference is applied across the layer, the electrons act very much as if they are trapped within a microscopic capacitor.

FIGURE 41.25a shows two capacitor plates separated by distance L . The left plate is positive, so the electric field points to the right with strength $E = \Delta V_0/L$. Because of its negative charge, an electron launched from the left plate is slowed by a *retarding* force. The electron makes it across to the right plate if it starts with sufficient kinetic energy; otherwise, it reaches a turning point and then is pushed back toward the positive plate.

This classical analysis is a valid model of a macroscopic capacitor. But if L becomes sufficiently small, comparable to the de Broglie wavelength of an electron, then the wave-like properties of the electron cannot be ignored. We need a quantum-mechanical model.

Let’s establish a coordinate system with $x = 0$ at the left plate and $x = L$ at the right plate. We define the electric potential to be zero at the positive plate. The potential *decreases* in the direction of the field, so the potential inside the capacitor (see Section 29.5) is

$$V(x) = -Ex = -\frac{\Delta V_0}{L}x$$

The electron, with charge $q = -e$, has potential energy

$$U(x) = qV(x) = +\frac{e\Delta V_0}{L}x \quad 0 < x < L \quad (41.50)$$

FIGURE 41.25 An electron in a capacitor.

