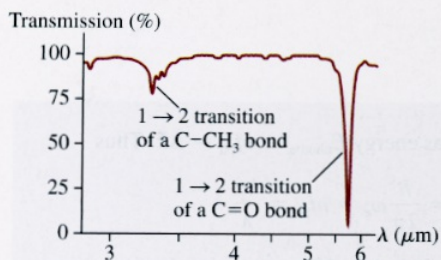


**FIGURE 41.24** The absorption spectrum of acetone.



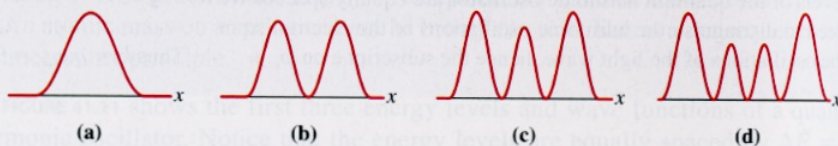
This frequency is usually in the infrared region of the spectrum, and these *vibrational transitions* give each molecule a unique and distinctive infrared absorption spectrum.

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.

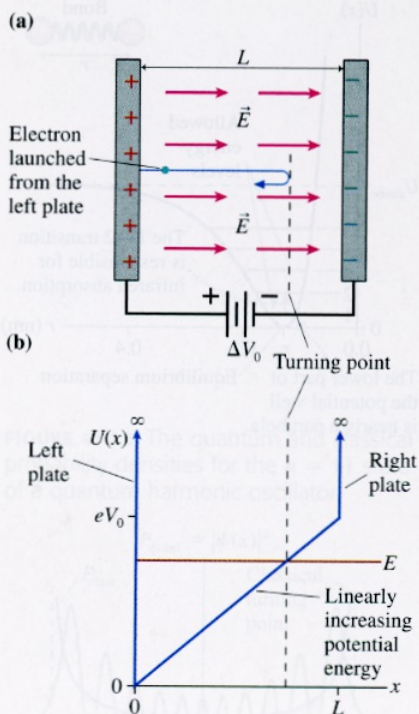
Let’s establish a coordinate system with  $x = 0$  at the left plate and  $x = L$  at the right plate. We define the electric potential to be zero at the positive plate. The potential *decreases* in the direction of the field, so the potential inside the capacitor (see Section 29.5) is

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

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.



This potential energy increases linearly for  $0 < x < L$ . If we assume that the capacitor plates act like the walls of a rigid box, then  $U(x) \rightarrow \infty$  at  $x = 0$  and  $x = L$ .

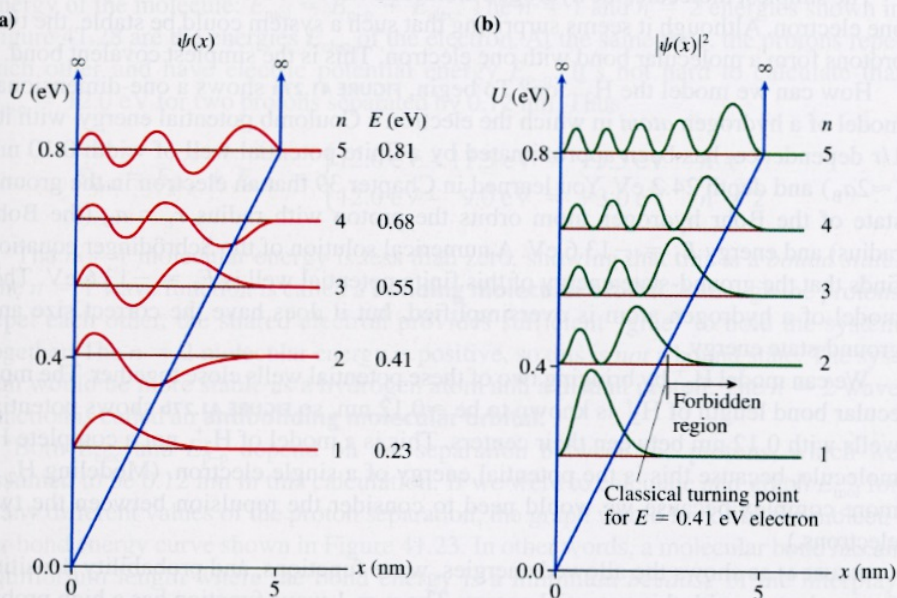
**FIGURE 41.25b** shows the electron's potential-energy function. It is the particle-in-a-rigid-box potential with a sloping "floor" due to the electric field. The figure also shows the total energy line  $E$  of an electron in the capacitor. The energy is purely kinetic at  $x = 0$ , where  $K = E$ , but it is converted to potential energy as the electron moves to the right. The right turning point occurs where the energy line  $E$  crosses the potential-energy curve  $U(x)$ . If the electron is a classical particle, it must reverse direction at this point.

**NOTE** ▶ This is also the shape of the potential energy for a microscopic bouncing ball that is trapped between a floor at  $y = 0$  and a ceiling at  $y = L$ . ◀

It is physically impossible for an electron to be outside the capacitor, so the wave function must be zero for  $x < 0$  and  $x > L$ . The continuity of  $\psi$  requires the same boundary conditions as for a particle in a rigid box:  $\psi = 0$  at  $x = 0$  and at  $x = L$ . The wave functions inside the capacitor are too complicated to find by guessing, so we have solved the Schrödinger equation numerically and will present the results graphically.

**FIGURE 41.26** shows the wave functions and probability densities for the first five quantum states of an electron confined in a 5.0-nm-thick layer that has a 0.80 V potential difference across it. Each allowed energy is represented as a horizontal line, with the numerical values shown on the right. They range from  $E_1 = 0.23$  eV up to  $E_5 = 0.81$  eV. An electron *must* have one of the allowed energies shown in the figure. An electron cannot have  $E = 0.30$  eV in this capacitor because no de Broglie wave with that energy can match the necessary boundary conditions.

**FIGURE 41.26** Energy levels, wave functions, and probability densities for an electron in a 5.0-nm-wide capacitor with a 0.80 V potential difference.



**NOTE** ▶ Remember that each wave function and probability density is graphed as if its energy line is the zero of the  $y$ -axis. ◀

We can make some observations about the Schrödinger equation solutions:

1. The energies  $E_n$  become more closely spaced as  $n$  increases. This behavior is in contrast to the particle in a box, for which  $E_n$  became more widely spaced.
2. The spacing between the nodes of a wave function is not constant but increases toward the right. This is because an electron on the right side of the capacitor has less kinetic energy and thus a slower speed and a larger de Broglie wavelength.

- The height of the probability density  $|\psi|^2$  increases toward the right. That is, we are more likely to find the electron on the right side of the capacitor than on the left. But this also makes sense if, classically, the electron is moving more slowly when on the right side and thus spending more time there than on the left side.
- The electron penetrates *beyond* the classical turning point into the classically forbidden region.

### EXAMPLE 41.10 The emission spectrum of an electron in a capacitor

What are the wavelengths of photons emitted by electrons in the  $n = 4$  state of Figure 41.26?

**SOLVE** Photon emission occurs as the electrons make  $4 \rightarrow 3$ ,  $4 \rightarrow 2$ , and  $4 \rightarrow 1$  quantum jumps. In each case, the photon frequency is  $f = \Delta E/h$  and the wavelength is

$$\lambda = \frac{c}{f} = \frac{hc}{\Delta E}$$

The energies of the quantum jumps, which can be read from Figure 41.26a, are  $\Delta E_{4 \rightarrow 3} = 0.13$  eV,  $\Delta E_{4 \rightarrow 2} = 0.27$  eV, and  $\Delta E_{4 \rightarrow 1} = 0.45$  eV. Thus

$$\lambda_{4 \rightarrow 3} = 9500 \text{ nm} = 9.5 \text{ } \mu\text{m}$$

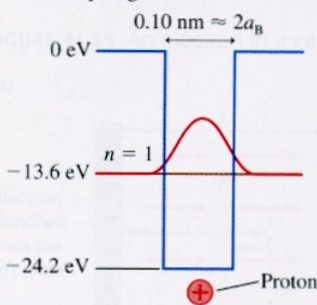
$$\lambda_{4 \rightarrow 2} = 4600 \text{ nm} = 4.6 \text{ } \mu\text{m}$$

$$\lambda_{4 \rightarrow 1} = 2800 \text{ nm} = 2.8 \text{ } \mu\text{m}$$

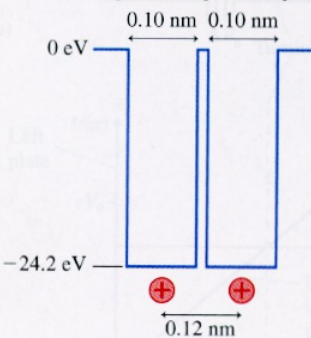
**ASSESS** The  $n = 4$  electrons in this device emit three distinct infrared wavelengths.

**FIGURE 41.27** A molecule can be modeled as two closely spaced potential wells, one representing each atom.

(a) Simple one-dimensional model of a hydrogen atom



(b) An  $\text{H}_2^+$  molecule modeled as an electron with two protons separated by 0.12 nm



## The Covalent Bond

You probably recall from chemistry that a **covalent molecular bond**, such as the bond between the two atoms in molecules such as  $\text{H}_2$  and  $\text{O}_2$ , is a bond in which the electrons are shared between the atoms. The basic idea of covalent bonding can be understood with a one-dimensional quantum-mechanical model.

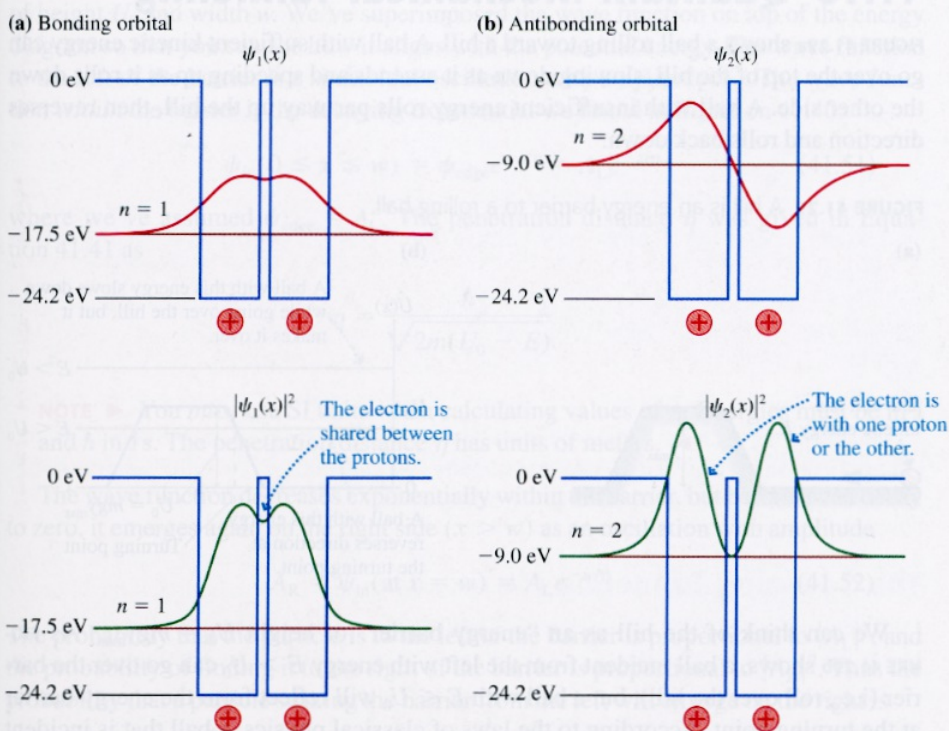
The simplest molecule, the hydrogen molecular ion  $\text{H}_2^+$ , consists of two protons and one electron. Although it seems surprising that such a system could be stable, the two protons form a molecular bond with one electron. This is the simplest covalent bond.

How can we model the  $\text{H}_2^+$  ion? To begin, **FIGURE 41.27a** shows a one-dimensional model of a hydrogen *atom* in which the electron's Coulomb potential energy, with its  $1/r$  dependence, has been approximated by a finite potential well of width 0.10 nm ( $\approx 2a_B$ ) and depth 24.2 eV. You learned in Chapter 39 that an electron in the ground state of the Bohr hydrogen atom orbits the proton with radius  $r_1 = a_B$  (the Bohr radius) and energy  $E_1 = -13.6$  eV. A numerical solution of the Schrödinger equation finds that the ground-state energy of this finite potential well is  $E_1 = -13.6$  eV. This model of a hydrogen atom is oversimplified, but it does have the correct size and ground-state energy.

We can model  $\text{H}_2^+$  by bringing two of these potential wells close together. The molecular bond length of  $\text{H}_2^+$  is known to be  $\approx 0.12$  nm, so **FIGURE 41.27b** shows potential wells with 0.12 nm between their centers. This is a model of  $\text{H}_2^+$ , not a complete  $\text{H}_2$  molecule, because this is the potential energy of a single electron. (Modeling  $\text{H}_2$  is more complex because we would need to consider the repulsion between the two electrons.)

**FIGURE 41.28** shows the allowed energies, wave functions, and probability densities for an electron with this potential energy. The  $n = 1$  wave function has a high probability of being found within the classically forbidden region *between* the two protons. In other words, an electron in this quantum state really is “shared” by the protons and spends most of its time between them.

In contrast, an electron in the  $n = 2$  energy level has zero probability of being found between the two protons because the  $n = 2$  wave function has a node at the center. The probability density shows that an  $n = 2$  electron is “owned” by one proton or the other rather than being shared.

**FIGURE 41.28** The wave functions and probability densities of the electron in  $\text{H}_2^+$ .

To learn the consequences of these wave functions we need to calculate the total energy of the molecule:  $E_{\text{mol}} = E_{\text{p-p}} + E_{\text{elec}}$ . The  $n = 1$  and  $n = 2$  energies shown in Figure 41.28 are the energies  $E_{\text{elec}}$  of the electron. At the same time, the protons repel each other and have electric potential energy  $E_{\text{p-p}}$ . It's not hard to calculate that  $E_{\text{p-p}} = 12.0$  eV for two protons separated by 0.12 nm. Thus

$$E_{\text{mol}} = E_{\text{p-p}} + E_{\text{elec}} = \begin{cases} 12.0 \text{ eV} - 17.5 \text{ eV} = -5.5 \text{ eV} & n = 1 \\ 12.0 \text{ eV} - 9.0 \text{ eV} = +3.0 \text{ eV} & n = 2 \end{cases}$$

The  $n = 1$  molecular energy is less than zero, showing that this is a *bound state*. The  $n = 1$  wave function is called a **bonding molecular orbital**. Although the protons repel each other, the shared electron provides sufficient “glue” to hold the system together. The  $n = 2$  molecular energy is positive, so this is *not* a bound state. The system would be more stable as a hydrogen atom and a distant proton. The  $n = 2$  wave function is called an **antibonding molecular orbital**.

Both  $E_{\text{elec}}$  and  $E_{\text{p-p}}$  depend on the separation between the protons, which we assumed to be 0.12 nm in this calculation. If we were to calculate and graph  $E_{\text{mol}}$  for many different values of the proton separation, the graph would look like the molecular-bond energy curve shown in Figure 41.23. In other words, a molecular bond has an equilibrium length where the bond energy is a minimum *because* of the interplay between  $E_{\text{p-p}}$  and  $E_{\text{elec}}$ .

Although real molecular wave functions are more complex than this one-dimensional model, the  $n = 1$  wave function captures the essential idea of a covalent bond. Notice that a “classical” molecule cannot have a covalent bond because the electron would not be able to exist in the classically forbidden region. Covalent bonds can be understood only within the context of quantum mechanics. In fact, the explanation of molecular bonds was one of the earliest successes of quantum mechanics.