

Molecules and Solids

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The most random atomic arrangement, that of a gas, was well understood in the 1800s as discussed in Chapter 21. In a crystalline solid, the atoms are not randomly arranged; rather, they form a regular array. The symmetry of the arrangement of atoms both stimulated and allowed rapid progress in the field of solid-state physics in the 20th century. Recently, our understanding of liquids and amorphous solids has advanced. (In an amorphous solid such as glass or paraffin, the atoms do not form a regular array.) The recent interest in the physics of low-cost amorphous materials has been driven by their use in such devices as solar cells, memory elements, and fiber-optic waveguides.

We begin this chapter by studying the aggregates of atoms known as molecules. We describe the bonding mechanisms in molecules, the various modes of molecular excitation, and the radiation emitted or absorbed by molecules. Next, we show how molecules combine to form solids. Then, by examining their energy-level structure, we explain the differences between insulating, conducting, semiconducting, and superconducting materials. The chapter also includes discussions of semiconducting junctions and several semiconductor devices.



This photograph relates to two topics discussed in this chapter. The diamond in the ring is a form of carbon. The ring gives a sense of scale for the pile below it, which contains thousands of tiny integrated circuits. In this chapter, we discuss arrangements of atoms in a crystal, such as the tetrahedral structure of diamond, and the development of integrated circuits for use in electronic devices. (Copyright 2009 © National Semiconductor Corporation)

43.1 Molecular Bonds

The bonding mechanisms in a molecule are fundamentally due to electric forces between atoms (or ions). The forces between atoms in the system of a molecule are related to a potential energy function. A stable molecule is expected at a configuration for which the potential energy function for the molecule has its minimum value. (See Section 7.9.)

A potential energy function that can be used to model a molecule should account for two known features of molecular bonding:

1. The force between atoms is repulsive at very small separation distances. When two atoms are brought close to each other, some of their electron shells overlap, resulting in repulsion between the shells. This repulsion is partly electrostatic in origin and partly the result of the exclusion principle. Because all electrons must obey the exclusion principle, some electrons in the overlapping shells are forced into higher energy states and the system energy increases as if a repulsive force existed between the atoms.
2. At somewhat larger separations, the force between atoms is attractive. If that were not true, the atoms in a molecule would not be bound together.

Taking into account these two features, the potential energy for a system of two atoms can be represented by an expression of the form

$$U(r) = -\frac{A}{r^n} + \frac{B}{r^m} \quad (43.1)$$

where r is the internuclear separation distance between the two atoms and n and m are small integers. The parameter A is associated with the attractive force and B with the repulsive force. Example 7.9 gives one common model for such a potential energy function, the Lennard-Jones potential.

Potential energy versus internuclear separation distance for a two-atom system is graphed in Figure 43.1. At large separation distances between the two atoms, the slope of the curve is positive, corresponding to a net attractive force. At the equilibrium separation distance, the attractive and repulsive forces just balance. At this point, the potential energy has its minimum value and the slope of the curve is zero.

A complete description of the bonding mechanisms in molecules is highly complex because bonding involves the mutual interactions of many particles. In this section, we discuss only some simplified models.

Ionic Bonding

When two atoms combine in such a way that one or more outer electrons are transferred from one atom to the other, the bond formed is called an **ionic bond**. Ionic bonds are fundamentally caused by the Coulomb attraction between oppositely charged ions.

A familiar example of an ionically bonded solid is sodium chloride, NaCl, which is common table salt. Sodium, which has the electronic configuration $1s^2 2s^2 2p^6 3s^1$, is ionized relatively easily, giving up its $3s$ electron to form a Na^+ ion. The energy required to ionize the atom to form Na^+ is 5.1 eV. Chlorine, which has the electronic configuration $1s^2 2s^2 2p^5$, is one electron short of the filled-shell structure of argon. If we compare the energy of a system of a free electron and a Cl atom with one in which the electron joins the atom to make the Cl^- ion, we find that the energy of the ion is lower. When the electron makes a transition from the $E = 0$ state to the negative energy state associated with the available shell in the atom, energy is released. This amount of energy is called the **electron affinity** of the atom. For chlorine, the electron affinity is 3.6 eV. Therefore, the energy required to form Na^+ and Cl^- from isolated atoms is $5.1 - 3.6 = 1.5$ eV. It costs 5.1 eV to remove the elec-

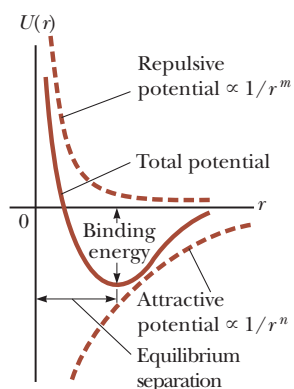


Figure 43.1 Total potential energy as a function of internuclear separation distance for a system of two atoms.

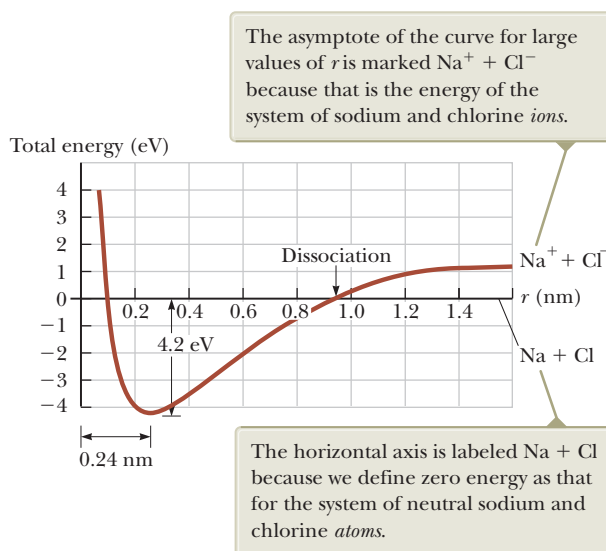


Figure 43.2 Total energy versus internuclear separation distance for Na^+ and Cl^- ions.

tron from the Na atom, but 3.6 eV of it is gained back when that electron is allowed to join with the Cl atom.

Now imagine that these two charged ions interact with one another to form a NaCl “molecule.”¹ The total energy of the NaCl molecule versus internuclear separation distance is graphed in Figure 43.2. At very large separation distances, the energy of the system of ions is 1.5 eV as calculated above. The total energy has a minimum value of -4.2 eV at the equilibrium separation distance, which is approximately 0.24 nm. Hence, the energy required to break the $\text{Na}^+ - \text{Cl}^-$ bond and form neutral sodium and chlorine atoms, called the **dissociation energy**, is 4.2 eV. The energy of the molecule is lower than that of the system of two neutral atoms. Consequently, it is **energetically favorable** for the molecule to form: if a lower energy state of a system exists, the system tends to emit energy to achieve this lower energy state. The system of neutral sodium and chlorine atoms can reduce its total energy by transferring energy out of the system (by electromagnetic radiation, for example) and forming the NaCl molecule.

Covalent Bonding

A **covalent bond** between two atoms is one in which electrons supplied by either one or both atoms are shared by the two atoms. Many diatomic molecules—such as H_2 , F_2 , and CO —owe their stability to covalent bonds. The bond between two hydrogen atoms can be described by using atomic wave functions. The ground-state wave function for a hydrogen atom (Chapter 42) is

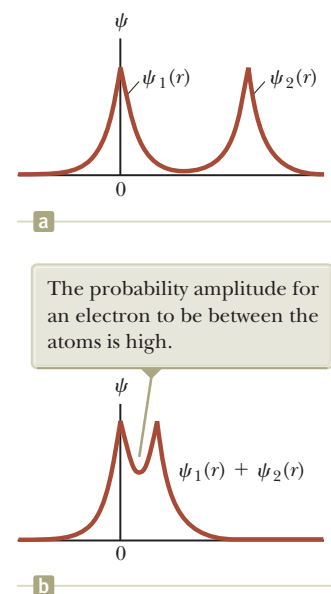
$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

This wave function is graphed in Active Figure 43.3a for two hydrogen atoms that are far apart. There is very little overlap of the wave functions $\psi_1(r)$ for atom 1, located at $r = 0$, and $\psi_2(r)$ for atom 2, located some distance away. Suppose now the two atoms are brought close together. As that happens, their wave functions overlap and form the compound wave function $\psi_1(r) + \psi_2(r)$ shown in Active Figure 43.3b. Notice that the probability amplitude is larger between the atoms than it is on either side of the combination of atoms. As a result, the probability is higher that the electrons associated with the atoms will be located between the atoms than on the outer regions of the system. Consequently, the average position of negative

Pitfall Prevention 43.1

Ionic and Covalent Bonds

In practice, these descriptions of ionic and covalent bonds represent extreme ends of a spectrum of bonds involving electron transfer. In a real bond, the electron may not be *completely* transferred as in an ionic bond or *equally* shared as in a covalent bond. Therefore, real bonds lie somewhere between these extremes.



ACTIVE FIGURE 43.3

Ground-state wave functions $\psi_1(r)$ and $\psi_2(r)$ for two atoms making a covalent bond. (a) The atoms are far apart, and their wave functions overlap minimally. (b) The atoms are close together, forming a composite wave function $\psi_1(r) + \psi_2(r)$ for the system.

¹NaCl does not tend to form as an isolated molecule at room temperature. In the solid state, NaCl forms a crystalline array of ions as described in Section 43.3. In the liquid state or in solution with water, the Na^+ and Cl^- ions dissociate and are free to move relative to each other.

charge in the system is halfway between the atoms. This scenario can be modeled as if there were a fixed negative charge between the atoms, exerting attractive Coulomb forces on both nuclei. Therefore, there is an overall attractive force between the atoms, resulting in a covalent bond.

Because of the exclusion principle, the two electrons in the ground state of H_2 must have antiparallel spins. Also because of the exclusion principle, if a third H atom is brought near the H_2 molecule, the third electron would have to occupy a higher energy level, which is not an energetically favorable situation. For this reason, the H_3 molecule is not stable and does not form.

Van der Waals Bonding

Ionic and covalent bonds occur between atoms to form molecules or ionic solids, so they can be described as bonds *within* molecules. Two additional types of bonds, van der Waals bonds and hydrogen bonds, can occur *between* molecules.

You might think that two neutral molecules would not interact by means of the electric force because they each have zero net charge. They are attracted to each other, however, by weak electrostatic forces called **van der Waals forces**. Likewise, atoms that do not form ionic or covalent bonds are attracted to each other by van der Waals forces. Noble gas atoms, for example, because of their filled shell structure, do not generally form molecules or bond to each other to form a liquid. Because of van der Waals forces, however, at sufficiently low temperatures at which thermal excitations are negligible, noble gases first condense to liquids and then solidify. (The exception is helium, which does not solidify at atmospheric pressure.)

The van der Waals force results from the following situation. While being electrically neutral, a molecule has a charge distribution with positive and negative centers at different positions in the molecule. As a result, the molecule may act as an electric dipole. (See Section 23.4.) Because of the dipole electric fields, two molecules can interact such that there is an attractive force between them.

There are three types of van der Waals forces. The first type, called the *dipole–dipole force*, is an interaction between two molecules each having a permanent electric dipole moment. For example, polar molecules such as HCl have permanent electric dipole moments and attract other polar molecules.

The second type, the *dipole–induced dipole force*, results when a polar molecule having a permanent electric dipole moment induces a dipole moment in a nonpolar molecule. In this case, the electric field of the polar molecule creates the dipole moment in the nonpolar molecule, which then results in an attractive force between the molecules.

The third type is called the *dispersion force*, an attractive force that occurs between two nonpolar molecules. In this case, although the average dipole moment of a nonpolar molecule is zero, the average of the square of the dipole moment is non-zero because of charge fluctuations. Two nonpolar molecules near each other tend to have dipole moments that are correlated in time so as to produce an attractive van der Waals force.

Hydrogen Bonding

Because hydrogen has only one electron, it is expected to form a covalent bond with only one other atom within a molecule. A hydrogen atom in a given molecule can also form a second type of bond between molecules called a **hydrogen bond**. Let's use the water molecule H_2O as an example. In the two covalent bonds in this molecule, the electrons from the hydrogen atoms are more likely to be found near the oxygen atom than near the hydrogen atoms, leaving essentially bare protons at the positions of the hydrogen atoms. This unshielded positive charge can be attracted to the negative end of another polar molecule. Because the proton is unshielded by electrons, the negative end of the other molecule can come very close to the proton to form a bond strong enough to form a solid crystalline structure, such as

that of ordinary ice. The bonds within a water molecule are covalent, but the bonds between water molecules in ice are hydrogen bonds.

The hydrogen bond is relatively weak compared with other chemical bonds and can be broken with an input energy of approximately 0.1 eV. Because of this weakness, ice melts at the low temperature of 0°C. Even though this bond is weak, however, hydrogen bonding is a critical mechanism responsible for the linking of biological molecules and polymers. For example, in the case of the DNA (deoxyribonucleic acid) molecule, which has a double-helix structure (Fig. 43.4), hydrogen bonds formed by the sharing of a proton between two atoms create linkages between the turns of the helix.

Quick Quiz 43.1 For each of the following atoms or molecules, identify the most likely type of bonding that occurs between the atoms or between the molecules. Choose from the following list: ionic, covalent, van der Waals, hydrogen. (a) atoms of krypton (b) potassium and chlorine atoms (c) hydrogen fluoride (HF) molecules (d) chlorine and oxygen atoms in a hypochlorite ion (ClO^-)

43.2 Energy States and Spectra of Molecules

Consider an individual molecule in the gaseous phase of a substance. The energy E of the molecule can be divided into four categories: (1) electronic energy, due to the interactions between the molecule's electrons and nuclei; (2) translational energy, due to the motion of the molecule's center of mass through space; (3) rotational energy, due to the rotation of the molecule about its center of mass; and (4) vibrational energy, due to the vibration of the molecule's constituent atoms:

$$E = E_{\text{el}} + E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}}$$

We explored the roles of translational, rotational, and vibrational energy of molecules in determining the molar specific heats of gases in Sections 21.2 and 21.4. Because the translational energy is unrelated to internal structure, this molecular energy is unimportant in interpreting molecular spectra. The electronic energy of a molecule is very complex because it involves the interaction of many charged particles, but various techniques have been developed to approximate its values. Although the electronic energies can be studied, significant information about a molecule can be determined by analyzing its quantized rotational and vibrational energy states. Transitions between these states give spectral lines in the microwave and infrared regions of the electromagnetic spectrum, respectively.

Rotational Motion of Molecules

Let's consider the rotation of a molecule around its center of mass, confining our discussion to the diatomic molecule (Active Fig. 43.5a on page 1300) but noting that the same ideas can be extended to polyatomic molecules. A diatomic molecule aligned along a y axis has only two rotational degrees of freedom, corresponding to rotations about the x and z axes passing through the molecule's center of mass. We discussed the rotation of such a molecule and its contribution to the specific heat of a gas in Section 21.4. If ω is the angular frequency of rotation about one of these axes, the rotational kinetic energy of the molecule about that axis can be expressed as

$$E_{\text{rot}} = \frac{1}{2}I\omega^2 \quad (43.2)$$

In this equation, I is the moment of inertia of the molecule about its center of mass, given by

$$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r^2 = \mu r^2 \quad (43.3)$$



Douglas Struthers/Stone/Getty Images

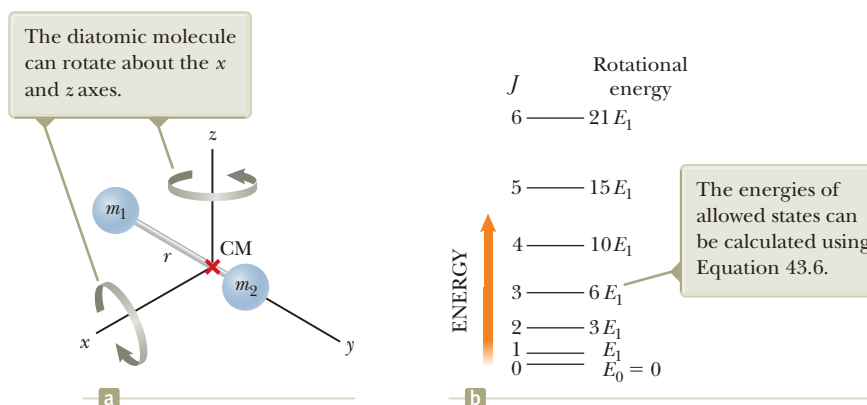
Figure 43.4 DNA molecules are held together by hydrogen bonds.

◀ Total energy of a molecule

◀ Moment of inertia for a diatomic molecule

ACTIVE FIGURE 43.5

Rotation of a diatomic molecule around its center of mass. (a) A diatomic molecule oriented along the y axis. (b) Allowed rotational energies of a diatomic molecule expressed as multiples of $E_1 = \hbar^2/I$.



where m_1 and m_2 are the masses of the atoms that form the molecule, r is the atomic separation, and μ is the **reduced mass** of the molecule (see Example 41.5 and Problem 40 in Chapter 41):

Reduced mass of a diatomic molecule ▶

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (43.4)$$

The magnitude of the molecule's angular momentum about its center of mass is $L = I\omega$, which classically can have any value. Quantum mechanics, however, restricts the molecule to certain quantized rotational frequencies such that the angular momentum of the molecule has the values²

Allowed values of rotational angular momentum ▶

$$L = \sqrt{J(J+1)} \hbar \quad J = 0, 1, 2, \dots \quad (43.5)$$

where J is an integer called the **rotational quantum number**. Combining Equations 43.5 and 43.2, we obtain an expression for the allowed values of the rotational kinetic energy of the molecule:

Allowed values of rotational energy ▶

$$E_{\text{rot}} = \frac{1}{2}I\omega^2 = \frac{1}{2I}(I\omega)^2 = \frac{L^2}{2I} = \frac{(\sqrt{J(J+1)} \hbar)^2}{2I} \quad (43.6)$$

The allowed rotational energies of a diatomic molecule are plotted in Active Figure 43.5b. As the quantum number J goes up, the states become farther apart as displayed earlier for rotational energy levels in Figure 21.8.

For most molecules, transitions between adjacent rotational energy levels result in radiation that lies in the microwave range of frequencies ($f \sim 10^{11}$ Hz). When a molecule absorbs a microwave photon, the molecule jumps from a lower rotational energy level to a higher one. The allowed rotational transitions of linear molecules are regulated by the selection rule $\Delta J = \pm 1$. Given this selection rule, all absorption lines in the spectrum of a linear molecule correspond to energy separations equal to $E_J - E_{J-1}$, where $J = 1, 2, 3, \dots$. From Equation 43.6, we see that the energies of the absorbed photons are given by

Energy of a photon absorbed in a transition between adjacent rotational levels ▶

$$E_{\text{photon}} = \Delta E_{\text{rot}} = E_J - E_{J-1} = \frac{\hbar^2}{2I}[J(J+1) - (J-1)J]$$

$$E_{\text{photon}} = \frac{\hbar^2}{I}J = \frac{\hbar^2}{4\pi^2 I}J \quad J = 1, 2, 3, \dots \quad (43.7)$$

²Equation 43.5 is similar to Equation 42.27 for orbital angular momentum in an atom. The relationship between the magnitude of the angular momentum of a system and the associated quantum number is the same as it is in these equations for *any* system that exhibits rotation as long as the potential energy function for the system is spherically symmetric.

where J is the rotational quantum number of the higher energy state. Because $E_{\text{photon}} = hf$, where f is the frequency of the absorbed photon, we see that the allowed frequency for the transition $J = 0$ to $J = 1$ is $f_1 = h/4\pi^2 I$. The frequency corresponding to the $J = 1$ to $J = 2$ transition is $2f_1$, and so on. These predictions are in excellent agreement with the observed frequencies.

Quick Quiz 43.2 A gas of identical diatomic molecules absorbs electromagnetic radiation over a wide range of frequencies. Molecule 1 is in the $J = 0$ rotation state and makes a transition to the $J = 1$ state. Molecule 2 is in the $J = 2$ state and makes a transition to the $J = 3$ state. Is the ratio of the frequency of the photon that excited molecule 2 to that of the photon that excited molecule 1 equal to (a) 1, (b) 2, (c) 3, (d) 4, or (e) impossible to determine?

Example 43.1

Rotation of the CO Molecule

The $J = 0$ to $J = 1$ rotational transition of the CO molecule occurs at a frequency of 1.15×10^{11} Hz.

(A) Use this information to calculate the moment of inertia of the molecule.

SOLUTION

Conceptualize Imagine that the two atoms in Active Figure 43.5a are carbon and oxygen. The center of mass of the molecule is not midway between the atoms because of the difference in masses of the C and O atoms.

Categorize The statement of the problem tells us to categorize this example as one involving a quantum-mechanical treatment and to restrict our investigation to the rotational motion of a diatomic molecule.

Analyze Use Equation 43.7 to find the energy of a photon that excites the molecule from the $J = 0$ to the $J = 1$ rotational level:

$$E_{\text{photon}} = \frac{h^2}{4\pi^2 I}(1) = \frac{h^2}{4\pi^2 I}$$

Equate this energy to $E = hf$ for the absorbed photon and solve for I :

$$\frac{h^2}{4\pi^2 I} = hf \rightarrow I = \frac{h}{4\pi^2 f}$$

Substitute the frequency given in the problem statement:

$$I = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{4\pi^2 (1.15 \times 10^{11} \text{ s}^{-1})} = 1.46 \times 10^{-46} \text{ kg} \cdot \text{m}^2$$

(B) Calculate the bond length of the molecule.

SOLUTION

Find the reduced mass μ of the CO molecule:

$$\begin{aligned} \mu &= \frac{m_1 m_2}{m_1 + m_2} = \frac{(12 \text{ u})(16 \text{ u})}{12 \text{ u} + 16 \text{ u}} = 6.86 \text{ u} \\ &= (6.86 \text{ u}) \left(\frac{1.66 \times 10^{-27} \text{ kg}}{1 \text{ u}} \right) = 1.14 \times 10^{-26} \text{ kg} \end{aligned}$$

Solve Equation 43.3 for r and substitute for the reduced mass and the moment of inertia from part (A):

$$\begin{aligned} r &= \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.46 \times 10^{-46} \text{ kg} \cdot \text{m}^2}{1.14 \times 10^{-26} \text{ kg}}} \\ &= 1.13 \times 10^{-10} \text{ m} = 0.113 \text{ nm} \end{aligned}$$

Finalize The moment of inertia of the molecule and the separation distance between the atoms are both very small, as expected for a microscopic system.

WHAT IF? What if another photon of frequency 1.15×10^{11} Hz is incident on the CO molecule while that molecule is in the $J = 1$ state? What happens?

continued

43.1 cont.

Answer Because the rotational quantum states are not equally spaced in energy, the $J = 1$ to $J = 2$ transition does not have the same energy as the $J = 0$ to $J = 1$ transition. Therefore, the molecule will *not* be excited to the $J = 2$ state. Two possibilities exist. The photon could pass by the molecule with no interaction, or the photon could induce a stimulated emission, similar to that for atoms and discussed in Section 42.9. In this case, the molecule makes a transition back to the $J = 0$ state and the original photon and a second identical photon leave the scene of the interaction.

Vibrational Motion of Molecules

If we consider a molecule to be a flexible structure in which the atoms are bonded together by “effective springs” as shown in Active Figure 43.6a, we can model the molecule as a simple harmonic oscillator as long as the atoms in the molecule are not too far from their equilibrium positions. Recall from Section 15.3 that the potential energy function for a simple harmonic oscillator is parabolic, varying as the square of the displacement from equilibrium. (See Eq. 15.20 and Active Fig. 15.9b.) Active Figure 43.6b shows a plot of potential energy versus atomic separation for a diatomic molecule, where r_0 is the equilibrium atomic separation. For separations close to r_0 , the shape of the potential energy curve closely resembles a parabola.

According to classical mechanics, the frequency of vibration for the system shown in Active Figure 43.6a is given by Equation 15.14:

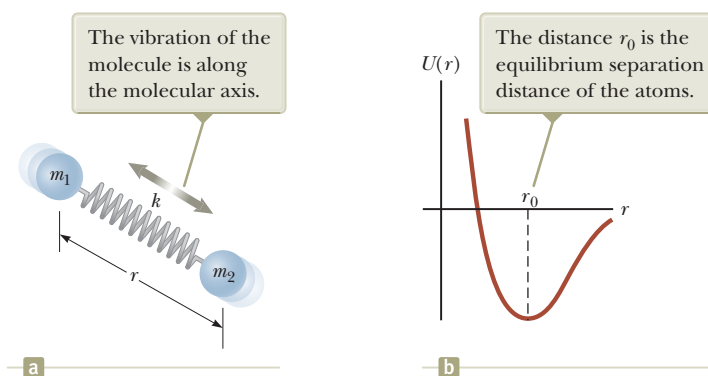
$$f = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (43.8)$$

where k is the effective spring constant and μ is the reduced mass given by Equation 43.4. In Section 21.4, we studied the contribution of a molecule’s vibration to the specific heats of gases.

Quantum mechanics predicts that a molecule vibrates in quantized states as described in Section 41.7. The vibrational motion and quantized vibrational energy can be altered if the molecule acquires energy of the proper value to cause a transition between quantized vibrational states. As discussed in Section 41.7, the allowed vibrational energies are

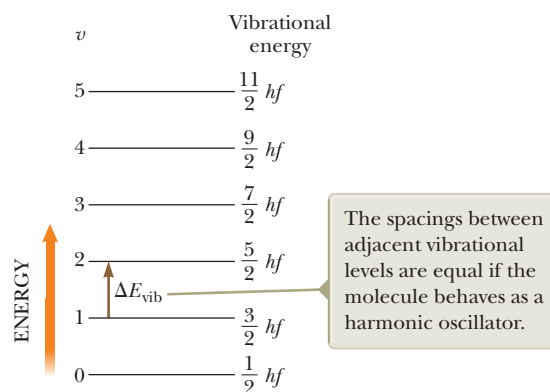
$$E_{\text{vib}} = (v + \frac{1}{2})hf \quad v = 0, 1, 2, \dots \quad (43.9)$$

where v is an integer called the **vibrational quantum number**. (We used n in Section 41.7 for a general harmonic oscillator, but v is often used for the quantum number when discussing molecular vibrations.) If the system is in the lowest vibrational state, for which $v = 0$, its ground-state energy is $\frac{1}{2}hf$. In the first excited vibrational state, $v = 1$ and the energy is $\frac{3}{2}hf$, and so on.



ACTIVE FIGURE 43.6

(a) Effective-spring model of a diatomic molecule. (b) Plot of the potential energy of a diatomic molecule versus atomic separation distance. Compare with Figure 15.11.

**ACTIVE FIGURE 43.7**

Allowed vibrational energies of a diatomic molecule, where f is the frequency of vibration of the molecule, given by Equation 43.8.

Substituting Equation 43.8 into Equation 43.9 gives the following expression for the allowed vibrational energies:

$$E_{\text{vib}} = \left(v + \frac{1}{2}\right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad v = 0, 1, 2, \dots \quad (43.10)$$

◀ **Allowed values of vibrational energy**

The selection rule for the allowed vibrational transitions is $\Delta v = \pm 1$. Transitions between vibrational levels are caused by absorption of photons in the infrared region of the spectrum. The energy of an absorbed photon is equal to the energy difference between any two successive vibrational levels. Therefore, the photon energy is given by

$$E_{\text{photon}} = \Delta E_{\text{vib}} = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad (43.11)$$

The vibrational energies of a diatomic molecule are plotted in Active Figure 43.7. At ordinary temperatures, most molecules have vibrational energies corresponding to the $v = 0$ state because the spacing between vibrational states is much greater than $k_{\text{B}}T$, where k_{B} is Boltzmann's constant and T is the temperature.

Quick Quiz 43.3 A gas of identical diatomic molecules absorbs electromagnetic radiation over a wide range of frequencies. Molecule 1, initially in the $v = 0$ vibrational state, makes a transition to the $v = 1$ state. Molecule 2, initially in the $v = 2$ state, makes a transition to the $v = 3$ state. What is the ratio of the frequency of the photon that excited molecule 2 to that of the photon that excited molecule 1? (a) 1 (b) 2 (c) 3 (d) 4 (e) impossible to determine

Example 43.2**Vibration of the CO Molecule**

The frequency of the photon that causes the $v = 0$ to $v = 1$ transition in the CO molecule is 6.42×10^{13} Hz. We ignore any changes in the rotational energy for this example.

(A) Calculate the force constant k for this molecule.

SOLUTION

Conceptualize Imagine that the two atoms in Active Figure 43.6a are carbon and oxygen. As the molecule vibrates, a given point on the imaginary spring is at rest. This point is not midway between the atoms because of the difference in masses of the C and O atoms.

Categorize The statement of the problem tells us to categorize this example as one involving a quantum-mechanical treatment and to restrict our investigation to the vibrational motion of a diatomic molecule.

continued

43.2 cont.

Analyze Set Equation 43.11 equal to the photon energy hf and solve for the force constant:

$$\frac{h}{2\pi} \sqrt{\frac{k}{\mu}} = hf \rightarrow k = 4\pi^2 \mu f^2$$

Substitute the frequency given in the problem statement and the reduced mass from Example 43.1:

$$k = 4\pi^2 (1.14 \times 10^{-26} \text{ kg}) (6.42 \times 10^{13} \text{ s}^{-1})^2 = 1.85 \times 10^3 \text{ N/m}$$

(B) What is the classical amplitude A of vibration for this molecule in the $v = 0$ vibrational state?

SOLUTION

Equate the maximum elastic potential energy $\frac{1}{2}kA^2$ in the molecule (Eq. 15.21) to the vibrational energy given by Equation 43.10 with $v = 0$ and solve for A :

$$\frac{1}{2}kA^2 = \frac{h}{4\pi} \sqrt{\frac{k}{\mu}} \rightarrow A = \sqrt{\frac{h}{2\pi} \left(\frac{1}{\mu k}\right)^{1/4}}$$

Substitute the value for k from part (A) and the value for μ :

$$A = \sqrt{\frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{2\pi} \left[\frac{1}{(1.14 \times 10^{-26} \text{ kg})(1.85 \times 10^3 \text{ N/m})} \right]^{1/4}}$$

$$= 4.79 \times 10^{-12} \text{ m} = 0.00479 \text{ nm}$$

Finalize Comparing this result with the bond length of 0.113 nm we calculated in Example 43.1 shows that the classical amplitude of vibration is approximately 4% of the bond length.

Molecular Spectra

In general, a molecule vibrates and rotates simultaneously. To a first approximation, these motions are independent of each other, so the total energy of the molecule for these motions is the sum of Equations 43.6 and 43.9:

$$E = (v + \frac{1}{2})hf + \frac{\hbar^2}{2I}J(J + 1) \quad (43.12)$$

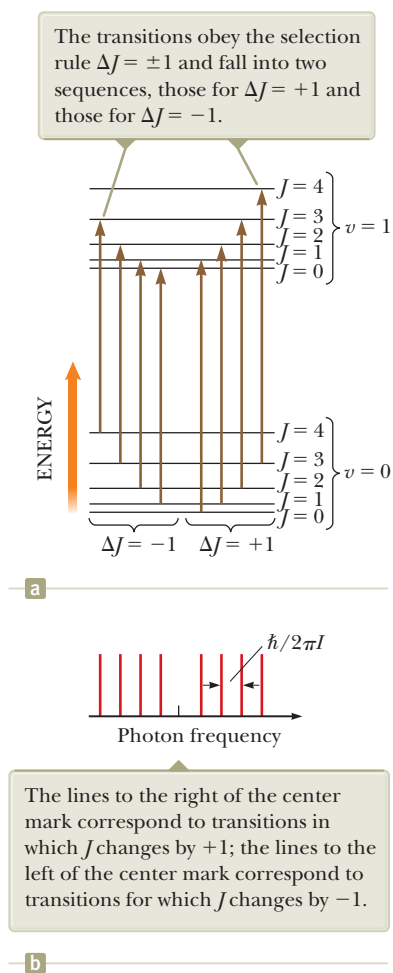
The energy levels of any molecule can be calculated from this expression, and each level is indexed by the two quantum numbers v and J . From these calculations, an energy-level diagram like the one shown in Active Figure 43.8a can be constructed. For each allowed value of the vibrational quantum number v , there is a complete set of rotational levels corresponding to $J = 0, 1, 2, \dots$. The energy separation between successive rotational levels is much smaller than the separation between successive vibrational levels. As noted earlier, most molecules at ordinary temperatures are in the $v = 0$ vibrational state; these molecules can be in various rotational states as Active Figure 43.8a shows.

When a molecule absorbs a photon with the appropriate energy, the vibrational quantum number v increases by one unit while the rotational quantum number J either increases or decreases by one unit as can be seen in Active Figure 43.8. Therefore, the molecular absorption spectrum in Active Figure 43.8b consists of two groups of lines: one group to the right of center and satisfying the selection rules $\Delta J = +1$ and $\Delta v = +1$, and the other group to the left of center and satisfying the selection rules $\Delta J = -1$ and $\Delta v = +1$.

The energies of the absorbed photons can be calculated from Equation 43.12:

$$E_{\text{photon}} = \Delta E = hf + \frac{\hbar^2}{I}(J + 1) \quad J = 0, 1, 2, \dots \quad (\Delta J = +1) \quad (43.13)$$

$$E_{\text{photon}} = \Delta E = hf - \frac{\hbar^2}{I}J \quad J = 1, 2, 3, \dots \quad (\Delta J = -1) \quad (43.14)$$

**ACTIVE FIGURE 43.8**

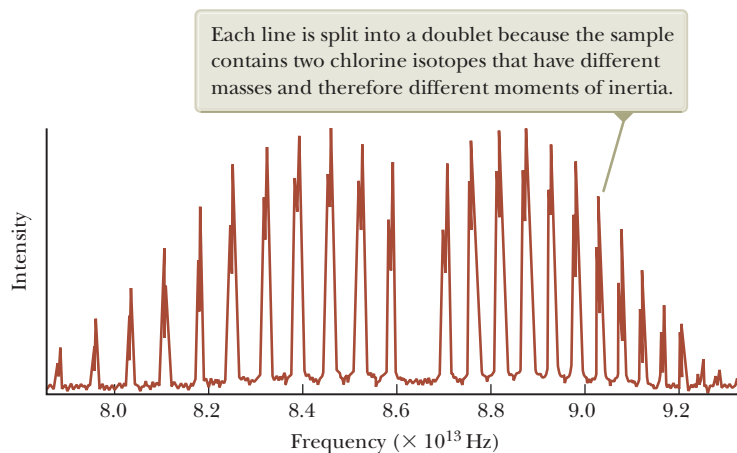
(a) Absorptive transitions between the $v = 0$ and $v = 1$ vibrational states of a diatomic molecule. Compare the energy levels in this figure with those in Figure 21.8. (b) Expected lines in the absorption spectrum of a molecule. These same lines appear in the emission spectrum.

where J is the rotational quantum number of the *initial* state. Equation 43.13 generates the series of equally spaced lines *higher* than the frequency f , whereas Equation 43.14 generates the series *lower* than this frequency. Adjacent lines are separated in frequency by the fundamental unit $\hbar/2\pi I$. Active Figure 43.8b shows the expected frequencies in the absorption spectrum of the molecule; these same frequencies appear in the emission spectrum.

The experimental absorption spectrum of the HCl molecule shown in Figure 43.9 on page 1306 follows this pattern very well and reinforces our model. One peculiarity is apparent, however: each line is split into a doublet. This doubling occurs because two chlorine isotopes (see Section 44.1) were present in the sample used to obtain this spectrum. Because the isotopes have different masses, the two HCl molecules have different values of I .

The intensity of the spectral lines in Figure 43.9 follows an interesting pattern, rising first as one moves away from the central gap (located at about 8.65×10^{13} Hz, corresponding to the forbidden $J = 0$ to $J = 0$ transition) and then falling. This intensity is determined by a product of two functions of J . The first function corresponds to the number of available states for a given value of J . This function is $2J + 1$, corresponding to the number of values of m_j , the molecular rotation analog to m_ℓ for atomic states. For example, the $J = 2$ state has five substates with five values of m_j ($m_j = -2, -1, 0, 1, 2$), whereas the $J = 1$ state has only three substates ($m_j = -1, 0, 1$). Therefore, on average and without regard for the second function described below, five-thirds as many molecules make the transition from the $J = 2$ state as from the $J = 1$ state.

Figure 43.9 Experimental absorption spectrum of the HCl molecule.



The second function determining the envelope of the intensity of the spectral lines is the Boltzmann factor, introduced in Section 21.5. The number of molecules in an excited rotational state is given by

$$n = n_0 e^{-h^2 J(J+1)/(2Ik_B T)}$$

where n_0 is the number of molecules in the $J = 0$ state.

Multiplying these factors together indicates that the intensity of spectral lines should be described by a function of J as follows:

$$I \propto (2J + 1) e^{-h^2 J(J+1)/(2Ik_B T)} \quad (43.15)$$

**Intensity variation in the
vibration–rotation spectrum
of a molecule** ▶

The factor $(2J + 1)$ increases with J while the exponential second factor decreases. The product of the two factors gives a behavior that closely describes the envelope of the spectral lines in Figure 43.9.

The excitation of rotational and vibrational energy levels is an important consideration in current models of global warming. Most of the absorption lines for CO_2 are in the infrared portion of the spectrum. Therefore, visible light from the Sun is not absorbed by atmospheric CO_2 but instead strikes the Earth's surface, warming it. In turn, the surface of the Earth, being at a much lower temperature than the Sun, emits thermal radiation that peaks in the infrared portion of the electromagnetic spectrum (Section 40.1). This infrared radiation is absorbed by the CO_2 molecules in the air instead of radiating out into space. Atmospheric CO_2 acts like a one-way valve for energy from the Sun and is responsible, along with some other atmospheric molecules, for raising the temperature of the Earth's surface above its value in the absence of an atmosphere. This phenomenon is commonly called the "greenhouse effect." The burning of fossil fuels in today's industrialized society adds more CO_2 to the atmosphere. This addition of CO_2 increases the absorption of infrared radiation, raising the Earth's temperature further. In turn, this increase in temperature causes substantial climatic changes. The increased temperature also results in melting of ice from polar regions, raising sea levels worldwide and endangering coastal population centers. In February 2007, the Intergovernmental Panel on Climate Change of the United Nations issued "Climate Change 2007: The Physical Science Basis." This survey, based on the work of more than 2 500 scientists from more than 130 countries, contains chilling statements that global warming is clearly linked to human activity and that the global warming issue is no longer a matter of debate. Solving the global warming problem is extremely important but will be difficult because of the worldwide contributions to the problem. Agreement among nations to address this problem will involve political, economic, and social issues that will necessitate international discussion and cooperation.

Conceptual Example 43.3**Comparing Figures 43.8 and 43.9**

In Active Figure 43.8a, the transitions indicated correspond to spectral lines that are equally spaced as shown in Active Figure 43.8b. The actual spectrum in Figure 43.9, however, shows lines that move closer together as the frequency increases. Why does the spacing of the actual spectral lines differ from the diagram in Active Figure 43.8?

SOLUTION

In Active Figure 43.8, we modeled the rotating diatomic molecule as a rigid object (Chapter 10). In reality, however, as the molecule rotates faster and faster, the effective spring in Active Figure 43.6a stretches and provides the increased force associated with the larger centripetal acceleration of each atom. As the molecule stretches along its length, its moment of inertia I increases. Therefore, the rotational part of the energy expression in Equation 43.12 has an extra dependence on J in the moment of inertia I . Because the increasing moment of inertia is in the denominator, as J increases, the energies do not increase as rapidly with J as indicated in Equation 43.12. With each higher energy level being lower than indicated by Equation 43.12, the energy associated with a transition to that level is smaller, as is the frequency of the absorbed photon, destroying the even spacing of the spectral lines and giving the uneven spacing seen in Figure 43.9.

43.3 Bonding in Solids

A crystalline solid consists of a large number of atoms arranged in a regular array, forming a periodic structure. The ions in the NaCl crystal are ionically bonded, as already noted, and the carbon atoms in diamond form covalent bonds with one another. The metallic bond described at the end of this section is responsible for the cohesion of copper, silver, sodium, and other solid metals.

Ionic Solids

Many crystals are formed by ionic bonding, in which the dominant interaction between ions is the Coulomb force. Consider a portion of the NaCl crystal shown in Figure 43.10a. The red spheres are sodium ions, and the blue spheres are chlorine ions. As shown in Figure 43.10b, each Na^+ ion has six nearest-neighbor Cl^- ions. Similarly, in Figure 43.10c, we see that each Cl^- ion has six nearest-neighbor Na^+ ions. Each Na^+ ion is attracted to its six Cl^- neighbors. The corresponding potential energy is $-6k_e e^2/r$, where k_e is the Coulomb constant and r is the separation distance between each Na^+ and Cl^- . In addition, there are 12 next-nearest-neighbor Na^+ ions at a distance of $\sqrt{2}r$ from the Na^+ ion, and these 12 positive ions exert weaker repulsive forces on the central Na^+ . Furthermore, beyond these 12 Na^+ ions

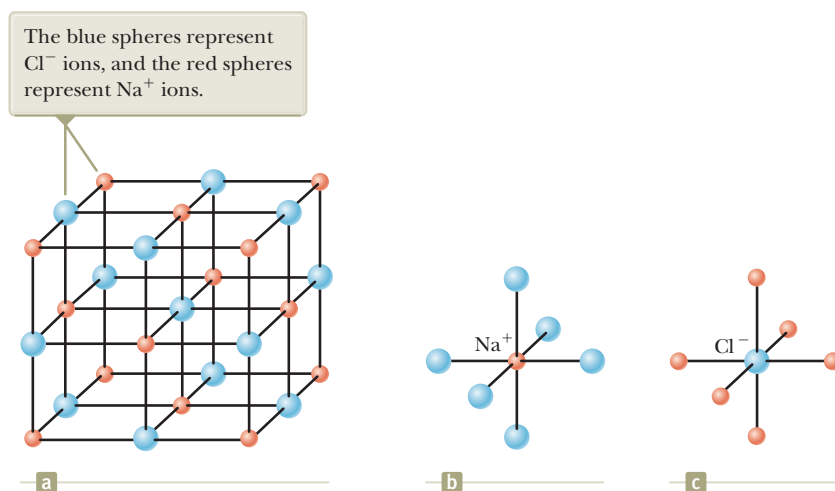


Figure 43.10 (a) Crystalline structure of NaCl. (b) Each positive sodium ion is surrounded by six negative chlorine ions. (c) Each chlorine ion is surrounded by six sodium ions.

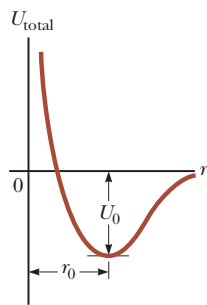


Figure 43.11 Total potential energy versus ion separation distance for an ionic solid, where U_0 is the ionic cohesive energy and r_0 is the equilibrium separation distance between ions.

are more Cl^- ions that exert an attractive force, and so on. The net effect of all these interactions is a resultant negative electric potential energy

$$U_{\text{attractive}} = -\alpha k_e \frac{e^2}{r} \quad (43.16)$$

where α is a dimensionless number known as the **Madelung constant**. The value of α depends only on the particular crystalline structure of the solid. For example, $\alpha = 1.7476$ for the NaCl structure. When the constituent ions of a crystal are brought close together, a repulsive force exists because of electrostatic forces and the exclusion principle as discussed in Section 43.1. The potential energy term B/r^m in Equation 43.1 accounts for this repulsive force. We do not include neighbors other than nearest neighbors here because the repulsive forces occur only for ions that are very close together. (Electron shells must overlap for exclusion-principle effects to become important.) Therefore, we can express the total potential energy of the crystal as

$$U_{\text{total}} = -\alpha k_e \frac{e^2}{r} + \frac{B}{r^m} \quad (43.17)$$

where m in this expression is some small integer.

A plot of total potential energy versus ion separation distance is shown in Figure 43.11. The potential energy has its minimum value U_0 at the equilibrium separation, when $r = r_0$. It is left as a problem (Problem 59) to show that

$$U_0 = -\alpha k_e \frac{e^2}{r_0} \left(1 - \frac{1}{m}\right) \quad (43.18)$$

This minimum energy U_0 is called the **ionic cohesive energy** of the solid, and its absolute value represents the energy required to separate the solid into a collection of isolated positive and negative ions. Its value for NaCl is -7.84 eV per ion pair.

To calculate the **atomic cohesive energy**, which is the binding energy relative to the energy of the neutral atoms, 5.14 eV must be added to the ionic cohesive energy value to account for the transition from Na^+ to Na and 3.62 eV must be subtracted to account for the conversion of Cl^- to Cl. Therefore, the atomic cohesive energy of NaCl is

$$-7.84 \text{ eV} + 5.14 \text{ eV} - 3.62 \text{ eV} = -6.32 \text{ eV}$$

In other words, 6.32 eV of energy per ion pair is needed to separate the solid into isolated neutral atoms of Na and Cl.

Ionic crystals form relatively stable, hard crystals. They are poor electrical conductors because they contain no free electrons; each electron in the solid is bound tightly to one of the ions, so it is not sufficiently mobile to carry current. Ionic crystals have high melting points; for example, the melting point of NaCl is 801°C . Ionic crystals are transparent to visible radiation because the shells formed by the electrons in ionic solids are so tightly bound that visible radiation does not possess sufficient energy to promote electrons to the next allowed shell. Infrared radiation is absorbed strongly because the vibrations of the ions have natural resonant frequencies in the low-energy infrared region.

Covalent Solids

Solid carbon, in the form of diamond, is a crystal whose atoms are covalently bonded. Because atomic carbon has the electronic configuration $1s^2 2s^2 2p^2$, it is four electrons short of filling its $n = 2$ shell, which can accommodate eight electrons. Because of this electron structure, two carbon atoms have a strong attraction for each other, with a cohesive energy of 7.37 eV. In the diamond structure, each carbon atom is covalently bonded to four other carbon atoms located at four corners of a cube as shown in Figure 43.12a.

The crystalline structure of diamond is shown in Figure 43.12b. Notice that each carbon atom forms covalent bonds with four nearest-neighbor atoms. The basic

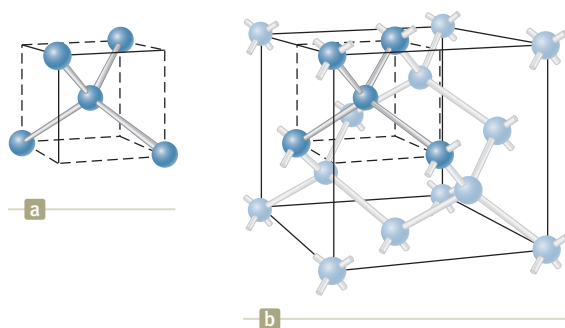


Figure 43.12 (a) Each carbon atom in a diamond crystal is covalently bonded to four other carbon atoms so that a tetrahedral structure is formed. (b) The crystal structure of diamond, showing the tetrahedral bond arrangement.

structure of diamond is called tetrahedral (each carbon atom is at the center of a regular tetrahedron), and the angle between the bonds is 109.5° . Other crystals such as silicon and germanium have the same structure.

Carbon is interesting in that it can form several different types of structures. In addition to the diamond structure, it forms graphite, with completely different properties. In this form, the carbon atoms form flat layers with hexagonal arrays of atoms. A very weak interaction between the layers allows the layers to be removed easily under friction, as occurs in the graphite used in pencil lead.

Carbon atoms can also form a large hollow structure; in this case, the compound is called **buckminsterfullerene** after the famous architect R. Buckminster Fuller, who invented the geodesic dome. The unique shape of this molecule (Fig. 43.13) provides a “cage” to hold other atoms or molecules. Related structures, called “buckytubes” because of their long, narrow cylindrical arrangements of carbon atoms, may provide the basis for extremely strong, yet lightweight, materials.

The atomic cohesive energies of some covalent solids are given in Table 43.1. The large energies account for the hardness of covalent solids. Diamond is particularly hard and has an extremely high melting point (about 4 000 K). Covalently bonded solids are usually very hard, have high bond energies and high melting points, and are good electrical insulators.

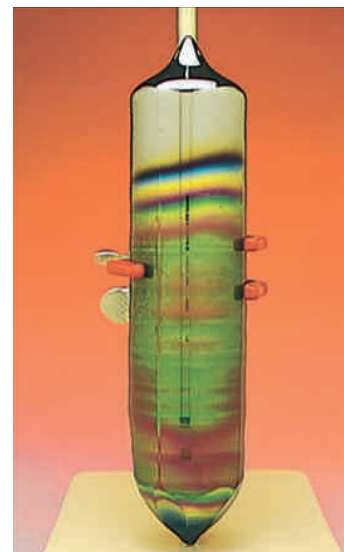
Metallic Solids

Metallic bonds are generally weaker than ionic or covalent bonds. The outer electrons in the atoms of a metal are relatively free to move throughout the material, and the number of such mobile electrons in a metal is large. The metallic structure can be viewed as a “sea” or a “gas” of nearly free electrons surrounding a lattice of positive ions (Fig. 43.14, page 1310). The bonding mechanism in a metal is the attractive force between the entire collection of positive ions and the electron gas. Metals have a cohesive energy in the range of 1 to 3 eV per atom, which is less than the cohesive energies of ionic or covalent solids.

Light interacts strongly with the free electrons in metals. Hence, visible light is absorbed and re-emitted quite close to the surface of a metal, which accounts for the shiny nature of metal surfaces. In addition to the high electrical conductivity

TABLE 43.1 Atomic Cohesive Energies of Some Covalent Solids

Solid	Cohesive Energy (eV per ion pair)
C (diamond)	7.37
Si	4.63
Ge	3.85
InAs	5.70
SiC	6.15
ZnS	6.32
CuCl	9.24



A cylinder of nearly pure crystalline silicon (Si), approximately 25 cm long. Such crystals are cut into wafers and processed to make various semiconductor devices.

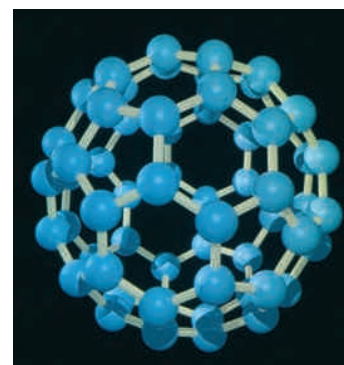


Figure 43.13 Computer rendering of a “buckyball,” short for the molecule buckminsterfullerene. These nearly spherical molecular structures that look like soccer balls were named for the inventor of the geodesic dome. This form of carbon, C_{60} , was discovered by astrophysicists investigating the carbon gas that exists between stars. Scientists are actively studying the properties and potential uses of buckminsterfullerene and related molecules.

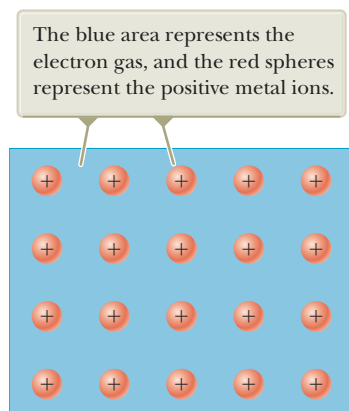


Figure 43.14 Highly schematic diagram of a metal.

of metals produced by the free electrons, the nondirectional nature of the metallic bond allows many different types of metal atoms to be dissolved in a host metal in varying amounts. The resulting *solid solutions*, or *alloys*, may be designed to have particular properties, such as tensile strength, ductility, electrical and thermal conductivity, and resistance to corrosion.

Because the bonding in metals is between all the electrons and all the positive ions, metals tend to bend when stressed. This bending is in contrast to nonmetallic solids, which tend to fracture when stressed. Fracturing results because bonding in nonmetallic solids is primarily with nearest-neighbor ions or atoms. When the distortion causes sufficient stress between some set of nearest neighbors, fracture occurs.

43.4 Free-Electron Theory of Metals

In Section 27.3, we described a classical free-electron theory of electrical conduction in metals that led to Ohm's law. According to this theory, a metal is modeled as a classical gas of conduction electrons moving through a fixed lattice of ions. Although this theory predicts the correct functional form of Ohm's law, it does not predict the correct values of electrical and thermal conductivities.

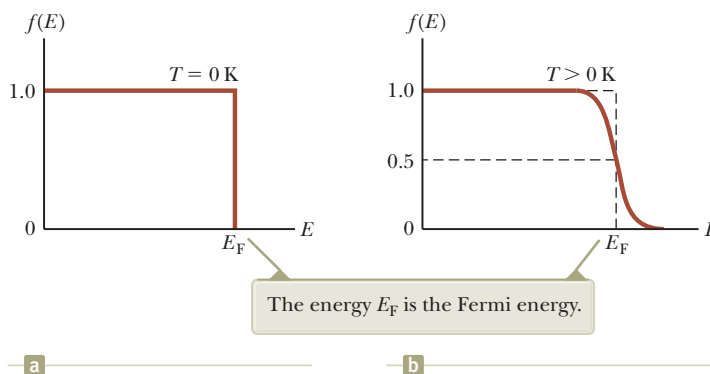
A quantum-based free-electron theory of metals remedies the shortcomings of the classical model by taking into account the wave nature of the electrons. In this model, the outer-shell electrons are free to move through the metal but are trapped within a three-dimensional box formed by the metal surfaces. Therefore, each electron is represented as a particle in a box. As discussed in Section 41.2, particles in a box are restricted to quantized energy levels.

Statistical physics can be applied to a collection of particles in an effort to relate microscopic properties to macroscopic properties as we saw with kinetic theory of gases in Chapter 21. In the case of electrons, it is necessary to use *quantum statistics*, with the requirement that each state of the system can be occupied by only two electrons (one with spin up and the other with spin down) as a consequence of the exclusion principle. The probability that a particular state having energy E is occupied by one of the electrons in a solid is

$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1} \quad (43.19)$$

Fermi–Dirac distribution function

where $f(E)$ is called the **Fermi–Dirac distribution function** and E_F is called the **Fermi energy**. A plot of $f(E)$ versus E at $T = 0$ K is shown in Active Figure 43.15a. Notice that $f(E) = 1$ for $E < E_F$ and $f(E) = 0$ for $E > E_F$. That is, at 0 K, all states having energies less than the Fermi energy are occupied and all states having energies greater than the Fermi energy are vacant. A plot of $f(E)$ versus E at some temperature $T > 0$ K is shown in Active Figure 43.15b. This curve shows that as T increases, the distribution rounds off slightly. Because of thermal excitation, states near and below E_F lose population and states near and above E_F gain population. The Fermi energy E_F also depends on temperature, but the dependence is weak in metals.



ACTIVE FIGURE 43.15

Plot of the Fermi–Dirac distribution function $f(E)$ versus energy at (a) $T = 0$ K and (b) $T > 0$ K.

Let's now follow up on our discussion of the particle in a box in Chapter 41 to generalize the results to a three-dimensional box. Recall that if a particle of mass m is confined to move in a one-dimensional box of length L , the allowed states have quantized energy levels given by Equation 41.14:

$$E_n = \left(\frac{\hbar^2}{8mL^2}\right)n^2 = \left(\frac{\hbar^2\pi^2}{2mL^2}\right)n^2 \quad n = 1, 2, 3, \dots$$

Now imagine a piece of metal in the shape of a solid cube of sides L and volume L^3 and focus on one electron that is free to move anywhere in this volume. Therefore, the electron is modeled as a particle in a three-dimensional box. In this model, we require that $\psi(x, y, z) = 0$ at the boundaries of the metal. It can be shown (see Problem 37) that the energy for such an electron is

$$E = \frac{\hbar^2\pi^2}{2m_eL^2}(n_x^2 + n_y^2 + n_z^2) \quad (43.20)$$

where m_e is the mass of the electron and n_x , n_y , and n_z are quantum numbers. As we expect, the energies are quantized, and each allowed value of the energy is characterized by this set of three quantum numbers (one for each degree of freedom) and the spin quantum number m_s . For example, the ground state, corresponding to $n_x = n_y = n_z = 1$, has an energy equal to $3\hbar^2\pi^2/2m_eL^2$ and can be occupied by two electrons, corresponding to spin up and spin down.

Because of the macroscopic size L of the box, the energy levels for the electrons are very close together. As a result, we can treat the quantum numbers as continuous variables. Under this assumption, the number of allowed states per unit volume that have energies between E and $E + dE$ is

$$g(E) dE = \frac{8\sqrt{2}\pi m_e^{3/2}}{h^3} E^{1/2} dE \quad (43.21)$$

(See Example 43.5.) The function $g(E)$ is called the **density-of-states function**.

If a metal is in thermal equilibrium, the number of electrons per unit volume $N(E) dE$ that have energy between E and $E + dE$ is equal to the product of the number of allowed states and the probability that a state is occupied; that is, $N(E) dE = g(E)f(E) dE$:

$$N(E) dE = \left(\frac{8\sqrt{2}\pi m_e^{3/2}}{h^3} E^{1/2}\right) \left(\frac{1}{e^{(E-E_F)/k_B T} + 1}\right) dE \quad (43.22)$$

Plots of $N(E)$ versus E for two temperatures are given in Figure 43.16.

If n_e is the total number of electrons per unit volume, we require that

$$n_e = \int_0^\infty N(E) dE = \frac{8\sqrt{2}\pi m_e^{3/2}}{h^3} \int_0^\infty \frac{E^{1/2} dE}{e^{(E-E_F)/k_B T} + 1} \quad (43.23)$$

We can use this condition to calculate the Fermi energy. At $T = 0$ K, the Fermi-Dirac distribution function $f(E) = 1$ for $E < E_F$ and $f(E) = 0$ for $E > E_F$. Therefore, at $T = 0$ K, Equation 43.23 becomes

$$n_e = \frac{8\sqrt{2}\pi m_e^{3/2}}{h^3} \int_0^{E_F} E^{1/2} dE = \frac{2}{3} \frac{8\sqrt{2}\pi m_e^{3/2}}{h^3} E_F^{3/2} \quad (43.24)$$

Solving for the Fermi energy at 0 K gives

$$E_F(0) = \frac{\hbar^2}{2m_e} \left(\frac{3n_e}{8\pi}\right)^{2/3} \quad (43.25)$$

The Fermi energies for metals are in the range of a few electron volts. Representative values for various metals are given in Table 43.2 (page 1312). It is left as a problem (Problem 39) to show that the average energy of a free electron in a metal at 0 K is

$$E_{\text{avg}} = \frac{3}{5} E_F \quad (43.26)$$

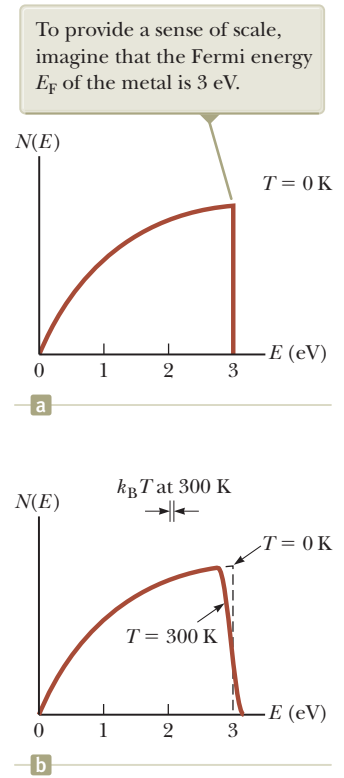


Figure 43.16 Plot of the electron distribution function versus energy in a metal at (a) $T = 0$ K and (b) $T = 300$ K.

◀ Fermi energy at $T = 0$ K

TABLE 43.2 Calculated Values of the Fermi Energy for Metals at 300 K Based on the Free-Electron Theory

Metal	Electron Concentration (m^{-3})	Fermi Energy (eV)
Li	4.70×10^{28}	4.72
Na	2.65×10^{28}	3.23
K	1.40×10^{28}	2.12
Cu	8.46×10^{28}	7.05
Ag	5.85×10^{28}	5.48
Au	5.90×10^{28}	5.53

In summary, we can consider a metal to be a system comprising a very large number of energy levels available to the free electrons. These electrons fill the levels in accordance with the Pauli exclusion principle, beginning with $E = 0$ and ending with E_F . At $T = 0$ K, all levels below the Fermi energy are filled and all levels above the Fermi energy are empty. At 300 K, a small fraction of the free electrons are excited above the Fermi energy.

Example 43.4 The Fermi Energy of Gold

Each atom of gold (Au) contributes one free electron to the metal. Compute the Fermi energy for gold.

SOLUTION

Conceptualize Imagine electrons filling available levels at $T = 0$ K in gold until the solid is neutral. The highest energy filled is the Fermi energy.

Categorize We evaluate the result using a result from this section, so we categorize this example as a substitution problem.

Substitute the concentration of free electrons in gold from Table 43.2 into Equation 43.25 to calculate the Fermi energy at 0 K:

$$E_F(0) = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2(9.11 \times 10^{-31} \text{ kg})} \left[\frac{3(5.90 \times 10^{28} \text{ m}^{-3})}{8\pi} \right]^{2/3}$$

$$= 8.85 \times 10^{-19} \text{ J} = 5.53 \text{ eV}$$

Example 43.5 Deriving Equation 43.21

Based on the allowed states of a particle in a three-dimensional box, derive Equation 43.21.

SOLUTION

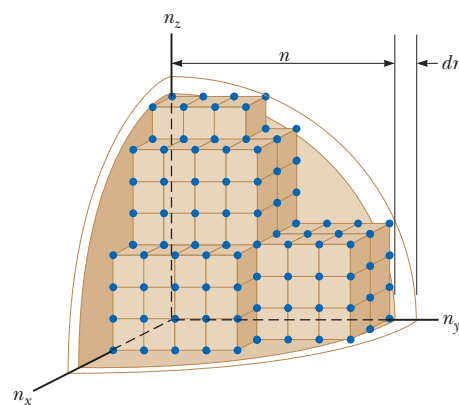
Conceptualize Imagine a particle confined to a three-dimensional box, subject to boundary conditions in three dimensions.

Categorize We categorize this problem as that of a quantum system in which the energies of the particle are quantized. Furthermore, we can base the solution to the problem on our understanding of the particle in a one-dimensional box.

Analyze As noted previously, the allowed states of the particle in a three-dimensional box are described by three quantum numbers n_x , n_y , and n_z . Imagine a

Figure 43.17 (Example 43.5)

The allowed states of particles in a three-dimensional box can be represented by dots (blue circles) in a quantum number space. This space is not traditional space in which a location is specified by coordinates x , y , and z ; rather, it is a space in which allowed states can be specified by coordinates representing the quantum numbers. The dots representing the allowed states are located at integer values of n_x , n_y , and n_z and are therefore at the corners of cubes with sides of “length” 1. The number of allowed states having energies between E and $E + dE$ corresponds to the number of dots in the spherical shell of radius n and thickness dn .



43.5 cont.

three-dimensional *quantum number space* whose axes represent n_x , n_y , and n_z . The allowed states in this space can be represented as dots located at integral values of the three quantum numbers as in Figure 43.17.

Defining $E_0 = \hbar^2\pi^2/2m_eL^2$ and $n = (E/E_0)^{1/2}$, rewrite Equation 43.20:

$$(1) \quad n_x^2 + n_y^2 + n_z^2 = \frac{2m_eL^2}{\hbar^2\pi^2} E = \frac{E}{E_0} = n^2$$

In the quantum number space, Equation (1) is the equation of a sphere of radius n . Therefore, the number of allowed states having energies between E and $E + dE$ is equal to the number of points in a spherical shell of radius n and thickness dn .

Find the “volume” of this shell, which represents the total number of states $G(E) dE$:

$$(2) \quad G(E) dE = \frac{1}{8}(4\pi n^2 dn) = \frac{1}{2}\pi n^2 dn$$

We have taken one-eighth of the total volume because we are restricted to the octant of a three-dimensional space in which all three quantum numbers are positive.

Replace n in Equation (2) with its equivalent in terms of E using the relation $n^2 = E/E_0$ from Equation (1):

$$G(E) dE = \frac{1}{2}\pi \left(\frac{E}{E_0}\right) d\left[\left(\frac{E}{E_0}\right)^{1/2}\right] = \frac{1}{2}\pi \frac{E}{(E_0)^{3/2}} d[(E)^{1/2}]$$

Evaluate the differential:

$$G(E) dE = \frac{1}{2}\pi \left[\frac{E}{(E_0)^{3/2}}\right] \left(\frac{1}{2}E^{-1/2} dE\right) = \frac{1}{4}\pi E_0^{-3/2} E^{1/2} dE$$

Substitute for E_0 from its definition above:

$$\begin{aligned} G(E) dE &= \frac{1}{4}\pi \left(\frac{\hbar^2\pi^2}{2m_eL^2}\right)^{-3/2} E^{1/2} dE \\ &= \frac{\sqrt{2}}{2} \frac{m_e^{3/2}L^3}{\hbar^3\pi^2} E^{1/2} dE \end{aligned}$$

Letting $g(E)$ represent the number of states per unit volume, where L^3 is the volume V of the cubical box in normal space, find $g(E) = G(E)/V$:

$$g(E) dE = \frac{G(E)}{V} dE = \frac{\sqrt{2}}{2} \frac{m_e^{3/2}}{\hbar^3\pi^2} E^{1/2} dE$$

Substitute $\hbar = h/2\pi$:

$$g(E) dE = \frac{4\sqrt{2}\pi m_e^{3/2}}{h^3} E^{1/2} dE$$

Multiply by 2 for the two possible spin states in each particle-in-a-box state:

$$g(E) dE = \frac{8\sqrt{2}\pi m_e^{3/2}}{h^3} E^{1/2} dE$$

Finalize This result is Equation 43.21, which is what we set out to derive.

43.5 Band Theory of Solids

In Section 43.4, the electrons in a metal were modeled as particles free to move around inside a three-dimensional box and we ignored the influence of the parent atoms. In this section, we make the model more sophisticated by incorporating the contribution of the parent atoms that form the crystal.

Recall from Section 41.1 that the probability density $|\psi|^2$ for a system is physically significant, but the probability amplitude ψ is not. Let's consider as an example an atom that has a single s electron outside of a closed shell. Both of the following wave functions are valid for such an atom with atomic number Z :

$$\psi_s^+(r) = +Af(r)e^{-Zr/na_0} \quad \psi_s^-(r) = -Af(r)e^{-Zr/na_0}$$

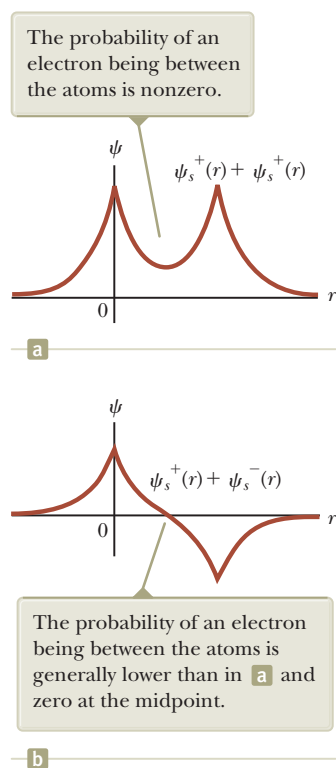


Figure 43.18 The wave functions of two atoms combine to form a composite wave function for the two-atom system when the atoms are close together. (a) Two atoms with wave functions $\psi_s^+(r)$ combine. (b) Two atoms with wave functions $\psi_s^+(r)$ and $\psi_s^-(r)$ combine.

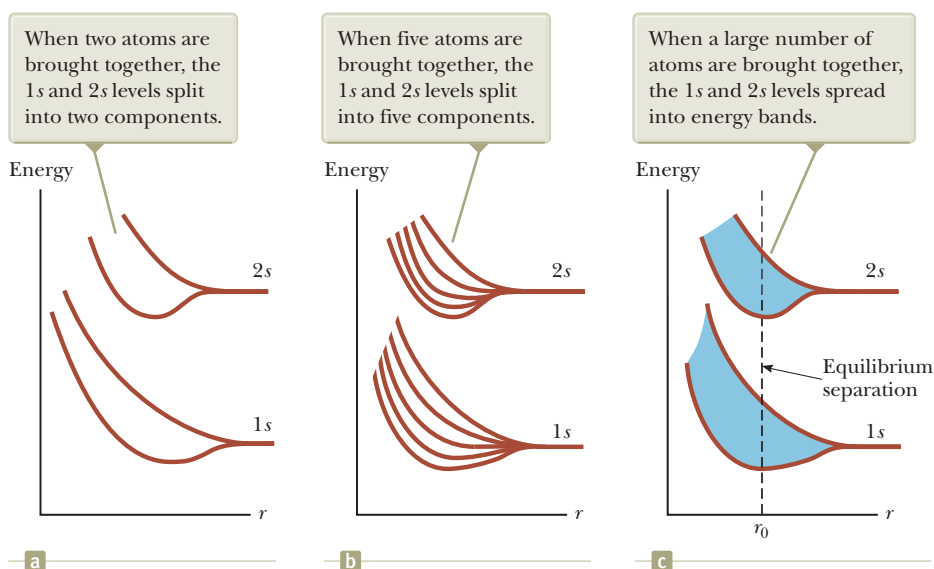
where A is the normalization constant and $f(r)$ is a function³ of r that varies with the value of n . Choosing either of these wave functions leads to the same value of $|\psi|^2$, so both choices are equivalent. A difference arises, however, when two atoms are combined.

If two identical atoms are very far apart, they do not interact and their electronic energy levels can be considered to be those of isolated atoms. Suppose the two atoms are sodium, each having a lone $3s$ electron that is in a well-defined quantum state. As the two sodium atoms are brought closer together, their wave functions begin to overlap as we discussed for covalent bonding in Section 43.1. The properties of the combined system differ depending on whether the two atoms are combined with wave functions $\psi_s^+(r)$ as in Figure 43.18a or whether they are combined with one having wave function $\psi_s^+(r)$ and the other $\psi_s^-(r)$ as in Figure 43.18b. The choice of two atoms with wave function $\psi_s^-(r)$ is physically equivalent to that with two positive wave functions, so we do not consider it separately. When two wave functions $\psi_s^+(r)$ are combined, the result is a composite wave function in which the probability amplitudes add between the atoms. If $\psi_s^+(r)$ combines with $\psi_s^-(r)$, however, the wave functions between the nuclei subtract. Therefore, the composite probability amplitudes for the two possibilities are different. These two possible combinations of wave functions represent two possible states of the two-atom system. We interpret these curves as representing the probability amplitude of finding an electron. The positive–positive curve shows some probability of finding the electron at the midpoint between the atoms. The positive–negative function shows no such probability. A state with a high probability of an electron *between* two positive nuclei must have a different energy than a state with a high probability of the electron being elsewhere! Therefore, the states are *split* into two energy levels due to the two ways of combining the wave functions. The energy difference is relatively small, so the two states are close together on an energy scale.

Figure 43.19a shows this splitting effect as a function of separation distance. For large separations r , the electron clouds do not overlap and there is no splitting. As the atoms are brought closer so that r decreases, the electron clouds overlap and we need to consider the system of two atoms.

When a large number of atoms are brought together to form a solid, a similar phenomenon occurs. The individual wave functions can be brought together in various combinations of $\psi_s^+(r)$ and $\psi_s^-(r)$, each possible combination correspond-

Figure 43.19 Energies of the $1s$ and $2s$ levels in sodium as a function of the separation distance r between atoms.



³The functions $f(r)$ are called *Laguerre polynomials*. They can be found in the quantum treatment of the hydrogen atom in modern physics textbooks.

ing to a different energy. As the atoms are brought close together, the various isolated-atom energy levels split into multiple energy levels for the composite system. This splitting in levels for five atoms in close proximity is shown in Figure 43.19b. In this case, there are five energy levels corresponding to five different combinations of isolated-atom wave functions.

If we extend this argument to the large number of atoms found in solids (on the order of 10^{23} atoms per cubic centimeter), we obtain a large number of levels of varying energy so closely spaced that they may be regarded as a continuous **band** of energy levels as shown in Figure 43.19c. In the case of sodium, it is customary to refer to the continuous distributions of allowed energy levels as *s* bands because the bands originate from the *s* levels of the individual sodium atoms.

Figure 43.20 shows the allowed energy bands of sodium at a fixed separation distance between the atoms. Notice that energy gaps, corresponding to *forbidden energies*, occur between the allowed bands. In addition, some bands exhibit sufficient spreading in energy that there is an overlap between bands arising from different quantum states (*3s* and *3p*).

As indicated by the blue-shaded areas in Figure 43.20, the *1s*, *2s*, and *2p* bands of sodium are each full of electrons because the *1s*, *2s*, and *2p* states of each atom are full. An energy level in which the orbital angular momentum is ℓ can hold $2(2\ell + 1)$ electrons. The factor 2 arises from the two possible electron spin orientations, and the factor $2\ell + 1$ corresponds to the number of possible orientations of the orbital angular momentum. The capacity of each band for a system of N atoms is $2(2\ell + 1)N$ electrons. Therefore, the *1s* and *2s* bands each contain $2N$ electrons ($\ell = 0$), and the *2p* band contains $6N$ electrons ($\ell = 1$). Because sodium has only one *3s* electron and there are a total of N atoms in the solid, the *3s* band contains only N electrons and is partially full as indicated by the blue coloring in Figure 43.20. The *3p* band, which is the higher region of the overlapping bands, is completely empty (all gold in the figure).

Band theory allows us to build simple models to understand the behavior of conductors, insulators, and semiconductors as well as that of semiconductor devices, as we shall discuss in the following sections.

43.6 Electrical Conduction in Metals, Insulators, and Semiconductors

Good electrical conductors contain a high density of free charge carriers, and the density of free charge carriers in insulators is nearly zero. Semiconductors, first introduced in Section 23.2, are a class of technologically important materials in which charge-carrier densities are intermediate between those of insulators and those of conductors. In this section, we discuss the mechanisms of conduction in these three classes of materials in terms of a model based on energy bands.

Metals

If a material is to be a good electrical conductor, the charge carriers in the material must be free to move in response to an applied electric field. Let's consider the electrons in a metal as the charge carriers. The motion of the electrons in response to an electric field represents an increase in energy of the system (the metal lattice and the free electrons) corresponding to the additional kinetic energy of the moving electrons. Therefore, when an electric field is applied to a conductor, electrons must move upward to an available higher energy state on an energy-level diagram.

Figure 43.21 shows a half-filled band in a metal at $T = 0$ K, where the blue region represents levels filled with electrons. Because electrons obey Fermi–Dirac statistics, all levels below the Fermi energy are filled with electrons and all levels above the Fermi energy are empty. The Fermi energy lies in the band at the highest filled state. At temperatures slightly greater than 0 K, some electrons are thermally

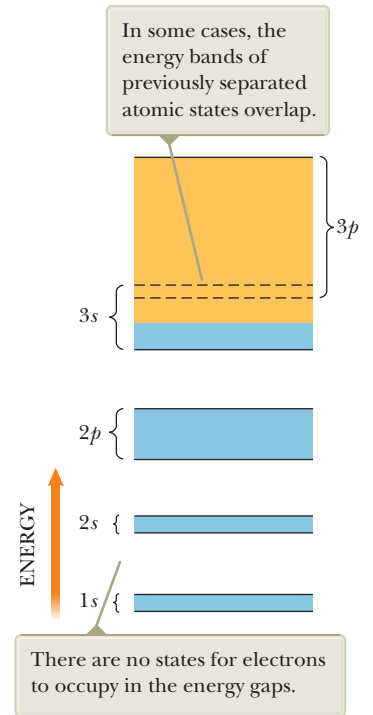


Figure 43.20 Energy bands of a sodium crystal. Blue represents energy bands occupied by the sodium electrons when the atom is in its ground state. Gold represents energy bands that are empty.

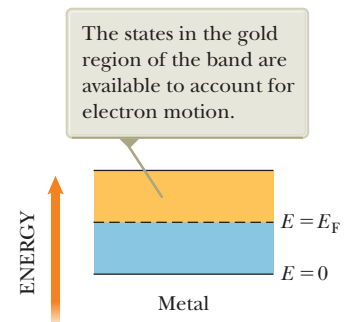


Figure 43.21 Half-filled band of a metal, an electrical conductor. At $T = 0$ K, the Fermi energy lies in the middle of the band.

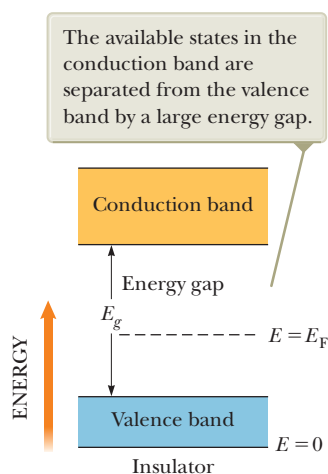


Figure 43.22 An electrical insulator at $T = 0$ K has a filled valence band and an empty conduction band. The Fermi level lies somewhere between these bands in the region known as the energy gap.

TABLE 43.3

Energy-Gap Values for Some Semiconductors

Crystal	E_g (eV)	
	0 K	300 K
Si	1.17	1.14
Ge	0.74	0.67
InP	1.42	1.34
GaP	2.32	2.26
GaAs	1.52	1.42
CdS	2.58	2.42
CdTe	1.61	1.56
ZnO	3.44	3.2
ZnS	3.91	3.6

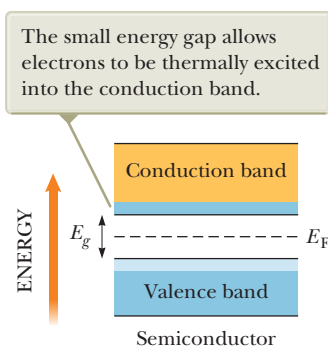


Figure 43.23 Band structure of a semiconductor at ordinary temperatures ($T \approx 300$ K). The energy gap is much smaller than in an insulator.

excited to levels above E_F , but overall there is little change from the 0 K case. If a potential difference is applied to the metal, however, electrons having energies near the Fermi energy require only a small amount of additional energy from the applied electric field to reach nearby empty energy states above the Fermi energy. Therefore, electrons in a metal experiencing only a weak applied electric field are free to move because many empty levels are available close to the occupied energy levels. The model of metals based on band theory demonstrates that metals are excellent electrical conductors.

Insulators

Now consider the two outermost energy bands of a material in which the lower band is filled with electrons and the higher band is empty at 0 K (Fig. 43.22). The lower, filled band is called the **valence band**, and the upper, empty band is the **conduction band**. (The conduction band is the one that is partially filled in a metal.) It is common to refer to the energy separation between the valence and conduction bands as the **energy gap** E_g of the material. The Fermi energy lies somewhere in the energy gap⁴ as shown in Figure 43.22.

Suppose a material has a relatively large energy gap of, for example, approximately 5 eV. At 300 K (room temperature), $k_B T = 0.025$ eV, which is much smaller than the energy gap. At such temperatures, the Fermi–Dirac distribution predicts that very few electrons are thermally excited into the conduction band. There are no available states that lie close in energy above the valence band and into which electrons can move upward to account for the extra kinetic energy associated with motion through the material in response to an electric field. Consequently, the electrons do not move; the material is an insulator. Although an insulator has many vacant states in its conduction band that can accept electrons, these states are separated from the filled states by a large energy gap. Only a few electrons occupy these states, so the overall electrical conductivity of insulators is very small.

Semiconductors

Semiconductors have the same type of band structure as an insulator, but the energy gap is much smaller, on the order of 1 eV. Table 43.3 shows the energy gaps for some representative materials. The band structure of a semiconductor is shown in Figure 43.23. Because the Fermi level is located near the middle of the gap for a semiconductor and E_g is small, appreciable numbers of electrons are thermally excited from the valence band to the conduction band. Because of the many empty levels above the thermally filled levels in the conduction band, a small applied potential difference can easily raise the energy of the electrons in the conduction band, resulting in a moderate current.

At $T = 0$ K, all electrons in these materials are in the valence band and no energy is available to excite them across the energy gap. Therefore, semiconductors are poor conductors at very low temperatures. Because the thermal excitation of electrons across the narrow gap is more probable at higher temperatures, the conductivity of semiconductors increases rapidly with temperature, contrasting sharply with the conductivity of metals, which decreases slowly with increasing temperature.

Charge carriers in a semiconductor can be negative, positive, or both. When an electron moves from the valence band into the conduction band, it leaves behind a vacant site, called a **hole**, in the otherwise filled valence band. This hole (electron-deficient site) acts as a charge carrier in the sense that a free electron from a nearby site can transfer into the hole. Whenever an electron does so, it creates a new hole at the site it abandoned. Therefore, the net effect can be viewed as the hole migrat-

⁴We defined the Fermi energy as the energy of the highest filled state at $T = 0$, which might suggest that the Fermi energy should be at the top of the valence band in Figure 43.22. A more sophisticated general treatment of the Fermi energy, however, shows that it is located at that energy at which the probability of occupation is one-half (see Active Fig. 43.15b). According to this definition, the Fermi energy lies in the energy gap between the bands.

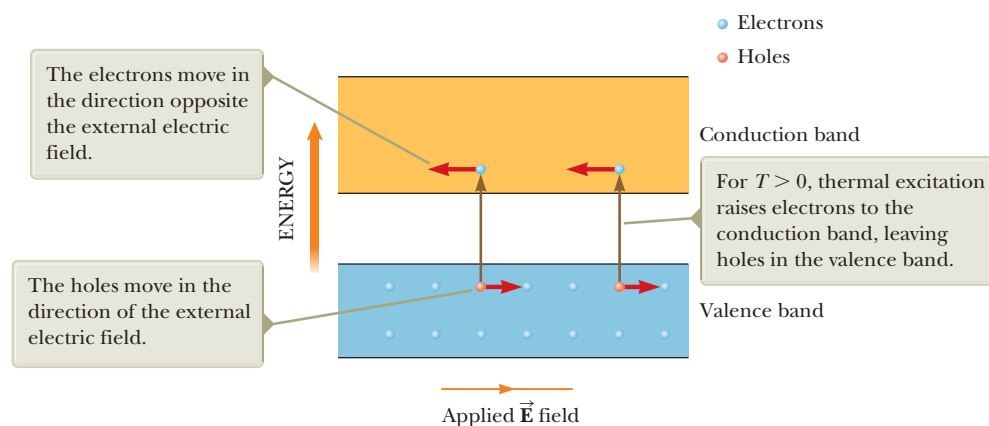


Figure 43.24 Movement of charges (holes and electrons) in an intrinsic semiconductor.

ing through the material in the direction opposite the direction of electron movement. The hole behaves as if it were a particle with a positive charge $+e$.

A pure semiconductor crystal containing only one element or one compound is called an **intrinsic semiconductor**. In these semiconductors, there are equal numbers of conduction electrons and holes. Such combinations of charges are called **electron–hole pairs**. In the presence of an external electric field, the holes move in the direction of the field and the conduction electrons move in the direction opposite the field (Fig. 43.24). Because the electrons and holes have opposite signs, both motions correspond to a current in the same direction.

Quick Quiz 43.4 Consider the data on three materials given in the table.

Material	Conduction Band	E_g
A	Empty	1.2 eV
B	Half full	1.2 eV
C	Empty	8.0 eV

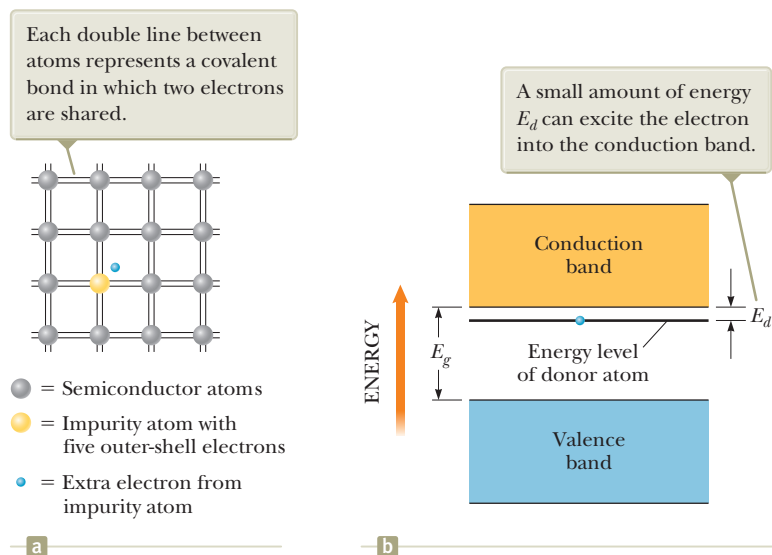
Identify each material as a conductor, an insulator, or a semiconductor.

Doped Semiconductors

When impurities are added to a semiconductor, both the band structure of the semiconductor and its resistivity are modified. The process of adding impurities, called **doping**, is important in controlling the conductivity of semiconductors. For example, when an atom containing five outer-shell electrons, such as arsenic, is added to a Group IV semiconductor, four of the electrons form covalent bonds with atoms of the semiconductor and one is left over (Fig. 43.25a on page 1318). This extra electron is nearly free of its parent atom and can be modeled as having an energy level that lies in the energy gap, immediately below the conduction band (Fig. 43.25b). Such a pentavalent atom in effect donates an electron to the structure and hence is referred to as a **donor atom**. Because the spacing between the energy level of the electron of the donor atom and the bottom of the conduction band is very small (typically, approximately 0.05 eV), only a small amount of thermal excitation is needed to cause this electron to move into the conduction band. (Recall that the average energy of an electron at room temperature is approximately $k_B T \approx 0.025$ eV.) Semiconductors doped with donor atoms are called ***n*-type semiconductors** because the majority of charge carriers are electrons, which are ***n*egatively charged**.

If a Group IV semiconductor is doped with atoms containing three outer-shell electrons, such as indium and aluminum, the three electrons form covalent bonds with neighboring semiconductor atoms, leaving an electron deficiency—a hole—where the fourth bond would be if an impurity-atom electron were available to form

Figure 43.25 (a) Two-dimensional representation of a semiconductor consisting of Group IV atoms (gray) and an impurity atom (yellow) that has five outer-shell electrons. (b) Energy-band diagram for a semiconductor in which the nearly free electron of the impurity atom lies in the energy gap, immediately below the bottom of the conduction band.



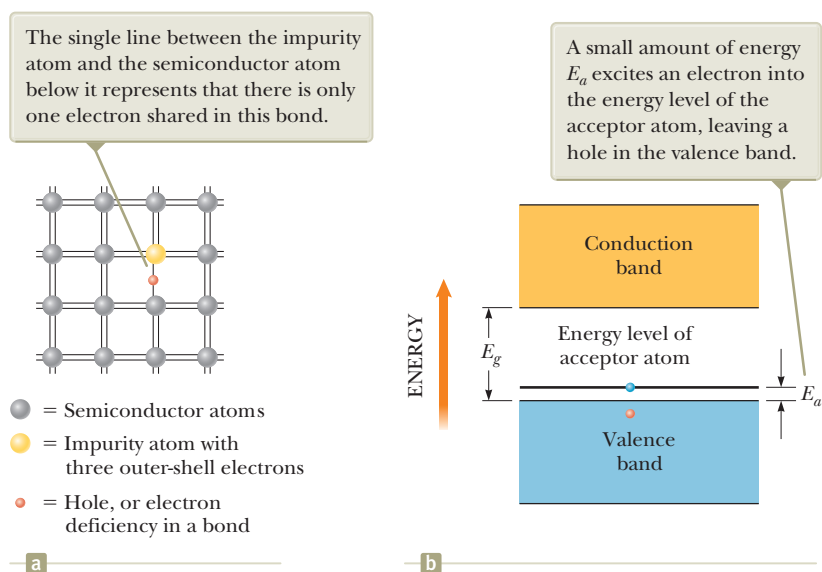
it (Fig. 43.26a). This situation can be modeled by placing an energy level in the energy gap, immediately above the valence band, as in Figure 43.26b. An electron from the valence band has enough energy at room temperature to fill this impurity level, leaving behind a hole in the valence band. This hole can carry current in the presence of an electric field. Because a trivalent atom accepts an electron from the valence band, such impurities are referred to as **acceptor atoms**. A semiconductor doped with trivalent (acceptor) impurities is known as a ***p*-type semiconductor** because the majority of charge carriers are *positively* charged holes.

When conduction in a semiconductor is the result of acceptor or donor impurities, the material is called an **extrinsic semiconductor**. The typical range of doping densities for extrinsic semiconductors is 10^{13} to 10^{19} cm^{-3} , whereas the electron density in a typical semiconductor is roughly 10^{21} cm^{-3} .

43.7 Semiconductor Devices

The electronics of the first half of the 20th century was based on vacuum tubes, in which electrons pass through empty space between a cathode and an anode. We have seen vacuum tubes in Figure 29.6 (the television picture tube), Figure 29.10

Figure 43.26 (a) Two-dimensional representation of a semiconductor consisting of Group IV atoms (gray) and an impurity atom (yellow) having three outer-shell electrons. (b) Energy-band diagram for a semiconductor in which the energy level associated with the trivalent impurity atom lies in the energy gap, immediately above the top of the valence band.



(circular electron beam), Figure 29.15a (Thomson's apparatus for measuring e/m_e for the electron), and Active Figure 40.9 (photoelectric effect apparatus).

The transistor was invented in 1948, leading to a shift away from vacuum tubes and toward semiconductors as the basis of electronic devices. This phase of electronics has been under way for several decades. As discussed in Chapter 41, there may be a new phase of electronics in the near future using nanotechnological devices employing quantum dots and other nanoscale structures.

In this section, we discuss electronic devices based on semiconductors, which are still in wide use and will be for many years to come.

The Junction Diode

A fundamental unit of a semiconductor device is formed when a p -type semiconductor is joined to an n -type semiconductor to form a p - n junction. A **junction diode** is a device that is based on a single p - n junction. The role of a diode of any type is to pass current in one direction but not the other. Therefore, it acts as a one-way valve for current.

The p - n junction shown in Figure 43.27a consists of three distinct regions: a p region, an n region, and a small area that extends several micrometers to either side of the interface, called a *depletion region*.

The depletion region may be visualized as arising when the two halves of the junction are brought together. The mobile n -side donor electrons nearest the junction (deep-blue area in Fig. 43.27a) diffuse to the p side and fill holes located there, leaving behind immobile positive ions. While this process occurs, we can model the holes that are being filled as diffusing to the n side, leaving behind a region (brown area in Fig. 43.27a) of fixed negative ions.

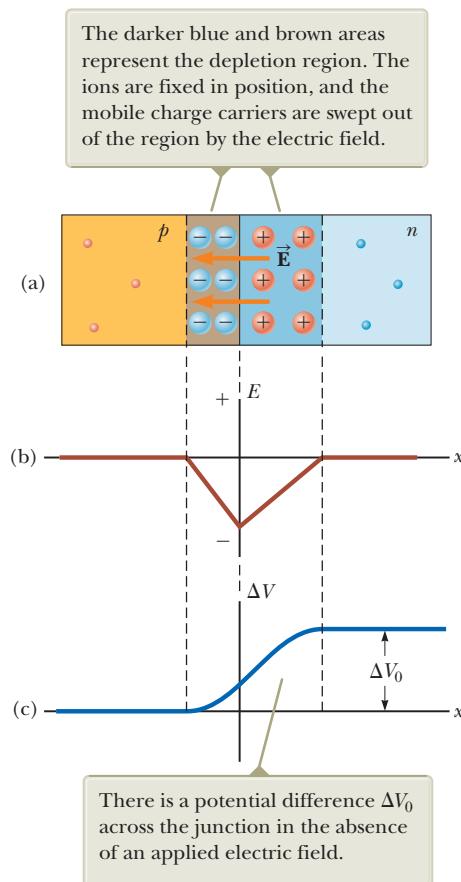
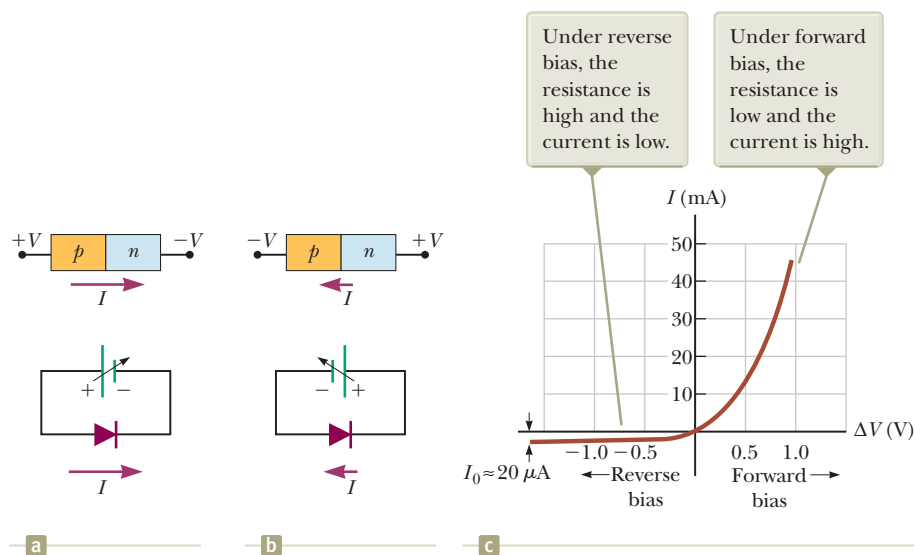


Figure 43.27 (a) Physical arrangement of a p - n junction. (b) Internal electric field magnitude versus x for the p - n junction. (c) Internal electric potential difference ΔV versus x for the p - n junction.

Figure 43.28 (a) A p - n junction under forward bias. The upper diagram shows the potentials applied at the ends of the junction. Below that is a circuit diagram showing a battery with an adjustable voltage. (b) When the battery is reversed and the p - n junction is under reverse bias, the current is very small. (c) The characteristic curve for a real p - n junction.



Because the two sides of the depletion region each carry a net charge, an internal electric field on the order of 10^4 to 10^6 V/cm exists in the depletion region (see Fig. 43.27b). This field produces an electric force on any remaining mobile charge carriers that sweeps them out of the depletion region, so named because it is a region depleted of mobile charge carriers. This internal electric field creates an internal potential difference ΔV_0 that prevents further diffusion of holes and electrons across the junction and thereby ensures zero current in the junction when no potential difference is applied.

The operation of the junction as a diode is easiest to understand in terms of the potential difference graph shown in Figure 43.27c. If a voltage ΔV is applied to the junction such that the p side is connected to the positive terminal of a voltage source as shown in Figure 43.28a, the internal potential difference ΔV_0 across the junction decreases; the decrease results in a current that increases exponentially with increasing forward voltage, or *forward bias*. For *reverse bias* (where the n side of the junction is connected to the positive terminal of a voltage source), the internal potential difference ΔV_0 increases with increasing reverse bias; the increase results in a very small reverse current that quickly reaches a saturation value I_0 . The current–voltage relationship for an ideal diode is

$$I = I_0 (e^{e\Delta V/k_B T} - 1) \quad (43.27)$$

where the first e is the base of the natural logarithm, the second e represents the magnitude of the electron charge, k_B is Boltzmann's constant, and T is the absolute temperature. Figure 43.28b shows a circuit diagram for a diode under reverse bias, and Figure 43.28c shows an I - ΔV plot characteristic of a real p - n junction, demonstrating the diode behavior.

Light-Emitting and Light-Absorbing Diodes

Light-emitting diodes (LEDs) and semiconductor lasers are common examples of devices that depend on the behavior of semiconductors. LEDs are used in traffic signals, in electronic displays, and as indicator lights for electronic equipment. Semiconductor lasers are often used for pointers in presentations and in compact disc and DVD playback equipment.

Light emission and absorption in semiconductors is similar to light emission and absorption by gaseous atoms except that in the discussion of semiconductors we must incorporate the concept of energy bands rather than the discrete energy levels in single atoms. As shown in Figure 43.29a, an electron excited electrically into the conduction band can easily recombine with a hole (especially if the electron

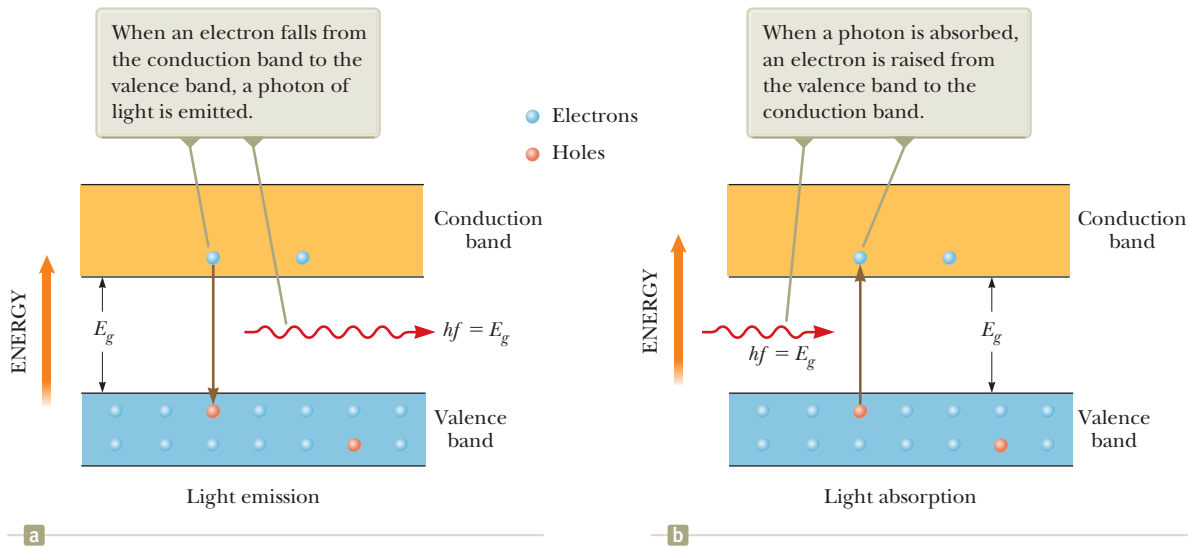


Figure 43.29 (a) Light emission from a semiconductor. (b) Light absorption by a semiconductor.

is injected into a p region). As this recombination takes place, a photon of energy E_g is emitted. With proper design of the semiconductor and the associated plastic envelope or mirrors, the light from a large number of these transitions serves as the source of an LED or a semiconductor laser.

Conversely, an electron in the valence band may absorb an incoming photon of light and be promoted to the conduction band, leaving a hole behind (Fig. 43.29b). This absorbed energy can be used to operate an electrical circuit.

One device that operates on this principle is the **photovoltaic solar cell**, which appears in many handheld calculators. An early large-scale application of arrays of photovoltaic cells is the energy supply for orbiting spacecraft. The solar panels of the Hubble Space Telescope can be seen in the chapter-opening photograph for Chapter 38 on page 1111.

During the early years of the current century, application of photovoltaics for ground-based generation of electricity has been one of the world's fastest-growing energy technologies. At the time of this printing, the global generation of energy by means of photovoltaics is over 10 GW. A homeowner can install arrays of photovoltaic panels on the roof of his or her house and generate enough energy to operate the home as well as feed excess energy back into the electrical grid. Several photovoltaic power plants have recently been completed in Europe, including the 60-MW Olmedilla Photovoltaic Park in Olmedilla de Alarcón, Spain. Several large solar power plants have been proposed in the United States, including one that would provide over 500 MW in California.

Example 43.6

Where's the Remote?

Estimate the band gap of the semiconductor in the infrared LED of a typical television remote control.

SOLUTION

Conceptualize Imagine electrons in Figure 43.29a falling from the conduction band to the valence band, emitting infrared photons in the process.

Categorize We use concepts discussed in this section, so we categorize this example as a substitution problem.

In Chapter 34, we learned that the wavelength of infrared light ranges from 700 nm to 1 mm. Let's pick a number that is easy to work with, such as 1 000 nm (which is not a bad estimate because remote controls typically operate in the range of 880 to 950 nm.)

continued

43.6 cont.

Estimate the energy hf of the photons from the remote control:

$$E = hf = \frac{hc}{\lambda} = \frac{1\,240 \text{ eV} \cdot \text{nm}}{1\,000 \text{ nm}} = 1.2 \text{ eV}$$

This value corresponds to an energy gap E_g of approximately 1.2 eV in the LED's semiconductor.

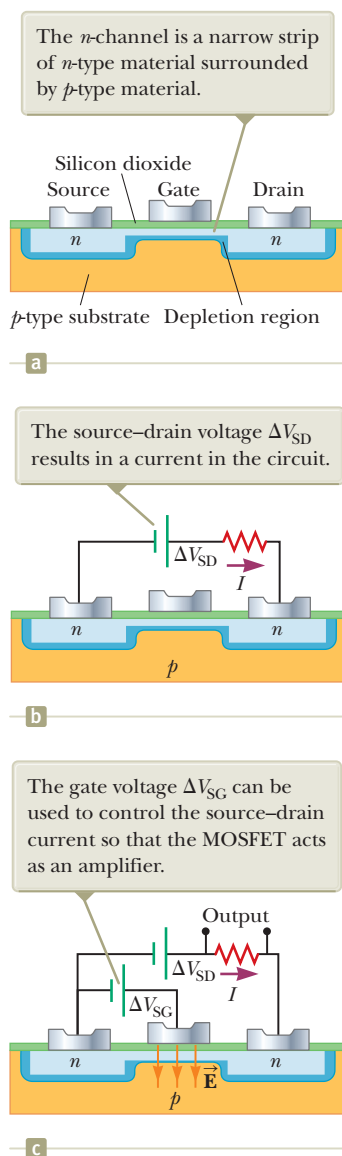


Figure 43.30 (a) The structure of a metal-oxide-semiconductor field-effect transistor (MOSFET). (b) A source–drain voltage is applied. (c) A gate voltage is applied.

The Transistor

The invention of the transistor by John Bardeen (1908–1991), Walter Brattain (1902–1987), and William Shockley (1910–1989) in 1948 totally revolutionized the world of electronics. For this work, these three men shared the Nobel Prize in Physics in 1956. By 1960, the transistor had replaced the vacuum tube in many electronic applications. The advent of the transistor created a multitrillion-dollar industry that produces such popular devices as MP3 players, handheld calculators, computers, wireless telephones, and electronic games.

A **junction transistor** consists of a semiconducting material in which a very narrow n region is sandwiched between two p regions or a p region is sandwiched between two n regions. In either case, the transistor is formed from two p - n junctions. These types of transistors were used widely in the early days of semiconductor electronics.

During the 1960s, the electronics industry converted many electronic applications from the junction transistor to the **field-effect transistor**, which is much easier to manufacture and just as effective. Figure 43.30a shows the structure of a very common device, the **MOSFET**, or **metal-oxide-semiconductor field-effect transistor**. You are likely using millions of MOSFET devices when you are working on your computer.

There are three metal connections (the M in MOSFET) to the transistor: the *source*, *drain*, and *gate*. The source and drain are connected to n -type semiconductor regions (the S in MOSFET) at either end of the structure. These regions are connected by a narrow channel of additional n -type material, the n channel. The source and drain regions and the n channel are embedded in a p -type substrate material, which forms a depletion region, as in the junction diode, along the bottom of the n channel. (Depletion regions also exist at the junctions underneath the source and drain regions, but we will ignore them because the operation of the device depends primarily on the behavior in the channel.)

The gate is separated from the n channel by a layer of insulating silicon dioxide (the O in MOSFET, for oxide). Therefore, it does not make electrical contact with the rest of the semiconducting material.

Imagine that a voltage source ΔV_{SD} is applied across the source and drain as shown in Figure 43.30b. In this situation, electrons flow through the upper region of the n channel. Electrons cannot flow through the depletion region in the lower part of the n channel because this region is depleted of charge carriers. Now a second voltage ΔV_{SG} is applied across the source and gate as in Figure 43.30c. The positive potential on the gate electrode results in an electric field below the gate that is directed downward in the n channel (the field in “field-effect”). This electric field exerts upward forces on electrons in the region below the gate, causing them to move into the n channel. Consequently, the depletion region becomes smaller, widening the area through which there is current between the top of the n channel and the depletion region. As the area becomes wider, the current increases.

If a varying voltage, such as that generated from music stored on a compact disc, is applied to the gate, the area through which the source–drain current exists var-

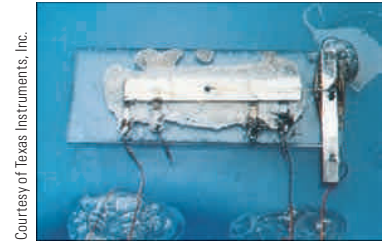
ies in size according to the varying gate voltage. A small variation in gate voltage results in a large variation in current and a correspondingly large voltage across the resistor in Figure 43.30c. Therefore, the MOSFET acts as a voltage amplifier. A circuit consisting of a chain of such transistors can result in a very small initial signal from a microphone being amplified enough to drive powerful speakers at an outdoor concert.

The Integrated Circuit

Invented independently by Jack Kilby (1923–2005, Nobel Prize in Physics, 2000) at Texas Instruments in late 1958 and by Robert Noyce (1927–1990) at Fairchild Camera and Instrument in early 1959, the integrated circuit has been justly called “the most remarkable technology ever to hit mankind.” Kilby’s first device is shown in Figure 43.31. Integrated circuits have indeed started a “second industrial revolution” and are found at the heart of computers, watches, cameras, automobiles, aircraft, robots, space vehicles, and all sorts of communication and switching networks.

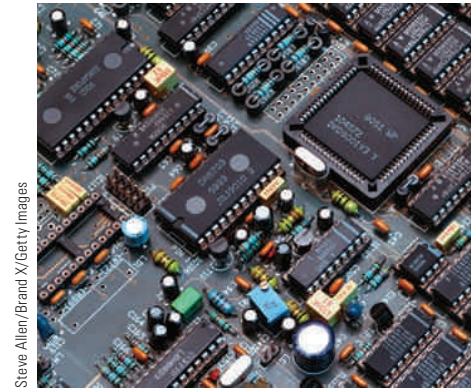
In simplest terms, an **integrated circuit** is a collection of interconnected transistors, diodes, resistors, and capacitors fabricated on a single piece of silicon known as a *chip*. Contemporary electronic devices often contain many integrated circuits (Fig. 43.32). State-of-the-art chips easily contain several million components within a 1-cm² area, and the number of components per square inch has increased steadily since the integrated circuit was invented. Figure 43.33 illustrates the dramatic advances made in chip technology since Intel introduced the first microprocessor in 1971.

Integrated circuits were invented partly to solve the interconnection problem spawned by the transistor. In the era of vacuum tubes, power and size considerations



Courtesy of Texas Instruments, Inc.

Figure 43.31 Jack Kilby’s first integrated circuit, tested on September 12, 1958.



Steve Allen/Brand X/Getty Images

Figure 43.32 Integrated circuits are prevalent in many electronic devices. All the flat circuit elements with black-topped surfaces in this photograph are integrated circuits.

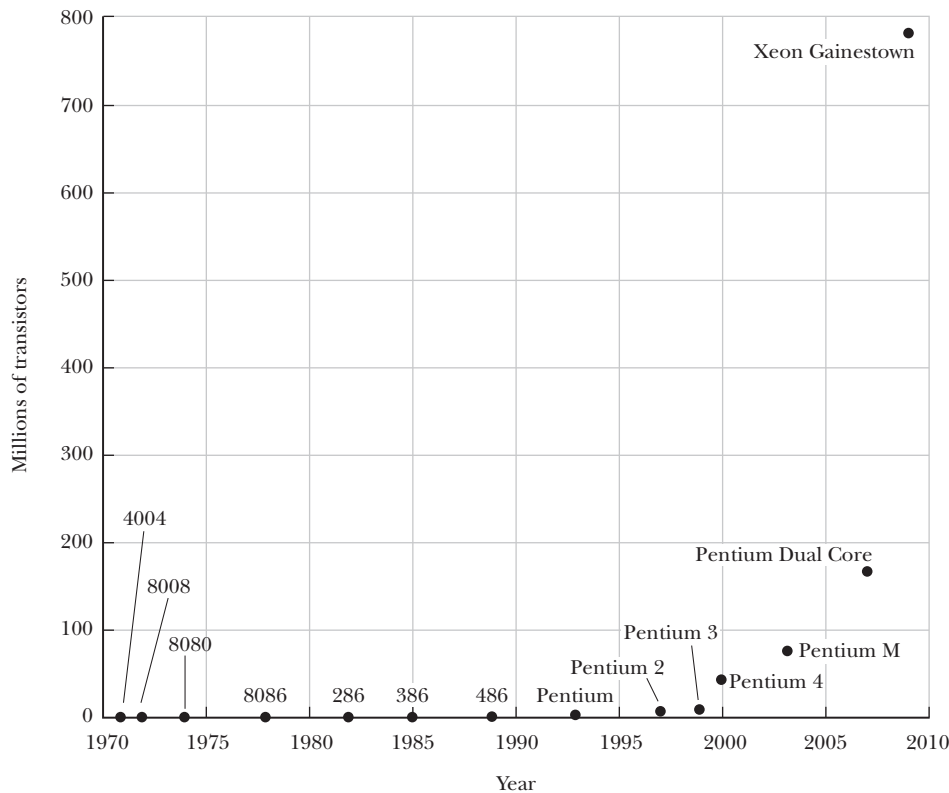


Figure 43.33 Dramatic advances in chip technology related to computer microchips manufactured by Intel, shown by a plot of the number of transistors on a single computer chip versus year of manufacture.

of individual components set modest limits on the number of components that could be interconnected in a given circuit. With the advent of the tiny, low-power, highly reliable transistor, design limits on the number of components disappeared and were replaced by the problem of wiring together hundreds of thousands of components. The magnitude of this problem can be appreciated when we consider that second-generation computers (consisting of discrete transistors rather than integrated circuits) contained several hundred thousand components requiring more than a million joints that had to be hand-soldered and tested.

In addition to solving the interconnection problem, integrated circuits possess the advantages of miniaturization and fast response, two attributes critical for high-speed computers. Because the response time of a circuit depends on the time interval required for electrical signals traveling at the speed of light to pass from one component to another, miniaturization and close packing of components result in fast response times.

43.8 Superconductivity

We learned in Section 27.5 that there is a class of metals and compounds known as **superconductors** whose electrical resistance decreases to virtually zero below a certain temperature T_c called the *critical temperature* (Table 27.3). Let's now look at these amazing materials in greater detail, using what we know about the properties of solids to help us understand the behavior of superconductors.

Let's start by examining the Meissner effect, introduced in Section 30.6 as the exclusion of magnetic flux from the interior of superconductors. The Meissner effect is illustrated in Figure 43.34 for a superconducting material in the shape of a long cylinder. Notice that the magnetic field penetrates the cylinder when its temperature is greater than T_c (Fig. 43.34a). As the temperature is lowered to below T_c , however, the field lines are spontaneously expelled from the interior of the superconductor (Fig. 43.34b). Therefore, a superconductor is more than a perfect conductor (resistivity $\rho = 0$); it is also a perfect diamagnet ($\vec{\mathbf{B}} = 0$). The property that $\vec{\mathbf{B}} = 0$ in the interior of a superconductor is as fundamental as the property of zero resistance. If the magnitude of the applied magnetic field exceeds a critical value B_c , defined as the value of B that destroys a material's superconducting properties, the field again penetrates the sample.

Because a superconductor is a perfect diamagnet, it repels a permanent magnet. In fact, one can perform a demonstration of the Meissner effect by floating a small permanent magnet above a superconductor and achieving magnetic levitation as seen in Figure 30.27 in Section 30.6.

Recall from our study of electricity that a good conductor expels static electric fields by moving charges to its surface. In effect, the surface charges produce an electric field that exactly cancels the externally applied field inside the conductor. In a similar manner, a superconductor expels magnetic fields by forming surface currents. To see why that happens, consider again the superconductor shown in Figure 43.34. Let's assume the sample is initially at a temperature $T > T_c$ as illustrated in Figure 43.34a so that the magnetic field penetrates the cylinder. As the cylinder is cooled to a temperature $T < T_c$, the field is expelled as shown in Figure 43.34b. Surface currents induced on the superconductor's surface produce a magnetic field that exactly cancels the externally applied field inside the superconductor. As you would expect, the surface currents disappear when the external magnetic field is removed.

A successful theory for superconductivity in metals was published in 1957 by J. Bardeen (1908–1991), L. N. Cooper (b. 1930), and J. R. Schrieffer (b. 1931); it is

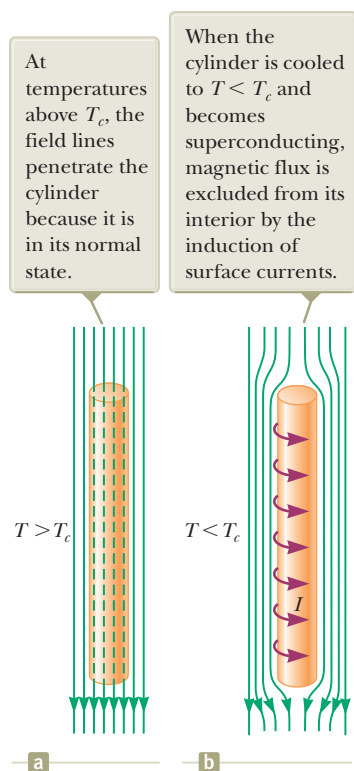


Figure 43.34 A superconductor in the form of a long cylinder in the presence of an external magnetic field.

generally called BCS theory, based on the first letters of their last names. This theory led to a Nobel Prize in Physics for the three scientists in 1972. In this theory, two electrons can interact via distortions in the array of lattice ions so that there is a net attractive force between the electrons.⁵ As a result, the two electrons are bound into an entity called a *Cooper pair*, which behaves like a particle with integral spin. Particles with integral spin are called *bosons*. (As noted in Pitfall Prevention 42.6, *fermions* make up another class of particles, those with half-integral spin.) An important feature of bosons is that they do not obey the Pauli exclusion principle. Consequently, at very low temperatures, it is possible for all bosons in a collection of such particles to be in the lowest quantum state. The entire collection of Cooper pairs in the metal is described by a single wave function. Above the energy level associated with this wave function is an energy gap equal to the binding energy of a Cooper pair. Under the action of an applied electric field, the Cooper pairs experience an electric force and move through the metal. A random scattering event of a Cooper pair from a lattice ion would represent resistance to the electric current. Such a collision would change the energy of the Cooper pair because some energy would be transferred to the lattice ion. There are no available energy levels below that of the Cooper pair (it is already in the lowest state), however, and none available above because of the energy gap. As a result, collisions do not occur and there is no resistance to the movement of Cooper pairs.

An important development in physics that elicited much excitement in the scientific community was the discovery of high-temperature copper oxide-based superconductors. The excitement began with a 1986 publication by J. Georg Bednorz (b. 1950) and K. Alex Müller (b. 1927), scientists at the IBM Zurich Research Laboratory in Switzerland. In their seminal paper,⁶ Bednorz and Müller reported strong evidence for superconductivity at 30 K in an oxide of barium, lanthanum, and copper. They were awarded the Nobel Prize in Physics in 1987 for their remarkable discovery. Shortly thereafter, a new family of compounds was open for investigation and research activity in the field of superconductivity proceeded vigorously. In early 1987, groups at the University of Alabama at Huntsville and the University of Houston announced superconductivity at approximately 92 K in an oxide of yttrium, barium, and copper (YBa₂Cu₃O₇). Later that year, teams of scientists from Japan and the United States reported superconductivity at 105 K in an oxide of bismuth, strontium, calcium, and copper. Superconductivity at temperatures as high as 150 K have been reported in an oxide containing mercury. In 2006, Japanese scientists discovered superconductivity for the first time in iron-based materials, beginning with LaFePO, with a critical temperature of 4 K. The highest critical temperature that has been reported so far in the iron-based materials is 55 K, a milestone held by fluorine-doped SmFeAsO. These newly discovered materials have rejuvenated the field of high- T_c superconductivity. Today, one cannot rule out the possibility of room-temperature superconductivity, and the mechanisms responsible for the behavior of high-temperature superconductors are still under investigation. The search for novel superconducting materials continues both for scientific reasons and because practical applications become more probable and widespread as the critical temperature is raised.

Although BCS theory was very successful in explaining superconductivity in metals, there is currently no widely accepted theory for high-temperature superconductivity. It remains an area of active research.

⁵A highly simplified explanation of this attraction between electrons is as follows. The attractive Coulomb force between one electron and the surrounding positively charged lattice ions causes the ions to move inward slightly toward the electron. As a result, there is a higher concentration of positive charge in this region than elsewhere in the lattice. A second electron is attracted to the higher concentration of positive charge.

⁶J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**:189, 1986.

Concepts and Principles

Two or more atoms combine to form molecules because of a net attractive force between the atoms. The mechanisms responsible for molecular bonding can be classified as follows:

- **Ionic bonds** form primarily because of the Coulomb attraction between oppositely charged ions. Sodium chloride (NaCl) is one example.
- **Covalent bonds** form when the constituent atoms of a molecule share electrons. For example, the two electrons of the H_2 molecule are equally shared between the two nuclei.
- **Van der Waals bonds** are weak electrostatic bonds between molecules or between atoms that do not form ionic or covalent bonds. These bonds are responsible for the condensation of noble gas atoms and nonpolar molecules into the liquid phase.
- **Hydrogen bonds** form between the center of positive charge in a polar molecule that includes one or more hydrogen atoms and the center of negative charge in another polar molecule.

The allowed values of the rotational energy of a diatomic molecule are

$$E_{\text{rot}} = E_J = \frac{\hbar^2}{2I} J(J+1) \quad J = 0, 1, 2, \dots \quad (43.6)$$

where I is the moment of inertia of the molecule and J is an integer called the **rotational quantum number**. The selection rule for transitions between rotational states is $\Delta J = \pm 1$.

The allowed values of the vibrational energy of a diatomic molecule are

$$E_{\text{vib}} = (v + \frac{1}{2}) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad v = 0, 1, 2, \dots \quad (43.10)$$

where v is the **vibrational quantum number**, k is the force constant of the “effective spring” bonding the molecule, and μ is the **reduced mass** of the molecule. The selection rule for allowed vibrational transitions is $\Delta v = \pm 1$, and the energy difference between any two adjacent levels is the same, regardless of which two levels are involved.

Bonding mechanisms in solids can be classified in a manner similar to the schemes for molecules. For example, the Na^+ and Cl^- ions in NaCl form **ionic bonds**, whereas the carbon atoms in diamond form **covalent bonds**. The **metallic bond** is characterized by a net attractive force between positive ion cores and the mobile free electrons of a metal.

In the **free-electron theory of metals**, the free electrons fill the quantized levels in accordance with the Pauli exclusion principle. The number of states per unit volume available to the conduction electrons having energies between E and $E + dE$ is

$$N(E) dE = \left(\frac{8\sqrt{2} \pi m_e^{3/2}}{h^3} E^{1/2} \right) \left(\frac{1}{e^{(E-E_F)/k_B T} + 1} \right) dE \quad (43.22)$$

where E_F is the **Fermi energy**. At $T = 0$ K, all levels below E_F are filled, all levels above E_F are empty, and

$$E_F(0) = \frac{\hbar^2}{2m_e} \left(\frac{3n_e}{8\pi} \right)^{2/3} \quad (43.25)$$

where n_e is the total number of conduction electrons per unit volume. Only those electrons having energies near E_F can contribute to the electrical conductivity of the metal.

continued

In a crystalline solid, the energy levels of the system form a set of **bands**. Electrons occupy the lowest energy states, with no more than one electron per state. Energy gaps are present between the bands of allowed states.

A **semiconductor** is a material having an energy gap of approximately 1 eV and a valence band that is filled at $T = 0$ K. Because of the small energy gap, a significant number of electrons can be thermally excited from the valence band into the conduction band. The band structures and electrical properties of a Group IV semiconductor can be modified by the addition of either donor atoms containing five outer-shell electrons or acceptor atoms containing three outer-shell electrons. A semiconductor **doped** with donor impurity atoms is called an ***n*-type semiconductor**, and one doped with acceptor impurity atoms is called a ***p*-type semiconductor**.

Objective Questions

denotes answer available in Student Solutions Manual/Study Guide

- Consider a typical material composed of covalently bonded diatomic molecules. Rank the following energies from the largest in magnitude to the smallest in magnitude. (a) the latent heat of fusion per molecule (b) the molecular binding energy (c) the energy of the first excited state of molecular rotation (d) the energy of the first excited state of molecular vibration
- An infrared absorption spectrum of a molecule is shown in Figure OQ43.2. Notice that the highest peak on either side of the gap is the third peak from the gap. After this spectrum is taken, the temperature of the sample of molecules is raised to a much higher value. Compared with Figure OQ43.2, in this new spectrum is the highest absorption peak (a) at the same frequency, (b) farther from the gap, or (c) closer to the gap?
- What kind of bonding likely holds the atoms together in the following solids (i), (ii), and (iii)? Choose your answers from these possibilities: (a) ionic bonding, (b) covalent bonding, and (c) metallic bonding. (i) The solid is opaque, shiny, flexible, and a good electric conductor. (ii) The crystal is transparent, brittle, and soluble in water. It is a poor conductor of electricity. (iii) The crystal is opaque, brittle, very hard, and a good electric insulator.
- The Fermi energy for silver is 5.48 eV. In a piece of solid silver, free-electron energy levels are measured near 2 eV and near 6 eV. (i) Near which of these energies are the energy levels closer together? (a) 2 eV (b) 6 eV (c) The spacing is the same. (ii) Near which of these energies are more electrons occupying energy levels? (a) 2 eV (b) 6 eV (c) The number of electrons is the same.
- As discussed in Chapter 27, the conductivity of metals decreases with increasing temperature due to electron collisions with vibrating atoms. In contrast, the conductivity of semiconductors increases with increasing temperature. What property of a semiconductor is responsible for this behavior? (a) Atomic vibrations decrease as temperature increases. (b) The number of conduction electrons and the number of holes increase steeply with increasing temperature. (c) The energy gap decreases with increasing temperature. (d) Electrons do not collide with atoms in a semiconductor.
- (i) Should you expect an *n*-type doped semiconductor to have (a) higher, (b) lower, or (c) the same conductivity as an intrinsic (pure) semiconductor? (ii) Should you

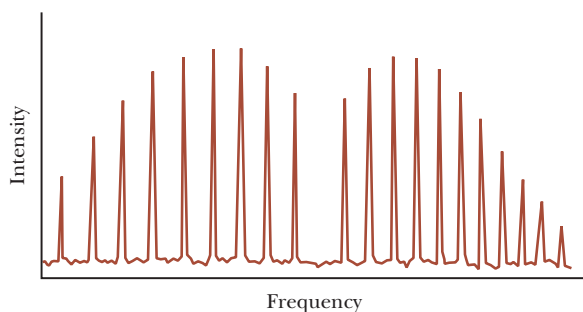


Figure OQ43.2

expect a *p*-type doped semiconductor to have (a) higher, (b) lower, or (c) the same conductivity as an intrinsic (pure) semiconductor?

7. Is each one of the following statements true or false for a superconductor below its critical temperature? (a) It can

carry infinite current. (b) It must carry some nonzero current. (c) Its interior electric field must be zero. (d) Its internal magnetic field must be zero. (e) No internal energy appears when it carries electric current.

Conceptual Questions

Note: Conceptual Questions 4 and 5 in Chapter 27 can be assigned with this chapter.

- Discuss models for the different types of bonds that form stable molecules.
- Discuss the three major forms of excitation of a molecule (other than translational motion) and the relative energies associated with these three forms.
- How can the analysis of the rotational spectrum of a molecule lead to an estimate of the size of that molecule?
- (a) Discuss the differences in the band structures of metals, insulators, and semiconductors. (b) How does the band-structure model enable you to understand the electrical properties of these materials better?
- When a photon is absorbed by a semiconductor, an electron–hole pair is created. Give a physical explanation of this statement using the energy-band model as the basis for your description.

denotes answer available in Student Solutions Manual/Study Guide

- Pentavalent atoms such as arsenic are donor atoms in a semiconductor such as silicon, whereas trivalent atoms such as indium are acceptors. Inspect the periodic table in Appendix C and determine what other elements might make good donors or acceptors.
- (a) What essential assumptions are made in the free-electron theory of metals? (b) How does the energy-band model differ from the free-electron theory in describing the properties of metals?
- How do the vibrational and rotational levels of heavy hydrogen (D_2) molecules compare with those of H_2 molecules?
- The energies of photons of visible light range between the approximate values 1.8 eV and 3.1 eV. Explain why silicon, with an energy gap of 1.14 eV at room temperature (see Table 43.3), appears opaque, whereas diamond, with an energy gap of 5.47 eV, appears transparent.
- Discuss the differences between crystalline solids, amorphous solids, and gases.

Problems

WebAssign The problems found in this chapter may be assigned online in Enhanced WebAssign

1. denotes straightforward problem; 2. denotes intermediate problem; 3. denotes challenging problem

full solution available in the Student Solutions Manual/Study Guide

denotes problems most often assigned in Enhanced WebAssign; these provide students with targeted feedback and either a Master It tutorial or a Watch It solution video.

Q/C denotes asking for quantitative and conceptual reasoning

S denotes symbolic reasoning problem

M denotes Master It tutorial available in Enhanced WebAssign

GP denotes guided problem

shaded denotes “paired problems” that develop reasoning with symbols and numerical values

Section 43.1 Molecular Bonds

- Potassium chloride is an ionically bonded molecule that is sold as a salt substitute for use in a low-sodium diet. The electron affinity of chlorine is 3.6 eV. An energy input of 0.70 eV

is required to form separate K^+ and Cl^- ions from separate K and Cl atoms. What is the ionization energy of K?

- Review.** A K^+ ion and a Cl^- ion are separated by a distance of 5.00×10^{-10} m. Assuming the two ions act like charged

particles, determine (a) the force each ion exerts on the other and (b) the potential energy of the two-ion system in electron volts.

3. A van der Waals dispersion force between helium atoms produces a very shallow potential well, with a depth on the order of 1 meV. At approximately what temperature would you expect helium to condense?
4. In the potassium iodide (KI) molecule, assume the K and I atoms bond ionically by the transfer of one electron from K to I. (a) The ionization energy of K is 4.34 eV, and the electron affinity of I is 3.06 eV. What energy is needed to transfer an electron from K to I, to form K^+ and I^- ions from neutral atoms? This quantity is sometimes called the activation energy E_a . (b) A model potential energy function for the KI molecule is the Lennard–Jones potential:

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + E_a$$

where r is the internuclear separation distance and ϵ and σ are adjustable parameters. The E_a term is added to ensure the correct asymptotic behavior at large r . At the equilibrium separation distance, $r = r_0 = 0.305$ nm, $U(r)$ is a minimum, and $dU/dr = 0$. In addition, $U(r_0)$ is the negative of the dissociation energy: $U(r_0) = -3.37$ eV. Find σ and ϵ . (c) Calculate the force needed to break up a KI molecule. (d) Calculate the force constant for small oscillations about $r = r_0$. *Suggestion:* Set $r = r_0 + s$, where $s/r_0 \ll 1$, and expand $U(r)$ in powers of s/r_0 up to second-order terms.

5. One description of the potential energy of a diatomic molecule is given by the Lennard–Jones potential,

$$U = \frac{A}{r^{12}} - \frac{B}{r^6}$$

where A and B are constants and r is the separation distance between the atoms. For the H_2 molecule, take $A = 0.124 \times 10^{-120}$ eV \cdot m¹² and $B = 1.488 \times 10^{-60}$ eV \cdot m⁶. Find (a) the separation distance r_0 at which the energy of the molecule is a minimum and (b) the energy E required to break up the H_2 molecule.

6. **S** One description of the potential energy of a diatomic molecule is given by the Lennard–Jones potential,

$$U = \frac{A}{r^{12}} - \frac{B}{r^6}$$

where A and B are constants and r is the separation distance between the atoms. Find, in terms of A and B , (a) the value r_0 at which the energy is a minimum and (b) the energy E required to break up a diatomic molecule.

Section 43.2 Energy States and Spectra of Molecules

7. Assume the distance between the protons in the H_2 molecule is 0.750×10^{-10} m. (a) Find the energy of the first excited rotational state, with $J = 1$. (b) Find the wavelength of radiation emitted in the transition from $J = 1$ to $J = 0$.

8. The cesium iodide (CsI) molecule has an atomic separation of 0.127 nm. (a) Determine the energy of the second excited rotational state, with $J = 2$. (b) Find the frequency of the photon absorbed in the $J = 1$ to $J = 2$ transition.

9. **M** An HCl molecule is excited to its second rotational energy level, corresponding to $J = 2$. If the distance between its nuclei is 0.1275 nm, what is the angular speed of the molecule about its center of mass?

10. **Q|C** The photon frequency that would be absorbed by the NO molecule in a transition from vibration state $v = 0$ to $v = 1$, with no change in rotation state, is 56.3 THz. The bond between the atoms has an effective spring constant of 1530 N/m. (a) Use this information to calculate the reduced mass of the NO molecule. (b) Compute a value for μ using Equation 43.4. (c) Compare your results to parts (a) and (b) and explain their difference, if any.

11. **Q|C** The CO molecule makes a transition from the $J = 1$ to the $J = 2$ rotational state when it absorbs a photon of frequency 2.30×10^{11} Hz. (a) Find the moment of inertia of this molecule from these data. (b) Compare your answer with that obtained in Example 43.1 and comment on the significance of the two results.

12. *Why is the following situation impossible?* The effective force constant of a vibrating HCl molecule is $k = 480$ N/m. A beam of infrared radiation of wavelength 6.20×10^3 nm is directed through a gas of HCl molecules. As a result, the molecules are excited from the ground vibrational state to the first excited vibrational state.

13. The effective spring constant describing the potential energy of the HI molecule is 320 N/m and that for the HF molecule is 970 N/m. Calculate the minimum amplitude of vibration for (a) the HI molecule and (b) the HF molecule.

14. **S** A diatomic molecule consists of two atoms having masses m_1 and m_2 separated by a distance r . Show that the moment of inertia about an axis through the center of mass of the molecule is given by Equation 43.3, $I = \mu r^2$.

15. The atoms of an NaCl molecule are separated by a distance $r = 0.280$ nm. Calculate (a) the reduced mass of an NaCl molecule, (b) the moment of inertia of an NaCl molecule, and (c) the wavelength of radiation emitted when an NaCl molecule undergoes a transition from the $J = 2$ state to the $J = 1$ state.

16. The rotational spectrum of the HCl molecule contains lines with wavelengths of 0.060 4, 0.069 0, 0.080 4, 0.096 4, and 0.120 4 mm. What is the moment of inertia of the molecule?
17. The nuclei of the O_2 molecule are separated by a distance 1.20×10^{-10} m. The mass of each oxygen atom in the molecule is 2.66×10^{-26} kg. (a) Determine the rotational energies of an oxygen molecule in electron volts for the levels corresponding to $J = 0, 1,$ and 2 . (b) The effective force constant k between the atoms in the oxygen molecule is 1.177 N/m. Determine the vibrational energies (in electron volts) corresponding to $v = 0, 1,$ and 2 .
18. Figure P43.18 is a model of a benzene molecule. All atoms lie in a plane, and the carbon atoms ($m_C = 1.99 \times 10^{-26}$ kg) form a regular hexagon, as do the hydrogen atoms ($m_H = 1.67 \times 10^{-27}$ kg). The carbon atoms are 0.110 nm apart center to center, and the adjacent carbon and hydrogen atoms are 0.100 nm apart center to center. (a) Calculate the moment of inertia of the molecule about an axis perpendicular to the plane of the paper through the center point O . (b) Determine the allowed rotational energies about this axis.

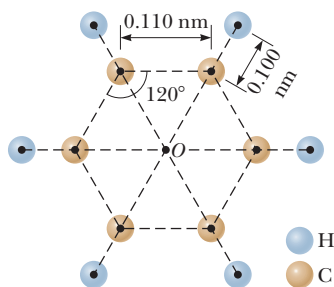


Figure P43.18

19. (a) In an HCl molecule, take the Cl atom to be the isotope ^{35}Cl . The equilibrium separation of the H and Cl atoms is $0.127\ 46$ nm. The atomic mass of the H atom is $1.007\ 825$ u and that of the ^{35}Cl atom is $34.968\ 853$ u. Calculate the longest wavelength in the rotational spectrum of this molecule. (b) **What If?** Repeat the calculation in part (a), but take the Cl atom to be the isotope ^{37}Cl , which has atomic mass $36.965\ 903$ u. The equilibrium separation distance is the same as in part (a). (c) Naturally occurring chlorine contains approximately three parts of ^{35}Cl to one part of ^{37}Cl . Because of the two different Cl masses, each line in the microwave rotational spectrum of HCl is split into a doublet as shown in Figure P43.19. Calculate the separation in wavelength between the doublet lines for the longest wavelength.

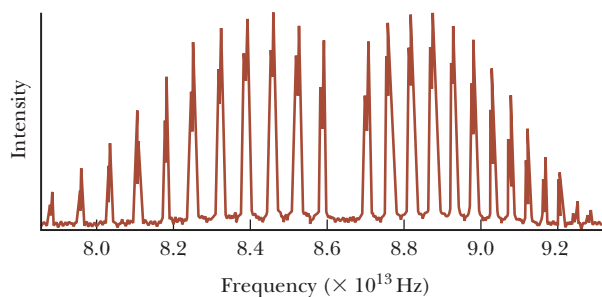


Figure P43.19 Problems 19 and 20.

20. Estimate the moment of inertia of an HCl molecule from its infrared absorption spectrum shown in Figure P43.19.
21. An H_2 molecule is in its vibrational and rotational ground states. It absorbs a photon of wavelength $2.211\ 2\ \mu\text{m}$ and makes a transition to the $v = 1, J = 1$ energy level. It then drops to the $v = 0, J = 2$ energy level while emitting a photon of wavelength $2.405\ 4\ \mu\text{m}$. Calculate (a) the moment of inertia of the H_2 molecule about an axis through its center of mass and perpendicular to the H-H bond, (b) the vibrational frequency of the H_2 molecule, and (c) the equilibrium separation distance for this molecule.
22. Photons of what frequencies can be spontaneously emitted by CO molecules in the state with $v = 1$ and $J = 0$?
23. Most of the mass of an atom is in its nucleus. Model the mass distribution in a diatomic molecule as two spheres of uniform density, each of radius 2.00×10^{-15} m and mass 1.00×10^{-26} kg, located at points along the y axis as in Active Figure 43.5a, and separated by 2.00×10^{-10} m. Rotation about the axis joining the nuclei in the diatomic molecule is ordinarily ignored because the first excited state would have an energy that is too high to access. To see why, calculate the ratio of the energy of the first excited state for rotation about the y axis to the energy of the first excited state for rotation about the x axis.

Section 43.3 Bonding in Solids

24. Use a magnifying glass to look at the grains of table salt that come out of a salt shaker. Compare what you see with Figure 43.10a. The distance between a sodium ion and a nearest-neighbor chlorine ion is 0.261 nm. (a) Make an order-of-magnitude estimate of the number N of atoms in a typical grain of salt. (b) **What If?** Suppose you had a number of grains of salt equal to this number N . What would be the volume of this quantity of salt?

25. Use Equation 43.18 to calculate the ionic cohesive energy for NaCl. Take $\alpha = 1.7476$, $r_0 = 0.281$ nm, and $m = 8$.

26. **S** Consider a one-dimensional chain of alternating singly-ionized positive and negative ions. Show that the potential energy associated with one of the ions and its interactions with the rest of this hypothetical crystal is

$$U(r) = -k_e \alpha \frac{e^2}{r}$$

where the Madelung constant is $\alpha = 2 \ln 2$ and r is the distance between ions. *Suggestion:* Use the series expansion for $\ln(1+x)$.

Section 43.4 Free-Electron Theory of Metals

Section 43.5 Band Theory of Solids

27. **M** Sodium is a monovalent metal having a density of 0.971 g/cm³ and a molar mass of 23.0 g/mol. Use this information to calculate (a) the density of charge carriers and (b) the Fermi energy of sodium.

28. **Q|C** (a) State what the Fermi energy depends on according to the free-electron theory of metals and how the Fermi energy depends on that quantity. (b) Show that Equation 43.25 can be expressed as $E_F = (3.65 \times 10^{-19}) n_e^{2/3}$, where E_F is in electron volts when n_e is in electrons per cubic meter. (c) According to Table 43.2, by what factor does the free-electron concentration in copper exceed that in potassium? (d) Which of these metals has the larger Fermi energy? (e) By what factor is the Fermi energy larger? (f) Explain whether this behavior is predicted by Equation 43.25.

29. When solid silver starts to melt, what is the approximate fraction of the conduction electrons that are thermally excited above the Fermi level?

30. **Q|C** (a) Find the typical speed of a conduction electron in copper, taking its kinetic energy as equal to the Fermi energy, 7.05 eV. (b) Suppose the copper is a current-carrying wire. How does the speed found in part (a) compare with a typical drift speed (see Section 27.1) of electrons in the wire of 0.1 mm/s?

31. The Fermi energy of copper at 300 K is 7.05 eV. (a) What is the average energy of a conduction electron in copper at 300 K? (b) At what temperature would the average translational energy of a molecule in an ideal gas be equal to the energy calculated in part (a)?

32. Consider a cube of gold 1.00 mm on an edge. Calculate the approximate number of conduction electrons in this cube whose energies lie in the range 4.000 to 4.025 eV.

33. Calculate the energy of a conduction electron in silver at 800 K, assuming the probability of finding an electron in that state is 0.950 . The Fermi energy of silver is 5.48 eV at this temperature.

34. **M Q|C** (a) Consider a system of electrons confined to a three-dimensional box. Calculate the ratio of the number of allowed energy levels at 8.50 eV to the number at 7.05 eV. (b) **What If?** Copper has a Fermi energy of 7.05 eV at 300 K. Calculate the ratio of the number of occupied levels in copper at an energy of 8.50 eV to the number at the Fermi energy. (c) How does your answer to part (b) compare with that obtained in part (a)?

35. For copper at 300 K, calculate the probability that a state with an energy equal to 99.0% of the Fermi energy is occupied.

36. **S** For a metal at temperature T , calculate the probability that a state with an energy equal to βE_F is occupied where β is a fraction between 0 and 1 .

37. **S Review.** An electron moves in a three-dimensional box of edge length L and volume L^3 . The wave function of the particle is $\psi = A \sin(k_x x) \sin(k_y y) \sin(k_z z)$. Show that its energy is given by Equation 43.20,

$$E = \frac{\hbar^2 \pi^2}{2m_e L^2} (n_x^2 + n_y^2 + n_z^2)$$

where the quantum numbers (n_x, n_y, n_z) are integers ≥ 1 . *Suggestion:* The Schrödinger equation in three dimensions may be written

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

38. *Why is the following situation impossible?* A hypothetical metal has the following properties: its Fermi energy is 5.48 eV, its density is 4.90×10^3 kg/m³, its molar mass is 100 g/mol, and it has one free electron per atom.

39. **S** Show that the average kinetic energy of a conduction electron in a metal at 0 K is $E_{\text{avg}} = \frac{3}{5} E_F$. *Suggestion:* In general, the average kinetic energy is

$$E_{\text{avg}} = \frac{1}{n_e} \int_0^\infty EN(E) dE$$

where n_e is the density of particles, $N(E) dE$ is given by Equation 43.22, and the integral is over all possible values of the energy.

Section 43.6 Electrical Conduction in Metals, Insulators, and Semiconductors

40. The longest wavelength of radiation absorbed by a certain semiconductor is $0.512 \mu\text{m}$. Calculate the energy gap for this semiconductor.
41. The energy gap for silicon at 300 K is 1.14 eV. (a) Find the lowest-frequency photon that can promote an electron from the valence band to the conduction band. (b) What is the wavelength of this photon?
42. Light from a hydrogen discharge tube is incident on a CdS crystal. (a) Which spectral lines from the Balmer series are absorbed and (b) which are transmitted?
43. A light-emitting diode (LED) made of the semiconductor GaAsP emits red light ($\lambda = 650 \text{ nm}$). Determine the energy-band gap E_g for this semiconductor.
44. **Q/C** Most solar radiation has a wavelength of $1 \mu\text{m}$ or less. (a) What energy gap should the material in a solar cell have if it is to absorb this radiation? (b) Is silicon an appropriate solar cell material (see Table 43.3)? Explain your answer.
45. You are asked to build a scientific instrument that is thermally isolated from its surroundings. The isolation container may be a calorimeter, but these design criteria could apply to other containers as well. You wish to use a laser external to the container to raise the temperature of a target inside the instrument. You decide to use a diamond window in the container. Diamond has an energy gap of 5.47 eV. What is the shortest laser wavelength you can use to warm the sample inside the instrument?
46. **CP Review.** When a phosphorus atom is substituted for a silicon atom in a crystal, four of the phosphorus valence electrons form bonds with neighboring atoms and the remaining electron is much more loosely bound. You can model the electron as free to move through the crystal lattice. The phosphorus nucleus has one more positive charge than does the silicon nucleus, however, so the extra electron provided by the phosphorus atom is attracted to this single nuclear charge $+e$. The energy levels of the extra electron are similar to those of the electron in the Bohr hydrogen atom with two important exceptions. First, the Coulomb attraction between the electron and the positive charge on the phosphorus nucleus is reduced by a factor of $1/\kappa$ from what it would be in free space (see Eq. 26.21), where κ is the dielectric constant of the crystal. As

a result, the orbit radii are greatly increased over those of the hydrogen atom. Second, the influence of the periodic electric potential of the lattice causes the electron to move as if it had an effective mass m^* , which is quite different from the mass m_e of a free electron. You can use the Bohr model of hydrogen to obtain relatively accurate values for the allowed energy levels of the extra electron. We wish to find the typical energy of these donor states, which play an important role in semiconductor devices. Assume $\kappa = 11.7$ for silicon and $m^* = 0.220m_e$. (a) Find a symbolic expression for the smallest radius of the electron orbit in terms of a_0 , the Bohr radius. (b) Substitute numerical values to find the numerical value of the smallest radius. (c) Find a symbolic expression for the energy levels E_n' of the electron in the Bohr orbits around the donor atom in terms of m_e , m^* , κ , and E_n , the energy of the hydrogen atom in the Bohr model. (d) Find the numerical value of the energy for the ground state of the electron.

Section 43.7 Semiconductor Devices

47. Assuming $T = 300 \text{ K}$, (a) for what value of the bias voltage ΔV in Equation 43.27 does $I = 9.00I_0$? (b) **What If?** What if $I = -0.900I_0$?
48. **M** A diode is at room temperature so that $k_B T = 0.025 \text{ eV}$. Taking the applied voltages across the diode to be $+1.00 \text{ V}$ (under forward bias) and -1.00 V (under reverse bias), calculate the ratio of the forward current to the reverse current if the diode is described by Equation 43.27.
49. You put a diode in a microelectronic circuit to protect the system in case an untrained person installs the battery backward. In the correct forward-bias situation, the current is 200 mA with a potential difference of 100 mV across the diode at room temperature (300 K). If the battery were reversed, so that the potential difference across the diode is still 100 mV but with the opposite sign, what would be the magnitude of the current in the diode?
50. **Q/C** A diode, a resistor, and a battery are connected in a series circuit. The diode is at a temperature for which $k_B T = 25.0 \text{ meV}$, and the saturation value of the current is $I_0 = 1.00 \mu\text{A}$. The resistance of the resistor is $R = 745 \Omega$, and the battery maintains a constant potential difference of $\mathcal{E} = 2.42 \text{ V}$ between its terminals. (a) Use Kirchhoff's loop rule to show that

$$\mathcal{E} - \Delta V = I_0 R (e^{e\Delta V/k_B T} - 1)$$

where ΔV is the voltage across the diode. (b) To solve this transcendental equation for the voltage ΔV , graph the left-hand side of the above equation and the right-hand side as functions of ΔV and find the value of ΔV at which the

curves cross. (c) Find the current I in the circuit. (d) Find the ohmic resistance of the diode, defined as the ratio $\Delta V/I$, at the voltage in part (b). (e) Find the dynamic resistance of the diode, which is defined as the derivative $d(\Delta V)/dI$, at the voltage in part (b).

Section 43.8 Superconductivity

Note: Problem 30 in Chapter 30 and Problems 69 through 72 in Chapter 32 can also be assigned with this section.

51. A superconducting ring of niobium metal 2.00 cm in diameter is immersed in a uniform 0.020 T magnetic field directed perpendicular to the ring and carries no current. Determine the current generated in the ring when the magnetic field is suddenly decreased to zero. The inductance of the ring is 3.10×10^{-8} H.

52. Q C A direct and relatively simple demonstration of zero DC resistance can be carried out using the four-point probe method. The probe shown in Figure P43.52 consists of a disk of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (a high- T_c superconductor) to which four wires are attached. Current is maintained through the sample by applying a DC voltage between points a and b , and it is measured with a DC ammeter. The current can be varied with the variable resistance R . The potential difference ΔV_{cd} between c and d is measured with a digital voltmeter. When the probe is immersed in liquid nitrogen, the sample quickly cools to 77 K, below the critical temperature of the material, 92 K. The current remains approximately constant, but ΔV_{cd} drops abruptly to zero. (a) Explain this observation on the basis of what you know about superconductors. (b) The data in the accompanying table represent actual values of ΔV_{cd} for different values of I taken on the sample at room temperature in the senior author's laboratory. A 6-V battery in series with a variable resistor R supplied the current. The values of R ranged from 10 Ω to 100 Ω . Make an I - ΔV plot of the data and determine

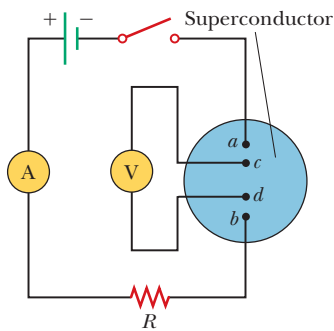


Figure P43.52

whether the sample behaves in a linear manner. (c) From the data, obtain a value for the DC resistance of the sample at room temperature. (d) At room temperature, it was found that $\Delta V_{cd} = 2.234$ mV for $I = 100.3$ mA, but after the sample was cooled to 77 K, $\Delta V_{cd} = 0$ and $I = 98.1$ mA. What do you think might have caused the slight decrease in current?

Current Versus Potential Difference ΔV_{cd} Measured in a Bulk Ceramic Sample of $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ at Room Temperature

I (mA)	ΔV_{cd} (mV)
57.8	1.356
61.5	1.441
68.3	1.602
76.8	1.802
87.5	2.053
102.2	2.398
123.7	2.904
155	3.61

53. A thin rod of superconducting material 2.50 cm long is placed into a 0.540-T magnetic field with its cylindrical axis along the magnetic field lines. (a) Sketch the directions of the applied field and the induced surface current. (b) Find the magnitude of the surface current on the curved surface of the rod.

Additional Problems

54. The effective spring constant associated with bonding in the N_2 molecule is 2 297 N/m. The nitrogen atoms each have a mass of 2.32×10^{-26} kg, and their nuclei are 0.120 nm apart. Assume the molecule is rigid. The first excited vibrational state of the molecule is above the vibrational ground state by an energy difference ΔE . Calculate the J value of the rotational state that is above the rotational ground state by the same energy difference ΔE .

55. The hydrogen molecule comes apart (dissociates) when it is excited internally by 4.48 eV. Assuming this molecule behaves like a harmonic oscillator having classical angular frequency $\omega = 8.28 \times 10^{14}$ rad/s, find the highest vibrational quantum number for a state below the 4.48-eV dissociation energy.

56. The Fermi–Dirac distribution function can be written as

$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1} = \frac{1}{e^{(E/E_F - 1)T_F/T} + 1}$$

where T_F is the Fermi temperature, defined according to

$$k_B T_F \equiv E_F$$

- (a) Write a spreadsheet to calculate and plot $f(E)$ versus E/E_F at a fixed temperature T . (b) Describe the curves obtained for $T = 0.1T_F$, $0.2T_F$, and $0.5T_F$.
57. Under pressure, liquid helium can solidify as each atom bonds with four others, and each bond has an average energy of 1.74×10^{-23} J. Find the latent heat of fusion for helium in joules per gram. (The molar mass of He is 4.00 g/mol.)
58. The dissociation energy of ground-state molecular hydrogen is 4.48 eV, but it only takes 3.96 eV to dissociate it when it starts in the first excited vibrational state with $J = 0$. Using this information, determine the depth of the H_2 molecular potential-energy function.
59. **S** Starting with Equation 43.17, show that the ionic cohesive energy of an ionically bonded solid is given by Equation 43.18.
60. **S** (a) Starting with Equation 43.17, show that the force exerted on an ion in an ionic solid can be written as

$$F = -k_e \alpha \frac{e^2}{r^2} \left[1 - \left(\frac{r_0}{r} \right)^{m-1} \right]$$

where α is the Madelung constant and r_0 is the equilibrium separation. (b) Imagine that an ion in the solid is displaced a small distance s from r_0 . Show that the ion experiences a restoring force $F = -Ks$, where

$$K = \frac{k_e \alpha e^2}{r_0^3} (m - 1)$$

(c) Use the result of part (b) to find the frequency of vibration of a Na^+ ion in NaCl. Take $m = 8$ and use the value $\alpha = 1.7476$.

61. A particle moves in one-dimensional motion through a field for which the potential energy of the particle–field system is

$$U(x) = \frac{A}{x^3} - \frac{B}{x}$$

where $A = 0.150 \text{ eV} \cdot \text{nm}^3$ and $B = 3.68 \text{ eV} \cdot \text{nm}$. The shape of this function is shown in Figure P43.61. (a) Find the equilibrium position x_0 of the particle. (b) Determine the depth U_0 of this potential well. (c) In moving along the x axis, what maximum force toward the negative x direction does the particle experience?

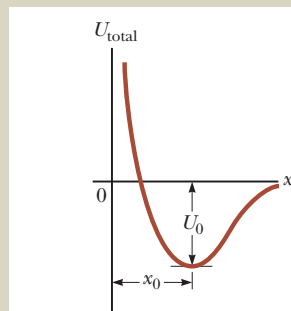


Figure P43.61 Problems 61 and 62.

62. **S** A particle of mass m moves in one-dimensional motion through a field for which the potential energy of the particle–field system is

$$U(x) = \frac{A}{x^3} - \frac{B}{x}$$

where A and B are constants. The general shape of this function is shown in Figure P43.61. (a) Find the equilibrium position x_0 of the particle in terms of m , A , and B . (b) Determine the depth U_0 of this potential well. (c) In moving along the x axis, what maximum force toward the negative x direction does the particle experience?

Challenge Problems

63. As you will learn in Chapter 44, carbon-14 (^{14}C) is an unstable isotope of carbon. It has the same chemical properties and electronic structure as the much more abundant isotope carbon-12 (^{12}C), but it has different nuclear properties. Its mass is 14 u, greater than that of carbon-12 because of the two extra neutrons in the carbon-14 nucleus. Assume the CO molecular potential energy is the same for both isotopes of carbon and the examples in Section 43.2 contain accurate data and results for carbon monoxide with carbon-12 atoms. (a) What is the vibrational frequency of ^{14}CO ? (b) What is the moment of inertia of ^{14}CO ? (c) What wavelengths of light can be absorbed by ^{14}CO in the ($v = 0$, $J = 10$) state that cause it to end up in the $v = 1$ state?
64. **S** As an alternative to Equation 43.1, another useful model for the potential energy of a diatomic molecule is the Morse potential

$$U(r) = B[e^{-a(r-r_0)} - 1]^2$$

where B , a , and r_0 are parameters used to adjust the shape of the potential and its depth. (a) What is the equilibrium separation of the nuclei? (b) What is the depth of the potential well, defined as the difference in energy between the potential's minimum value and its asymptote as r approaches infinity? (c) If μ is the reduced mass of the

system of two nuclei and assuming the potential is nearly parabolic about the well minimum, what is the vibrational frequency of the diatomic molecule in its ground state? (d) What amount of energy needs to be supplied to the ground-state molecule to separate the two nuclei to infinity?