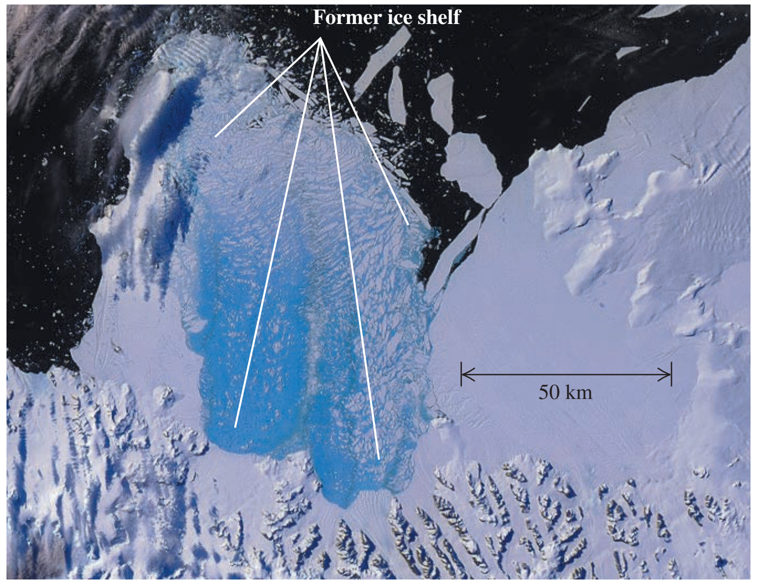
MOLECULES AND CONDENSED MATTER

42



? In 2002 a 10,000-year-old Antarctic ice shelf the size of Rhode Island abruptly collapsed in response to increasing summer temperatures. What property of carbon dioxide molecules in our atmosphere makes them a potent agent for triggering higher average temperatures worldwide?

LEARNING GOALS

By studying this chapter, you will learn:

- The various types of bonds that hold atoms together.
- How the rotational and vibrational dynamics of molecules are revealed by molecular spectra.
- How and why atoms form into crystalline structures.
- How to use the energy-band concept to explain the electrical properties of solids.
- A simple model for metals that explains many of their physical properties.
- How the character of a semiconductor can be radically transformed by adding small amounts of an impurity.
- Some of the technological applications of semiconductor devices.
- Why certain materials become superconductors at low temperature.

In Chapter 41 we discussed the structure and properties of isolated atoms. But such atoms are the exception; usually we find atoms combined to form molecules or more extended structures we call condensed matter (liquid or solid). It's the attractive forces between atoms, called molecular bonds, that causes them to combine. In this chapter we'll study several kinds of bonds as well as the energy levels and spectra associated with diatomic molecules. We will see that just as atoms have quantized energies determined by the quantum-mechanical state of their electrons, so molecules have quantized energies determined by their rotational and vibrational states.

The same physical principles behind molecular bonds also apply to the study of condensed matter, in which various types of bonding occur. We'll explore the concept of energy bands and see how it helps us understand the properties of solids. Then we'll look more closely at the properties of a special class of solids called semiconductors. Devices using semiconductors are found in every radio, TV, pocket calculator, and computer used today; they have revolutionized the entire field of electronics during the past half-century.

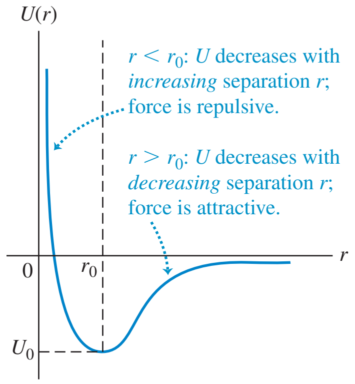
42.1 Types of Molecular Bonds

We can use our discussion of atomic structure in Chapters 41 as a basis for exploring the nature of *molecular bonds,* the interactions that hold atoms together to form stable structures such as molecules and solids.

Ionic Bonds

The **ionic bond** is an interaction between oppositely charged *ionized* atoms. The most familiar example is sodium chloride (NaCl), in which the sodium atom gives its one 3*s* electron to the chlorine atom, filling the vacancy in the 3*p* subshell of chlorine.

42.1 When the separation r between two oppositely charged ions is large, the potential energy $U(r)$ is proportional to $1/r$ as for point charges and the force is attractive. As r decreases, the charge clouds of the two atoms overlap and the force becomes less attractive. If r is less than the equilibrium separation r_0, the force is repulsive.



Let's look at the energy balance in this transaction. Removing the 3*s* electron from a neutral sodium atom requires 5.138 eV of energy; this is called the *ionization energy* or *ionization potential* of sodium. The neutral chlorine atom can attract an extra electron into the vacancy in the 3*p* subshell, where it is incompletely screened by the other electrons and therefore is attracted to the nucleus. This state has 3.613 eV lower energy than a neutral chlorine atom and a distant free electron; 3.613 eV is the magnitude of the *electron affinity* of chlorine. Thus creating the well-separated Na^+ and Cl^- ions requires a net investment of only $5.138\text{ eV} - 3.613\text{ eV} = 1.525\text{ eV}$. When the two oppositely charged ions are brought together by their mutual attraction, the magnitude of their negative potential energy is determined by how closely they can approach each other. This in turn is limited by the exclusion principle, which forbids extensive overlap of the electron clouds of the two ions. As the distance decreases, the exclusion principle distorts the charge clouds, so the ions no longer interact like point charges and the interaction eventually becomes repulsive (Fig. 42.1).

The minimum electric potential energy for NaCl turns out to be -5.7 eV at a separation of 0.24 nm The net energy released in creating the ions and letting them come together to the equilibrium separation of 0.24 nm is $5.7\text{ eV} - 1.525\text{ eV} = 4.2\text{ eV}$. Thus, if the kinetic energy of the ions is neglected, 4.2 eV is the *binding energy* of the NaCl molecule, the energy that is needed to dissociate the molecule into separate neutral atoms.

Example 42.1 Electric potential energy of the NaCl molecule

Find the electric potential energy of Na^+ and Cl^- ions separated by 0.24 nm if they can be treated as point charges.

SOLUTION

IDENTIFY: We use the ideas from Section 23.1 about the electric potential energy of two point charges.

SET UP: Equation (23.9) tells us that the electric potential energy of two point charges q and q_0 separated by a distance r is $U = qq_0/4\pi\epsilon_0 r$.

EXECUTE: The two charges are $q = +e$ (for Na^+) and $q_0 = -e$ (for Cl^-), and the separation is $r = 0.24\text{ nm} = 0.24 \times 10^{-9}\text{ m}$. From Eq. (23.9),

$$U = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r_0} = -(9.0 \times 10^9\text{ N}\cdot\text{m}^2/\text{C}^2)\frac{(1.6 \times 10^{-19}\text{ C})^2}{0.24 \times 10^{-9}\text{ m}}$$
$$= -9.6 \times 10^{-19}\text{ J} = -6.0\text{ eV}$$

EVALUATE: This result agrees fairly well with the observed value of -5.7 eV. The difference is because at the equilibrium separation the ions don't behave exactly like point charges; at this separation the electron clouds of the two ions are overlapping.

Covalent Bonds

Ionic bonds are interactions between charge distributions that are nearly spherically symmetric; hence they are not highly directional. They can involve more than one electron per atom. The alkaline earth elements form ionic compounds in which an atom loses *two* electrons; an example is $Mg^{2+}(Cl^-)_2$. Loss of more than two electrons is relatively rare; instead, a different kind of bond comes into operation.

The **covalent bond** is characterized by a more egalitarian participation of the two atoms than occurs with the ionic bond. The simplest covalent bond is found in the hydrogen molecule, a structure containing two protons and two electrons. This bond is shown schematically in Fig. 42.2. As the separate atoms (Fig. 42.2a) come together, the electron wave functions are distorted and become more concentrated in the region between the two protons (Fig. 42.2b). The net attraction of the electrons for each proton more than balances the repulsion of the two protons and of the two electrons.

The attractive interaction is then supplied by a *pair* of electrons, one contributed by each atom, with charge clouds that are concentrated primarily in the region between the two atoms. The energy of the covalent bond in the hydrogen molecule H_2 is -4.48 eV.

As we saw in Chapter 41, the exclusion principle permits two electrons to occupy the same region of space (that is, to be in the same spatial quantum state) only when they have opposite spins. When the spins are parallel, the exclusion principle forbids the molecular state that would be most favorable from energy considerations (with both electrons in the region between atoms). Opposite spins are an essential requirement for a covalent bond, and no more than two electrons can participate in such a bond.

However, an atom with several electrons in its outermost shell can form several covalent bonds. The bonding of carbon and hydrogen atoms, of central importance in organic chemistry, is an example. In the *methane* molecule (CH_4) the carbon atom is at the center of a regular tetrahedron, with a hydrogen atom at each corner. The carbon atom has four electrons in its *L* shell, and each of these four electrons forms a covalent bond with one of the four hydrogen atoms (Fig. 42.3). Similar patterns occur in more complex organic molecules.

Because of the role played by the exclusion principle, covalent bonds are highly directional. In the methane molecule the wave function for each of carbon's four valence electrons is a combination of the 2*s* and 2*p* wave functions called a *hybrid wave function.* The probability distribution for each one has a lobe protruding toward a corner of a tetrahedron. This symmetrical arrangement minimizes the overlap of wave functions for the electron pairs, minimizing their repulsive potential energy.

Ionic and covalent bonds represent two extremes in molecular bonding, but there is no sharp division between the two types. Often there is a *partial* transfer of one or more electrons from one atom to another. As a result, many molecules that have dissimilar atoms have electric dipole moments—that is, a preponderance of positive charge at one end and of negative charge at the other. Such molecules are called *polar* molecules. Water molecules have large electric dipole moments; these are responsible for the exceptionally large dielectric constant of liquid water (see Sections 24.4 and 24.5).

van der Waals Bonds

Ionic and covalent bonds, with typical bond energies of 1 to 5 eV, are called *strong bonds.* There are also two types of weaker bonds. One of these, the **van der Waals bond,** is an interaction between the electric dipole moments of atoms or molecules; typical energies are 0.1 eV or less. The bonding of water molecules in the liquid and solid states results partly from dipole–dipole interactions.

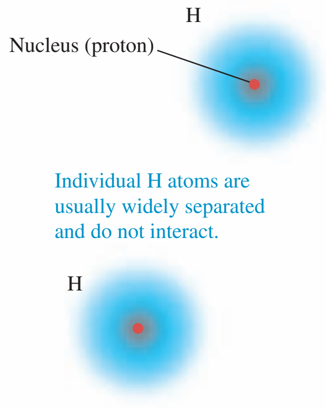
No atom has a permanent electric dipole moment, nor do many molecules. However, fluctuating charge distributions can lead to fluctuating dipole moments; these in turn can induce dipole moments in neighboring structures. Overall, the resulting dipole–dipole interaction is attractive, giving a weak bonding of atoms or molecules. The interaction potential energy drops off very quickly with distance r between molecules, usually as $1/r^6$. The liquefaction and solidification of the inert gases and of molecules such as H_2, O_2, and N_2 are due to induced-dipole van der Waals interactions. Not much thermal-agitation energy is needed to break these weak bonds, so such substances usually exist in the liquid and solid states only at very low temperatures.

Hydrogen Bonds

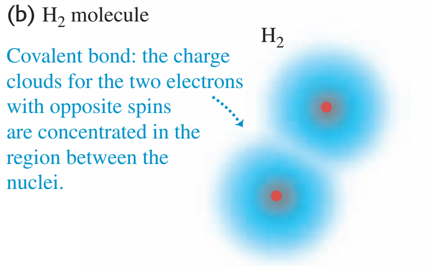
In the other type of weak bond, the **hydrogen bond,** a proton $(H^+$ ion) gets between two atoms, polarizing them and attracting them by means of the induced dipoles. This bond is unique to hydrogen-containing compounds because only hydrogen has a singly ionized state with no remaining electron cloud; the hydrogen ion is a bare proton, much smaller than any other singly ionized atom. The

42.2 Covalent bond in a hydrogen molecule.

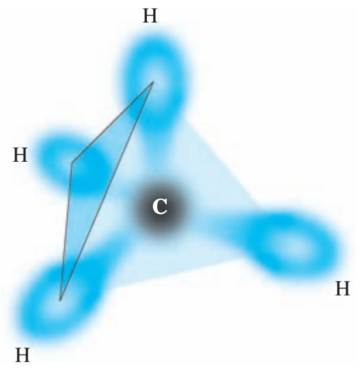
(a) Separate hydrogen atoms



(b) H_2 molecule



42.3 Schematic diagram of the methane (CH_4) molecule. The carbon atom is at the center of a regular tetrahedron and forms four covalent bonds with the hydrogen atoms at the corners. Each covalent bond includes two electrons with opposite spins, forming a charge cloud that is concentrated between the carbon atom and a hydrogen atom.



bond energy is usually less than 0.5 eV. The hydrogen bond plays an essential role in many organic molecules, including the cross-linking of polymer chains such as polyethylene and cross-link bonding between the two strands of the double-helix DNA molecule. Hydrogen bonding also plays a role in the structure of ice.

All these bond types hold the atoms together in *solids* as well as in molecules. Indeed, a solid is in many respects a giant molecule. Still another type of bonding, the *metallic bond,* comes into play in the structure of metallic solids. We'll return to this subject in Section 42.3.

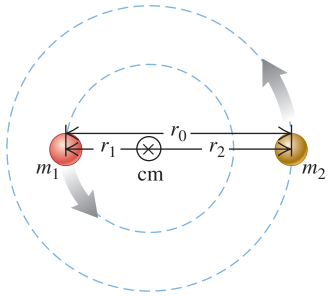
Test Your Understanding of Section 42.1 If electrons obeyed the exclusion principle but did *not* have spin, how many electrons could participate in a covalent bond? (i) one; (ii) two; (iii) three; (iv) more than three.

42.2 Molecular Spectra

Molecules have energy levels that are associated with rotational motion of a molecule as a whole and with vibrational motion of the atoms relative to each other. Just as transitions between energy levels in atoms lead to atomic spectra, transitions between rotational and vibrational levels in molecules lead to *molecular spectra.*

Rotational Energy Levels

42.4 A diatomic molecule modeled as two point masses m_1 and m_2 separated by a distance r_0. The distances of the masses from the center of mass are r_1 and r_2, where $r_1 + r_2 = r_0$.



In this discussion we'll concentrate mostly on *diatomic* molecules, to keep things as simple as possible. In Fig. 42.4 we picture a diatomic molecule as a rigid dumbbell (two point masses m_1 and m_2 separated by a constant distance r_0) that can *rotate* about axes through its center of mass, perpendicular to the line joining them. What are the energy levels associated with this motion?

We showed in Section 10.5 that when a rigid body rotates with angular speed ω about a perpendicular axis through its center of mass, the magnitude L of its angular momentum is given by Eq. (10.28), $L = I\omega$, where I is its moment of inertia about that symmetry axis. Its kinetic energy is given by Eq. (9.17), $K = \frac{1}{2}I\omega^2$. Combining these two equations, we find $K = L^2/2I$. There is no potential energy U, so the kinetic energy K is equal to the total mechanical energy E:

$$E = \frac{L^2}{2I} \qquad (42.1)$$

Zero potential energy U means no dependence of U on θ or ϕ. But the potential-energy function U in the hydrogen atom also has no dependence on θ or ϕ. Thus the angular solutions to the Schrödinger equation for rigid-body rotation are the same as for the hydrogen atom, and the angular momentum is quantized in the same way. As in Eq. (41.4),

$$L^2 = l(l+1)\hbar^2 \qquad (l = 0, 1, 2\ldots) \qquad (42.2)$$

Combining Eqs. (42.1) and (42.2), we obtain the *rotational energy levels:*

$$E_l = l(l+1)\frac{\hbar^2}{2I} \qquad (l = 0, 1, 2, \ldots) \qquad \text{(rotational energy levels, diatomic molecule)} \qquad (42.3)$$

42.5 The ground level and first four excited rotational energy levels for a diatomic molecule. The levels are not equally spaced.

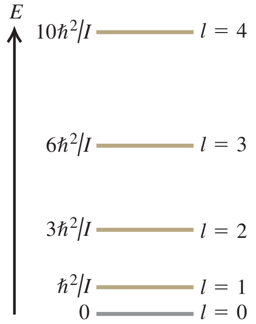


Figure 42.5 is an energy-level diagram showing these rotational levels. The ground level has zero quantum number l and zero energy E, corresponding to zero angular momentum (no rotation). The spacing of adjacent levels increases with increasing l.

We can express the moment of inertia I in Eqs. (42.1) and (42.3) in terms of the *reduced mass* m_r of the molecule:

$$m_r = \frac{m_1 m_2}{m_1 + m_2} \qquad (42.4)$$

We introduced this quantity in Section 38.5 to accommodate the finite nuclear mass of the hydrogen atom. In Fig. 42.4 the distances r_1 and r_2 are the distances from the center of mass to the nuclei of the atoms. By definition of the center of mass, $m_1 r_1 = m_2 r_2$, and the figure also shows that $r_0 = r_1 + r_2$. Solving these equations for r_1 and r_2, we find

$$r_1 = \frac{m_2}{m_1 + m_2}r_0 \qquad r_2 = \frac{m_1}{m_1 + m_2}r_0 \qquad (42.5)$$

The moment of inertia is $I = m_1 r_1^2 + m_2 r_2^2$; substituting Eq. (42.5), we find

$$I = m_1\frac{m_2^2}{(m_1 + m_2)^2}r_0^2 + m_2\frac{m_1^2}{(m_1 + m_2)^2}r_0^2 = \frac{m_1 m_2}{m_1 + m_2}r_0^2 \quad \text{or}$$

$$I = m_r r_0^2 \qquad \text{(moment of inertia of a diatomic molecule)} \qquad (42.6)$$

The reduced mass enables us to reduce this two-body problem to an equivalent one-body problem (a particle of mass m_r moving around a circle with radius r_0), just as we did with the hydrogen atom. Indeed, the only difference between this problem and the hydrogen atom is the difference in the radial forces. To conserve angular momentum, the allowed transitions are determined by the same selection rule as for the hydrogen atom: In allowed transitions, l must change by exactly one unit.

Example 42.2 Rotational spectrum of carbon monoxide

The two nuclei in the carbon monoxide (CO) molecule are 0.1128 nm apart. The mass of the most common carbon atom is exactly 12 u, or 1.993×10^{-26} kg. The mass of the most common oxygen atom is 15.995 u = 2.656×10^{-26} kg. (a) Find the energies of the lowest three rotational energy levels. Express your results in electron volts. (b) Find the wavelength of the photon emitted in the transition from the $l = 2$ to the $l = 1$ level.

SOLUTION

IDENTIFY: This problem uses the ideas developed in this section about the rotational energy levels of molecules.

SET UP: We are given the distance r_0 between the atoms and their masses m_1 and m_2. We calculate the reduced mass m_r using Eq. (42.4), the moment of inertia I of the molecule using Eq. (42.6), and the energies of the levels using Eq. (42.3). The energy E of the emitted photon is equal to the difference in energy between the $l = 2$ and $l = 1$ levels. We determine the wavelength using the relationship $E = hc/\lambda$ for a photon.

EXECUTE: (a) Using Eq. (42.4), we find that the reduced mass is $m_r = 1.139 \times 10^{-26}$ kg. From Eq. (42.6),

$$\begin{aligned} I = m_r r_0^2 &= (1.139 \times 10^{-26}\ \text{kg})(0.1128 \times 10^{-9}\ \text{m})^2 \\ &= 1.449 \times 10^{-46}\ \text{kg} \cdot \text{m}^2 \end{aligned}$$

The rotational levels are given by Eq. (42.3):

$$\begin{aligned} E_l &= l(l+1)\frac{\hbar^2}{2I} = l(l+1)\frac{(1.0546 \times 10^{-34}\ \text{J} \cdot \text{s})^2}{2(1.449 \times 10^{-46}\ \text{kg} \cdot \text{m}^2)} \\ &= l(l+1)(3.838 \times 10^{-23}\ \text{J}) = l(l+1)0.2395\ \text{meV} \end{aligned}$$

Substituting $l = 0, 1, 2$, we find

$$E_0 = 0 \qquad E_1 = 0.479\ \text{meV} \qquad E_2 = 1.437\ \text{meV}$$

(b) The photon energy is

$$E = E_2 - E_1 = 0.958\ \text{meV}$$

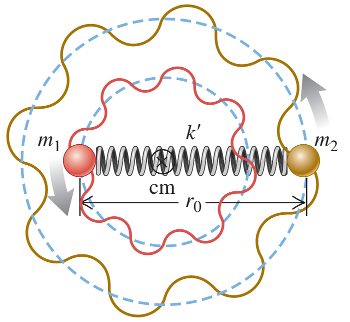
The photon wavelength is

$$\begin{aligned} \lambda = \frac{hc}{E} &= \frac{(4.136 \times 10^{-15}\ \text{eV} \cdot \text{s})(3.00 \times 10^8\ \text{m/s})}{0.958 \times 10^{-3}\ \text{eV}} \\ &= 1.29 \times 10^{-3}\ \text{m} = 1.29\ \text{mm} \end{aligned}$$

EVALUATE: The difference between the first two rotational energy levels of CO is very small (about $\frac{1}{2}$ meV, where 1 meV = 10^{-3} eV) compared to the difference between atomic energy levels (typically a few eV) associated with optical spectra. Hence a photon emitted by a CO molecule in a transition from the $l = 2$ to the $l = 1$ level has very low energy and a very long wavelength compared to visible light. Indeed, the wavelength calculated in part (b) is in the microwave part of the spectrum. Photon wavelengths for rotational transitions in other molecules are also long, falling within the microwave and far infrared regions of the spectrum.

In this example we were given the equilibrium separation between the atoms, also called the *bond length,* and we used it to calculate one of the wavelengths emitted by excited CO molecules. In actual experiments, scientists work this problem backward: By measuring the microwave emissions of a sample of diatomic molecules, they determine the moment of inertia of the molecule and hence the bond length.

42.6 A diatomic molecule modeled as two point masses m_1 and m_2 connected by a spring with force constant k'.



Vibrational Energy Levels

Molecules are never completely rigid. In a more realistic model of a diatomic molecule we represent the connection between atoms not as a rigid rod but as a *spring* (Fig. 42.6). Then in addition to rotating, the atoms of the molecule can *vibrate* about their equilibrium positions along the line joining them. For small oscillations the restoring force can be taken as proportional to the displacement from the equilibrium separation r_0 (like a spring that obeys Hooke's law with a force constant k'), and the system is a harmonic oscillator. We discussed the quantum-mechanical harmonic oscillator in Section 40.4. The energy levels are given by Eq. (40.25), with the mass m replaced with the reduced mass m_r:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{m_r}} \qquad (n = 0, 1, 2, \dots) \tag{42.7}$$

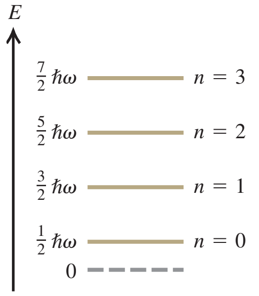
(vibrational energy levels of a diatomic molecule)

This represents a series of levels equally spaced in energy, with an energy separation of

$$\Delta E = \hbar\omega = \hbar\sqrt{\frac{k'}{m_r}} \tag{42.8}$$

Figure 42.7 is an energy-level diagram showing these vibrational levels. (Compare Fig. 40.18.)

42.7 The ground level and first three excited vibrational levels for a diatomic molecule, assuming small oscillations. The levels are equally spaced, with spacing $\Delta E = \hbar\omega$.



CAUTION **Watch out for k, k', and K** We're again using k' for the force constant, this time to minimize confusion with Boltzmann's constant k, the gas constant per molecule (introduced in Section 18.3). Besides the quantities k and k', we also use the absolute temperature unit 1 K = 1 kelvin.

Example 42.3 Force constant of carbon monoxide

For the carbon monoxide molecule of Example 42.2, the spacing of vibrational energy levels is found to be $\Delta E = 0.2690$ eV. Find the force constant k' for the interatomic force.

SOLUTION

IDENTIFY: The key idea of this problem is that the vibrational energy levels of a diatomic molecule have a uniform spacing ΔE that depends on the force constant of the "spring" force that holds the molecule together.

SET UP: We are given the value of ΔE, so we solve Eq. (42.8) for the force constant k' (our target variable).

EXECUTE: From Eq. (42.8),

$$k' = m_r\left(\frac{\Delta E}{\hbar}\right)^2 = (1.139 \times 10^{-26}\ \text{kg})\left(\frac{0.2690\ \text{eV}}{6.582 \times 10^{-16}\ \text{eV}\cdot\text{s}}\right)^2$$
$$= 1902\ \text{N/m}$$

EVALUATE: This corresponds to a fairly loose spring; to stretch a macroscopic spring with this force constant by 1.0 cm would require a pull of 19 N (about 4 lb). Force constants for diatomic molecules are typically about 100 to 2000 N/m.

Rotation and Vibration Combined

Visible-light photons have energies between 1.77 eV and 3.10 eV. The 0.2690-eV energy difference in Example 42.3 corresponds to a photon in the infrared region of the spectrum, though closer to the visible region than the photon in the *rotational* transition in Example 42.2. Vibrational energy differences, while usually much smaller than those that produce atomic spectra, are usually much *larger* than the rotational energy differences.

When we include *both* rotational and vibrational energies, the energy levels for our diatomic molecule are

$$E_{nl} = l(l + 1)\frac{\hbar^2}{2I} + \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{m_r}} \tag{42.9}$$

The energy-level diagram is shown in Fig. 42.8. For each value of n there are many values of l, forming a series of closely spaced levels.

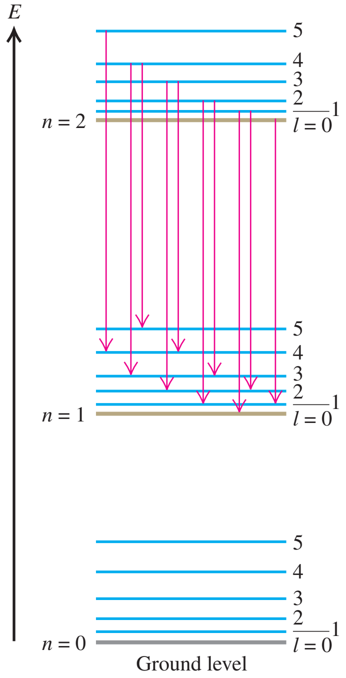
The arrows in Fig. 42.8 show several possible transitions in which a molecule goes from a level with $n = 2$ to a level with $n = 1$ by emitting a photon. Because the photon carries angular momentum, these molecular transitions obey a *selection rule* (see Section 41.3). This rule states that the angular momentum quantum number l must either increase by 1 or decrease by 1: $\Delta l = \pm 1$. An additional selection rule states that if the vibrational level changes, the vibrational quantum number n in Eq. (42.9) must increase by 1 $(\Delta n = 1)$ if a photon is absorbed or decrease by 1 $(\Delta n = -1)$ if a photon is emitted.

As an illustration of these selection rules, Fig. 42.8 shows that a molecule in the $n = 2$, $l = 4$ level can emit a photon and drop into the $n = 1$, $l = 5$ level $(\Delta n = -1, \Delta l = +1)$ or the $n = 1$, $l = 3$ level $(\Delta n = -1, \Delta l = -1)$, but is forbidden from making a $\Delta n = -1$, $\Delta l = 0$ transition into the $n = 1$, $l = 4$ level.

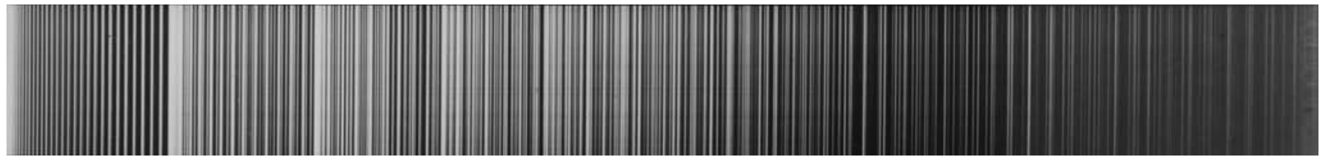
Transitions between states with various pairs of n-values give different series of spectrum lines, and the resulting spectrum has a series of *bands.* Each band corresponds to a particular vibrational transition, and each individual line in a band represents a particular rotational transition, with the selection rule $\Delta l = \pm 1$. A typical *band spectrum* is shown in Fig. 42.9.

All molecules can have excited states of the *electrons* in addition to the rotational and vibrational states that we have described. In general, these lie at higher energies than the rotational and vibrational states, and there is no simple rule relating them. When there is a transition between electronic states, the $\Delta n = \pm 1$ selection rule for the vibrational levels no longer holds.

42.8 Energy-level diagram for vibrational and rotational energy levels of a diatomic molecule. For each vibrational level (n) there is a series of more closely spaced rotational levels (l). Several transitions corresponding to a single band in a band spectrum are shown. These transitions obey the selection rule $\Delta l = \pm 1$.



42.9 A typical molecular band spectrum.



Example 42.4 Vibration-rotation spectrum of carbon monoxide

Again consider the CO molecule of Examples 42.2 and 42.3. Find the photon wavelength that is emitted when there is a change in its vibrational energy and its rotational energy is (a) initially zero and (b) finally zero.

SOLUTION

IDENTIFY: This problem uses the selection rules for the vibrational and rotational transitions of a diatomic molecule.

SET UP: In either case the energy of the emitted photon equals the difference between the initial and final energies of the molecule. Since a photon is emitted as the vibrational energy changes, the vibrational quantum number decreases by 1. For the case in part (a) the initial value of l is zero (no rotational energy), so the selection rule $\Delta l = \pm 1$ tells us that the *final* value of l is 1. For the case in part (b) the *final* value of l is zero, so the same selection rule tells us that the *initial* value of l is 1. Hence in part (a) the photon energy E is equal to the difference $\hbar\omega$ between adjacent vibrational energy levels *minus* the amount of rotational energy that the molecule *gains,* while in part (b) E is equal to $\hbar\omega$ *plus* the amount of rotational energy that the molecules *loses.* We use the results of Examples 42.2 and 42.3 to tell us the rotational and vibrational energy changes, respectively, and we use $E = hc/\lambda$ to determine the wavelengths (our target variables).

EXECUTE: (a) From Example 42.2 the energy difference between the $l = 0$ and $l = 1$ rotational levels of CO is 0.479 meV = 0.000479 meV, and from Example 42.3 the energy difference

Continued

between adjacent vibrational levels is 0.2690 eV. Hence the energy of this emitted photon is 0.2690 eV − 0.000479 eV = 0.2685 eV, and the photon wavelength is

$$\lambda = \frac{hc}{E} = \frac{(4.136 \times 10^{-15}\ \text{eV}\cdot\text{s})(2.998 \times 10^{8}\ \text{m/s})}{0.2685\ \text{eV}}$$

$$= 4.618 \times 10^{-6}\ \text{m} = 4.618\ \mu\text{m}$$

(b) Now the photon has 0.2690 eV from the decrease in vibrational energy and 0.000479 eV from the decrease in rotational energy for a total of $E = 0.2695$ eV for the photon. The photon's wavelength is then

$$\lambda = \frac{hc}{E} = \frac{(4.136 \times 10^{-15}\ \text{eV}\cdot\text{s})(2.998 \times 10^{8}\ \text{m/s})}{0.2695\ \text{eV}}$$

$$= 4.601 \times 10^{-6}\ \text{m} = 4.601\ \mu\text{m}$$

EVALUATE: In part (b) the molecule loses more energy than it does in part (a), so the emitted photon must have greater energy and a shorter wavelength. This is just what our results show.

Complex Molecules

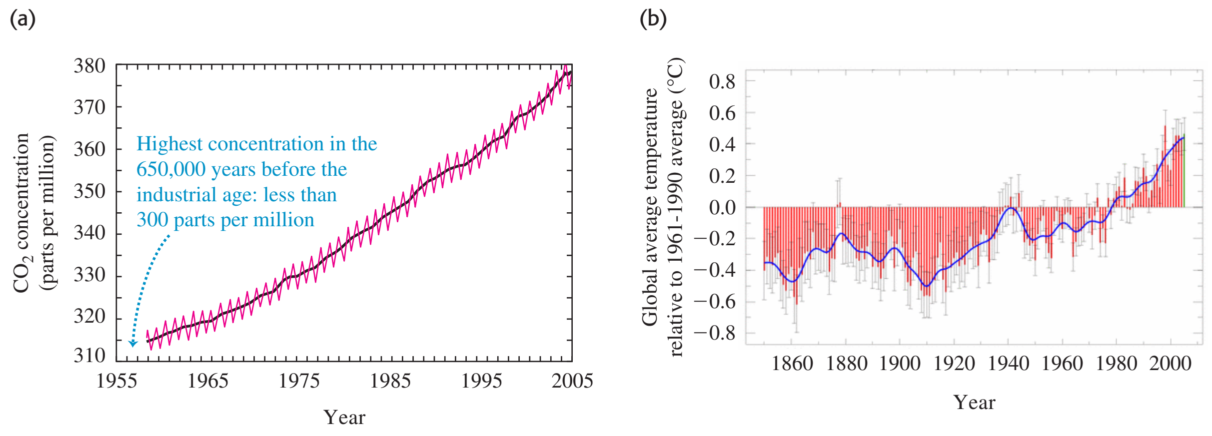
We can apply these same principles to more complex molecules. A molecule with three or more atoms has several different kinds or *modes* of vibratory motion. Each mode has its own set of energy levels, related to its frequency by Eq. (42.7). In nearly all cases the associated radiation lies in the infrared region of the electromagnetic spectrum.

Infrared spectroscopy has proved to be an extremely valuable analytical tool. It provides information about the strength, rigidity, and length of molecular bonds and the structure of complex molecules. Also, because every molecule (like every atom) has its characteristic spectrum, infrared spectroscopy can be used to identify unknown compounds.

One molecule that can readily absorb and emit infrared radiation is carbon dioxide (CO_2), which is the fourth most abundant constituent of the earth's atmosphere (after nitrogen, oxygen, and argon). This has important consequences for our planet's climate. To be in thermal equilibrium, the earth—which acts as a blackbody (see Section 38.8)—must radiate as much energy into space as it receives from the sun. The earth's surface temperature is such that most of the radiated energy is in the infrared part of the spectrum. However, CO_2 in the atmosphere absorbs some of this infrared radiation and re-radiates it toward the earth rather than allowing it to escape into space. In order to maintain thermal equilibrium, the earth's surface must compensate by increasing its temperature T and hence its total output of radiation (which is proportional to T^4). This means that our planet's surface temperature is higher than it would be if there were no atmospheric CO_2.

Measurements of air trapped in ancient Antarctic ice shows that over the past 650,000 years CO_2 has constituted less than 300 parts per million of our atmosphere. Since the beginning of the industrial age, however, the burning of fossil fuels such as coal and petroleum has elevated the atmospheric CO_2 concentration to unprecedented levels (Fig. 42.10a). As a consequence, since the 1950s the global average surface temperature has increased by 0.6°C and the earth has experienced the hottest years ever recorded (Fig. 42.10b). If we continue to consume fossil fuels at the same rate, by 2050 the atmospheric CO_2 concentration will reach 600 parts per million, well off the scale of Fig 42.10a. The resulting temperature increase in the polar regions will cause massive quantities of ice to melt and run from solid land to the sea, thus raising ocean levels worldwide and threatening the homes and lives of hundreds of millions of people who leave near the coast. Coping with this threat is one of the greatest challenges facing 21st-century civilization.

42.10 (a) The concentration of atmospheric CO_2 has increased by 18% since continuous measurements began in 1958. (The yearly variations are due to increased intake of CO_2 by plants in spring and summer.) (b) The increase in global average temperature since the beginning of the industrial era is a result of the increase in CO_2 concentration.



Test Your Understanding of Section 42.2 A rotating diatomic molecule emits a photon when it makes a transition from level l to level $l - 1$. If the value of l increases, does the wavelength of the emitted photon (i) increase, (ii) decrease, or (iii) remain unchanged?

42.3 Structure of Solids

The term *condensed matter* includes both solids and liquids. In both states, the interactions between atoms or molecules are strong enough to give the material a definite volume that changes relatively little with applied stress. In condensed matter, adjacent atoms attract one another until their outer electron charge clouds begin to overlap significantly. Thus the distances between adjacent atoms in condensed matter are about the same as the diameters of the atoms themselves, typically 0.1 to 0.5 nm. Also, when we speak of the distances between atoms, we mean the center-to-center (nucleus-to-nucleus) distances.

Ordinarily, we think of a liquid as a material that can flow and of a solid as a material with a definite shape. However, if you heat a horizontal glass rod in the flame of a burner, you'll find that the rod begins to sag (flow) more and more easily as its temperature rises. Glass has no definite transition from solid to liquid, and no definite melting point. On this basis, we can consider glass at room temperature as being an extremely viscous liquid. Tar and butter show similar behavior.

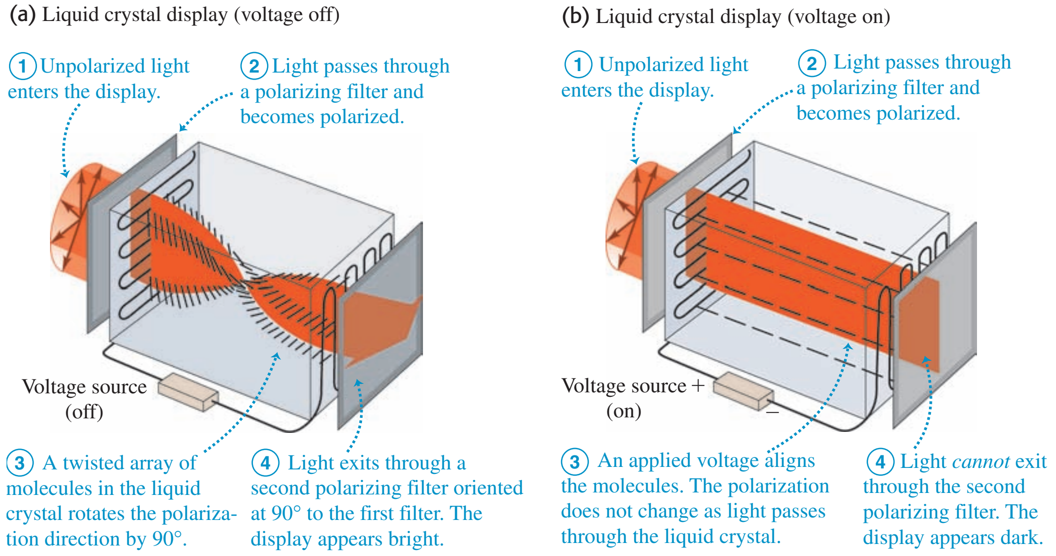
What is the microscopic difference between materials like glass or butter and solids like ice or copper, which do have definite melting points? Ice and copper are examples of *crystalline solids* in which the atoms have *long-range order,* a recurring pattern of atomic positions that extends over many atoms. This pattern is called the *crystal structure.* In contrast, glass at room temperature is an example of an *amorphous* solid, one that has no long-range order, but only *short-range order* (correlations between neighboring atoms or molecules). Liquids also have only short-range order. The boundaries between crystalline solid, amorphous solid, and liquid may be sometimes blurred. Some solids, crystalline when perfect, can form with so many imperfections in their structure that they have almost no long-range order. Conversely, some liquids have a fairly high degree of long-range order; a familiar example is the type of *liquid crystal* illustrated in Fig. 42.11 (next page).

Nearly everything we know about crystal structure has been learned from diffraction experiments, initially with x rays and later with electrons and neutrons. A typical distance between atoms is of the order of 0.1 nm. You can show that 12.4-keV x rays, 150-eV electrons, and 0.0818-eV neutrons all have wavelengths $\lambda = 0.1$ nm.

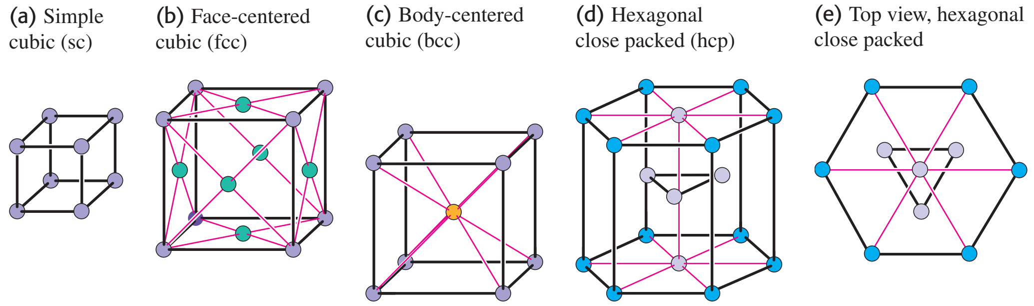
Crystal Lattices and Structures

A *crystal lattice* is a repeating pattern of mathematical points that extends throughout space. There are 14 general types of such patterns; Fig. 42.12 (next page) shows small portions of some common examples. The *simple cubic lattice* (sc) has a lattice point at each corner of a cubic array (Fig. 42.12a). The *face-centered cubic lattice* (fcc) is like the simple cubic but with an additional lattice point at the center of each cube face (Fig. 42.12b). The *body-centered cubic*

42.11 A simple version of a liquid-crystal display (LCD). A thin layer of liquid crystal—an organic compound whose cylindrical molecules tend to line up parallel to each other—is confined between two parallel glass plates and placed between two crossed polarizing filters. (a) The molecules tend to align with fine scratches on the glass plates, twisting them so that the light can pass through the second polarizing filter. (b) Each glass plate also has a pattern of fine electrodes. When a voltage is applied between the plates, the molecules align with the electric field and the light does not pass through the second polarizing filter. Hence switching the voltage on changes the display from light to dark.



42.12 Portions of some common types of crystal lattices.



lattice (bcc) is like the simple cubic but with an additional point at the center of each cube (Fig. 42.12c). The *hexagonal close-packed lattice* has layers of lattice points in hexagonal patterns, each hexagon made up of six equilateral triangles (Figs. 42.12d and 42.12e).

CAUTION **A perfect crystal lattice is infinitely large** Figure 42.12 shows just enough lattice points so you can easily visualize the pattern; the lattice, a mathematical abstraction, extends throughout space. Thus the lattice points shown repeat endlessly in all directions. ▮

In a crystal structure, a single atom or a group of atoms is associated with *each* lattice point. The group may contain the same or different kinds of atoms. This atom or group of atoms is called a *basis.* Thus a complete description of a crystal structure includes both the lattice and the basis. We initially consider *perfect crystals,* or *ideal single crystals,* in which the crystal structure extends uninterrupted throughout space.

The bcc and fcc structures are two common simple crystal structures. The alkali metals have a bcc structure—that is, a bcc lattice with a basis of one atom at each lattice point. Each atom in a bcc structure has eight nearest neighbors (Fig. 42.13a). The elements Al, Ca, Cu, Ag, and Au have an fcc structure—that is, an fcc lattice with a basis of one atom at each lattice point. Each atom in an fcc structure has 12 nearest neighbors (Fig. 42.13b).

42.13 (a) The bcc *structure* is composed of a bcc *lattice* with a basis of one atom for each lattice point. (b) The fcc *structure* is composed of an fcc *lattice* with a basis of one atom for each lattice point. These structures repeat precisely to make up perfect crystals.

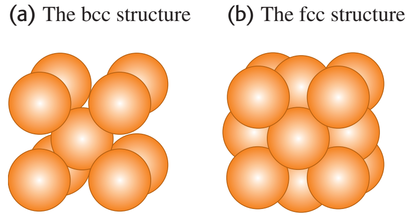

(a) The bcc structure (b) The fcc structure

Figure 42.14 shows a representation of the structure of sodium chloride (NaCl, ordinary salt). It may look like a simple cubic structure, but it isn't. The sodium and chloride ions each form an fcc structure, so we can think roughly of the sodium chloride structure as being composed of two interpenetrating fcc structures. More correctly, the sodium chloride crystal structure of Fig. 42.14 has an fcc lattice with one chloride ion at each lattice point and one sodium ion half a cube length above it. That is, its basis consists of one chloride and one sodium ion.

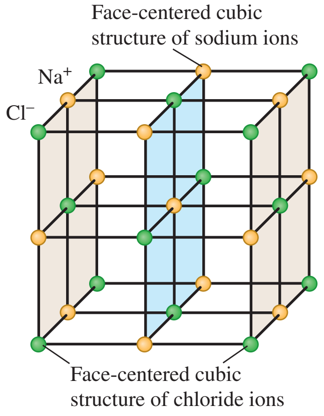
Another example is the *diamond structure;* it's called that because it is the crystal structure of carbon in the diamond form (Fig. 42.15). It's also the crystal structure of silicon, germanium, and gray tin (all four are Group IV elements in the periodic table). The diamond lattice is fcc; the basis consists of one atom at each lattice point and a second *identical* atom displaced a quarter of a cube length in each of the three cube-edge directions. Figure 42.16 will help you visualize this. The shaded volume in Fig. 42.16 shows the bottom right front eighth of the basic cube; the four atoms at alternate corners of this cube are at the corners of a regular tetrahedron, and there is an additional atom at the center. Thus each atom in the diamond structure is at the center of a regular tetrahedron with four nearest-neighbor atoms at the corners.

In the diamond structure, both the purple and green spheres in Fig. 42.16 represent *identical* atoms—for example, both carbon or both silicon. In the cubic zinc sulfide structure, the purple spheres represent one type of atom and the green spheres represent a *different* type. For example, in zinc sulfide (ZnS) each zinc atom (purple in Fig. 42.16) is at the center of a regular tetrahedron with four sulfur atoms (green in Fig. 42.16) at its corners, and vice versa. Gallium arsenide (GaAs) and similar compounds have this same structure.

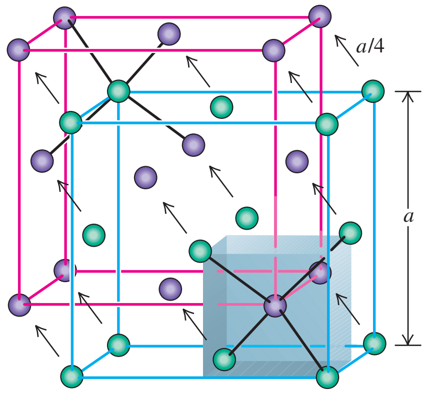
Bonding in Solids

The forces that are responsible for the regular arrangement of atoms in a crystal are the same as those involved in molecular bonds, plus one additional type. Not surprisingly, *ionic* and *covalent* molecular bonds are found in ionic and covalent crystals, respectively. The most familiar *ionic crystals* are the alkali halides, such as ordinary salt (NaCl). The positive sodium ions and the negative chloride ions occupy alternate positions in a cubic arrangement (Fig. 42.14). The attractive forces are the familiar Coulomb's-law forces between charged particles. These forces have no preferred direction, and the arrangement in which the material crystallizes is partly determined by the relative sizes of the two ions. Such a structure is *stable* in the sense that it has lower total energy than the separated ions (see the following example). The negative potential energies of pairs of opposite charges are greater in absolute value than the positive energies of pairs of like charges because the pairs of unlike charges are closer together, on average.

42.14 Representation of part of the sodium chloride crystal structure. The distances between ions are exaggerated.



42.15 The crystal structure of diamond is similar to that of many other, less highly coveted materials. What makes diamond unique are its beautiful optical properties. A large index of refraction makes diamond sparkle due to total internal reflection, and a large amount of dispersion turns white light into a rainbow of colors.



42.16 The diamond structure, shown as two interpenetrating face-centered cubic structures with distances between atoms exaggerated. Relative to the corresponding green atom, each purple atom is shifted up, back, and to the left by a distance $a/4$.

Example 42.5 Potential energy of an ionic crystal

Consider a fictitious one-dimensional ionic crystal consisting of a very large number of alternating positive and negative ions with charges e and $-e$, with equal spacing a along a line. Prove that the total interaction potential energy is negative.

SOLUTION

IDENTIFY: We can treat each ion as a point charge and then use our result from Section 23.1 for the electric potential energy of a collection of point charges.

SET UP: Equations (23.10) and (23.11) tell us to consider the electric potential energy U of each pair of charges. The total potential energy of the system is the sum of the values of U for every possible pair.

EXECUTE: Let's pick an ion somewhere in the middle of the string and add up the potential energies of its interactions with all the ions to one side of it. We get the series

$$\begin{aligned}\sum U &= -\frac{e^2}{4\pi\epsilon_0}\frac{1}{a} + \frac{e^2}{4\pi\epsilon_0}\frac{1}{2a} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{3a} + \cdots \\ &= -\frac{e^2}{4\pi\epsilon_0 a}\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots\right)\end{aligned}$$

You may notice the resemblance of the series in parentheses to the Taylor series for $\ln(1 + x)$:

$$\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots$$

When $x = 1$, we have the series in the parentheses, and

$$\sum U = -\frac{e^2}{4\pi\epsilon_0 a}\ln 2$$

This is certainly a negative quantity. The atoms on the other side of the ion that we're considering make an equal contribution to the potential energy. And if we include the potential energies of all pairs of atoms, the sum is certainly negative.

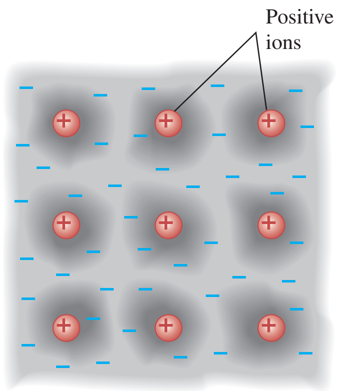
EVALUATE: We conclude that this structure is stable: It has lower energy than the zero electric potential energy that is obtained when all the ions are infinitely separated from each other.

Types of Crystals

Carbon, silicon, germanium, and tin in the diamond structure are simple examples of *covalent crystals.* These elements are in Group IV of the periodic table, meaning that each atom has four electrons in its outermost shell. Each atom forms a covalent bond with each of four adjacent atoms at the corners of a tetrahedron (Fig. 42.16). These bonds are strongly directional because of the asymmetrical electron distributions dictated by the exclusion principle, and the result is the tetrahedral diamond structure.

A third crystal type, less directly related to the chemical bond than are ionic or covalent crystals, is the **metallic crystal.** In this structure, one or more of the outermost electrons in each atom become detached from the parent atom (leaving a positive ion) and are free to move through the crystal. These electrons are not localized near the individual ions. The corresponding electron wave functions extend over many atoms.

42.17 In a metallic solid, one or more electrons are detached from each atom and are free to wander around the crystal, forming an "electron gas." The wave functions for these electrons extend over many atoms. The positive ions vibrate around fixed locations in the crystal.



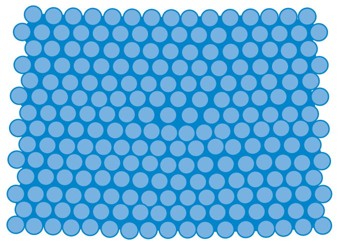
Thus we can picture a metallic crystal as an array of positive ions immersed in a sea of freed electrons whose attraction for the positive ions holds the crystal together (Fig. 42.17). These electrons also give metals their high electrical and thermal conductivities. This sea of electrons has many of the properties of a gas, and indeed we speak of the *electron-gas model* of metallic solids. The simplest version of this model is the *free-electron model,* which ignores interactions with the ions completely (except at the surface). We'll return to this model in Section 42.5.

In a metallic crystal the freed electrons are not localized but are shared among *many* atoms. This gives a bonding that is neither localized nor strongly directional. The crystal structure is determined primarily by considerations of *close packing*—that is, the maximum number of atoms that can fit into a given volume. The two most common metallic crystal lattices, the face-centered cubic and the hexagonal close-packed, are shown in Figs. 42.12b, 42.12d, and 42.12e. In structures composed of these lattices with a basis of one atom, each atom has 12 nearest neighbors.

As we mentioned in Section 42.1, van der Waals interactions and hydrogen bonding also play a role in the structure of some solids. In polyethylene and similar polymers, covalent bonding of atoms forms long-chain molecules, and hydrogen bonding forms cross-links between adjacent chains. In solid water, both van der Waals forces and hydrogen bonds are significant in determining the crystal structures of ice.

Our discussion has centered on perfect crystals, or ideal single crystals. Real crystals show a variety of departures from this idealized structure. Materials are often *polycrystalline,* composed of many small single crystals bonded together at *grain boundaries.* There may be *point defects* within a single crystal: *interstitial* atoms may occur in places where they do not belong, and there may be *vacancies,* positions that should be occupied by an atom but are not. A point defect of particular interest in semiconductors, which we will discuss in Section 42.6, is the *substitutional impurity,* a foreign atom replacing a regular atom (for example, arsenic in a silicon crystal).

42.18 An edge dislocation in two dimensions. In three dimensions an edge dislocation would look like an extra plane of atoms slipped partway into the crystal.



The irregularity is seen most easily by viewing the figure from various directions at a grazing angle with the page.

There are several basic types of extended defects called *dislocations.* One type is the *edge dislocation,* shown schematically in Fig. 42.18, in which one plane of atoms slips relative to another. The mechanical properties of metallic crystals are influenced strongly by the presence of dislocations. The ductility and malleability of some metals depend on the presence of dislocations that can move through the crystal during plastic deformations. Solid-state physicists often point out that the biggest extended defect of all, present in *all* real crystals, is the surface of the material with its dangling bonds and abrupt change in potential energy.

Test Your Understanding of Section 42.3 If a is the distance in an NaCl crystal from an Na^+ ion to one of its nearest-neighbor Cl^- ions, what is the distance from an Na^+ ion to one of its *next-to-nearest*-neighbor Cl^- ions? (i) $a\sqrt{2}$; (ii) $a\sqrt{3}$; (iii) $2a$ (iv) none of these.

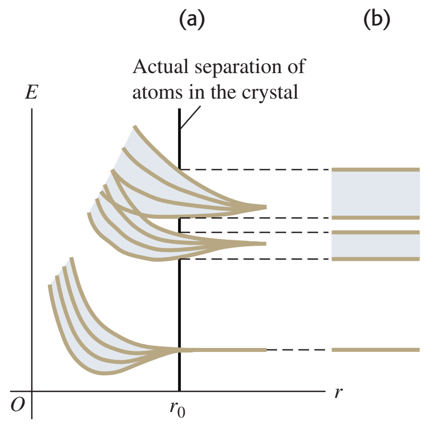
42.4 Energy Bands

The **energy-band** concept, introduced in 1928 (Fig. 42.19), is a great help in understanding several properties of solids. To introduce the idea, suppose we have a large number N of identical atoms, far enough apart that their interactions are negligible. Every atom has the same energy-level diagram. We can draw an energy-level diagram for the *entire system.* It looks just like the diagram for a single atom, but the exclusion principle, applied to the entire system, permits each state to be occupied by N electrons instead of just one.

42.19 The concept of energy bands was first developed by the Swiss-American physicist Felix Bloch (1905–1983) in his doctoral thesis. Our modern understanding of electrical conductivity stems from that landmark work. Bloch's work in nuclear physics brought him (along with Edward Purcell) the 1952 Nobel Prize in physics.

Now we begin to push the atoms uniformly closer together. Because of the electrical interactions and the exclusion principle, the wave functions begin to distort, especially those of the outer, or *valence,* electrons. The corresponding energies also shift, some upward and some downward, by varying amounts, as the valence electron wave functions become less localized and extend over more and more atoms. Thus the valence states that formerly gave the *system* a state with a sharp energy level that could accommodate N electrons now give a *band* containing N closely spaced levels (Fig. 42.20, next page). Ordinarily, N is very large, somewhere near the order of Avogadro's number (10^{24}), so we can accurately treat the levels as forming a *continuous* distribution of energies within a band. Between adjacent energy bands are gaps or forbidden regions where there are *no* allowed energy levels. The inner electrons in an atom are affected much less by nearby atoms than are the valence electrons, and their energy levels remain relatively sharp.

42.20 Origin of energy bands in a solid. (a) As the distance r between atoms decreases, the energy levels spread into bands. The vertical line at r_0 shows the actual atomic spacing in the crystal. (b) Symbolic representation of energy bands.



Insulators, Semiconductors, and Conductors

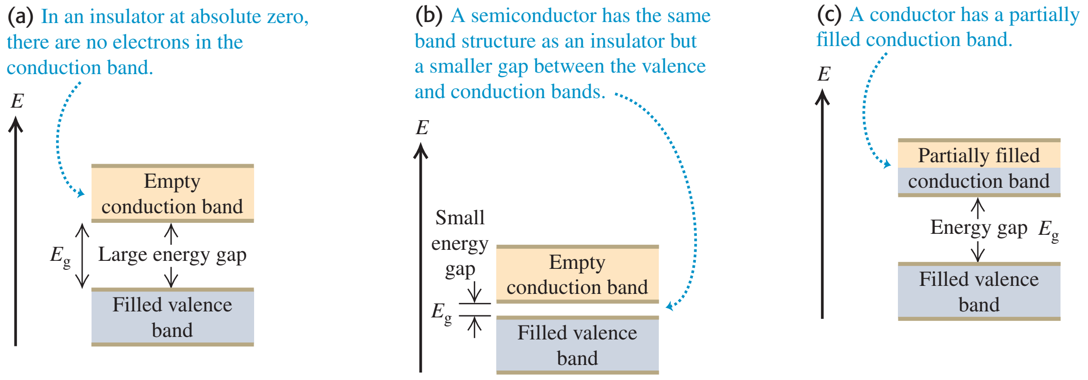
The nature of the energy bands determines whether the material is an electrical insulator, a semiconductor, or a conductor. In particular, what matters are the extent to which the states in each band are occupied and the spacing, or *energy gap,* between adjacent bands. A crucial factor is the exclusion principle (see Section 41.4), which states that only one electron can occupy a given quantum-mechanical state.

In an *insulator* at absolute zero temperature, the highest band that is completely filled, called the **valence band,** is also the highest band that has *any* electrons in it. The next higher band, called the **conduction band,** is completely empty; there are no electrons in its states (Fig. 42.21a). Imagine what happens if an electric field is applied to a material of this kind. To move in response to the field, an electron would have to go into a different quantum state with a slightly different energy. It can't do that, however, because all the neighboring states are already occupied. The only way such an electron can move is to jump across the energy gap into the conduction band, where there are plenty of nearby unoccupied states. At any temperature above absolute zero there is some probability this jump can happen, because an electron can gain energy from thermal motion. In an insulator, however, the energy gap between the valence and conduction bands can be 5 eV or more, and that much thermal energy is not ordinarily available. Hence little or no current flows in response to an applied electric field, and the electric conductivity (Section 25.2) is low. The thermal conductivity (Section 17.7), which also depends on mobile electrons, is likewise low.

We saw in Section 24.4 that an insulator becomes a conductor if it is subjected to a large enough electric field; this is called *dielectric breakdown.* If the electric field is of order 10^{10} V/m, there is a potential difference of a few volts over a distance comparable to atomic sizes. In this case the field can do enough work on a valence electron to boost it across the energy gap and into the conduction band. (In practice dielectric breakdown occurs for fields much less than 10^{10} V/m, because imperfections in the structure of an insulator provide some more accessible energy states *within* the energy gap.)

As in an insulator, a *semiconductor* at absolute zero has an empty conduction band above the full valence band. The difference is that in a semiconductor the energy gap between these bands is relatively small and electrons can more readily jump into the conduction band (Fig. 42.21b). As the temperature of a semiconductor increases, the population in the conduction band increases very rapidly, as does the electric conductivity. For example, in a semiconductor near room temperature with an energy gap of 1 eV, the number of conduction electrons doubles when the temperature rises by just 10°C. We will use the concept of energy bands to explore semiconductors in more depth in Section 42.6.

42.21 Three types of energy-band structure.


(a) In an insulator at absolute zero, there are no electrons in the conduction band.

(b) A semiconductor has the same band structure as an insulator but a smaller gap between the valence and conduction bands.

(c) A conductor has a partially filled conduction band.

In a *conductor* such as a metal, there are electrons in the conduction band even at absolute zero (Fig. 42.21c). The metal sodium is an example. An analysis of the atomic energy-level diagram for sodium (Fig. 38.10a) shows that for an isolated sodium atom, the six lowest excited states (all $3p$ states) are about 2.1 eV above the two $3s$ ground states. In solid sodium, however, the atoms are so close together that the $3s$ and $3p$ *bands* spread out and overlap into a single band. Each sodium atom contributes one electron to the band, leaving an Na^+ ion behind. Each atom also contributes eight *states* to that band (two $3s$, six $3p$), so the band is only one-eighth occupied. We call this structure a *conduction* band because it is only partially occupied. Electrons near the top of the filled portion of the band have many adjacent unoccupied states available, and they can easily gain or lose small amounts of energy in response to an applied electric field. Therefore these electrons are mobile, giving solid sodium its high electrical and thermal conductivity. A similar description applies to other conducting materials.

Example 42.6 Photoconductivity in germanium

Even at room temperature, pure germanium has an almost completely filled valence band separated by a gap of 0.67 eV from an almost completely empty conduction band. It is a poor electrical conductor, but its conductivity increases substantially when it is irradiated with electromagnetic waves of a certain maximum wavelength. What maximum wavelength is appropriate?

SOLUTION

IDENTIFY: The conductivity of a semiconductor increases greatly when electrons are excited from the valence band into the conduction band. In this example, the excitation occurs when an electron absorbs a photon with an energy of at least E_{min}.

SET UP: From the relationship $E = hc/\lambda$ for photons, the *maximum* wavelength corresponds to the *minimum* photon energy.

EXECUTE: An electron at the top of the valence band can absorb a photon with energy of 0.67 eV (no less) and move to the bottom of the conduction band, where it is a mobile charge. Thus the maximum wavelength is

$$\lambda_{\text{max}} = \frac{hc}{E_{\text{min}}} = \frac{(4.136 \times 10^{-15}\ \text{eV} \cdot \text{s})(3.00 \times 10^{8}\ \text{m/s})}{0.67\ \text{eV}}$$

$$= 1.9 \times 10^{-6}\ \text{m} = 1.9\ \mu\text{m} = 1900\ \text{nm}$$

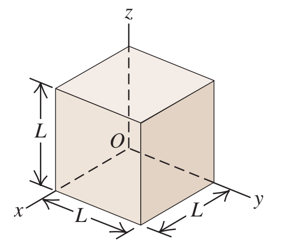
EVALUATE: This wavelength is in the infrared part of the spectrum, so visible-light photons (which have shorter wavelength) will also induce conductivity in germanium. As we will see in Section 42.7, semiconductor crystals are widely used as photocells as well as for many other applications.

Test Your Understanding of Section 42.4 One type of thermometer works by measuring the temperature-dependent electrical resistivity of a sample. Which of the following types of material displays the greatest change in resistivity for a given temperature change? (i) insulator; (ii) semiconductor; (iii) resistor.

42.5 Free-Electron Model of Metals

Studying the energy states of electrons in metals can give us a lot of insight into their electrical and magnetic properties, the electron contributions to heat capacities, and other behavior. As we discussed in Section 42.3, one of the distinguishing features of a metal is that one or more valence electrons are detached from their home atom and can move freely within the metal, with wave functions that extend over many atoms.

42.22 A cubical box with rigid walls and side length L. This is the three-dimensional version of the infinite square well discussed in Section 40.1. The energy levels for a particle in this box are given by Eq. (42.11).



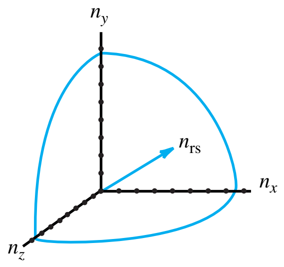
The **free-electron model** assumes that these electrons are completely free inside the material, that they don't interact at all with the ions or with each other, but that there are infinite potential-energy barriers at the surfaces. The wave functions and energy levels are then the three-dimensional versions of those for the particle in a box that we analyzed in Section 40.1 in one dimension. Suppose the box is a cube with side length L (Fig. 42.22). Then the possible wave functions, analogous to Eq. (40.10), are

$$\psi(x, y, z) = A \sin\frac{n_x \pi x}{L} \sin\frac{n_y \pi y}{L} \sin\frac{n_z \pi z}{L} \qquad (42.10)$$

where (n_x, n_y, n_z) is a set of three positive-integer quantum numbers that identify the state. We invite you to verify that these functions are zero at the surfaces of the cube, satisfying the boundary conditions. You can also substitute Eq. (42.10) into the three-dimensional Schrödinger equation, Eq. (40.28), with $U = 0$ to show that the energies of the states are

$$E = \frac{(n_x^2 + n_y^2 + n_z^2)\pi^2\hbar^2}{2mL^2} \qquad (42.11)$$

This equation is the three-dimensional analog of Eq. (40.9) for the energy levels of a particle in a box.



42.23 The allowed values of n_x, n_y, and n_z are positive integers for the electron states in the free-electron gas model. Including spin, there are two states for each unit volume in n space.

Density of States

Later we'll need to know the *number dn* of quantum states that have energies in a given range *dE*. The number of states per unit energy range dn/dE is called the **density of states,** denoted by $g(E)$. We'll begin by working out an expression for $g(E)$. Think of a three-dimensional space with coordinates (n_x, n_y, n_z) (Fig. 42.23). The radius n_{rs} of a sphere centered at the origin in that space is given by $n_{rs}^2 = n_x^2 + n_y^2 + n_z^2$. Each point with integer coordinates in that space represents one spatial quantum state. Thus each point corresponds to one unit of volume in the space, and the total number of points with integer coordinates inside a sphere equals the volume of the sphere, $\frac{4}{3}\pi n_{rs}^3$. Because all our n's are positive, we must take only one *octant* of the sphere, with $\frac{1}{8}$ the total volume, or $(\frac{1}{8})(\frac{4}{3}\pi n_{rs}^3) = \frac{1}{6}\pi n_{rs}^3$. The particles are electrons, so each point corresponds to *two* states with opposite spin components $(m_s = \pm\frac{1}{2})$, and the total number n of electron states corresponding to points inside the octant is twice $\frac{1}{6}\pi n_{rs}^3$, or

$$n = \frac{\pi n_{rs}^3}{3} \qquad (42.12)$$

The energy E of states at the surface of the sphere can be expressed in terms of n_{rs}. Equation (42.11) becomes

$$E = \frac{n_{rs}^2\pi^2\hbar^2}{2mL^2} \qquad (42.13)$$

We can combine Eqs. (42.12) and (42.13) to get a relationship between E and n that doesn't contain n_{rs}. We'll leave the details as an exercise (Exercise 42.24); the result is

$$n = \frac{(2m)^{3/2}VE^{3/2}}{3\pi^2\hbar^3} \qquad (42.14)$$

where $V = L^3$ is the volume of the box. Equation (42.14) gives the total number of states with energies of E or less.

To get the number of states dn in an energy interval dE, we treat n and E as continuous variables and take differentials of both sides of Eq. (42.14). We get

$$dn = \frac{(2m)^{3/2}VE^{1/2}}{2\pi^2\hbar^3}\,dE \qquad (42.15)$$

The density of states $g(E)$ is equal to dn/dE, so from Eq. (42.15) we get

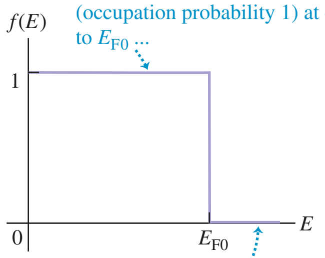
$$g(E) = \frac{(2m)^{3/2}V}{2\pi^2\hbar^3}E^{1/2} \quad \text{(density of states, free-electron model)} \qquad (42.16)$$

Fermi-Dirac Distribution

Now we need to know how the electrons are distributed among the various quantum states at any given temperature. The *Maxwell-Boltzmann distribution* states that the average number of particles in a state of energy E is proportional to $e^{-E/kT}$ (see Section 38.6). However, there are two very important reasons why it wouldn't be right to use the Maxwell-Boltzmann distribution. The first reason is the *exclusion principle.* At absolute zero the Maxwell-Boltzmann function predicts that *all* the electrons would go into the two ground states of the system, with $n_x = n_y = n_z = 1$ and $m_s = \pm\frac{1}{2}$. But the exclusion principle allows only one electron in each state. At absolute zero the electrons can fill up the lowest *available* states, but there's not enough room for *all* of them to go into the lowest states. Thus a reasonable guess as to the shape of the distribution would be Fig. 42.24. At absolute zero temperature the states are filled up to some value E_{F0}, and all states above this value are empty.

42.24 The probability distribution for occupation of free-electron energy states at absolute zero.

At absolute zero, all states are occupied (occupation probability 1) at energies up to E_{F0} ...



... and all states are empty (occupation probability zero) at energies above E_{F0}.

The second reason we can't use the Maxwell-Boltzmann distribution is more subtle. That distribution assumes that we are dealing with *distinguishable* particles. It might seem that we could put a tag on each electron and know which is which. But overlapping electrons in a system such as a metal are *indistinguishable.* Suppose we have two electrons; a state in which the first is in an energy level E_1 and the second is in level E_2 is not distinguishable from a state in which the two electrons are reversed, because we can't tell which electron is which.

The statistical distribution function that emerges from the exclusion principle and the indistinguishability requirement is called (after its inventors) the **Fermi-Dirac distribution.** Because of the exclusion principle, the probability that a particular state with energy E is occupied by an electron is the same as $f(E)$, the fraction of states with that energy that are occupied:

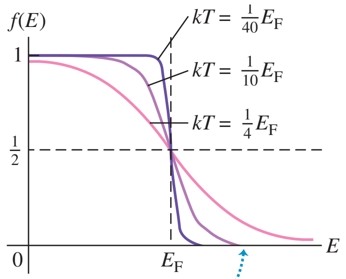
$$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1} \quad \text{(Fermi-Dirac distribution)} \qquad (42.17)$$

The energy E_F is called the **Fermi energy** or the *Fermi level;* we'll discuss its significance below. We use E_{F0} for its value at absolute zero $(T = 0)$ and E_F for other temperatures. We can accurately let $E_F = E_{F0}$ for metals because the Fermi energy does not change much with temperature for solid conductors. However, it is not safe to assume that $E_F = E_{F0}$ for semiconductors, in which the Fermi energy usually does change with temperature.

Figure 42.25 shows graphs of Eq. (42.17) for three temperatures. The trend of this function as kT approaches zero confirms our guess. When $E = E_F$, the exponent is zero and $f(E_F) = \frac{1}{2}$. That is, the probability is $\frac{1}{2}$ that a state at the Fermi energy contains an electron. Alternatively, at $E = E_F$, half the states are filled (and half are empty).

For $E < E_F$ the exponent is negative, and $f(E) > \frac{1}{2}$. For $E > E_F$ the exponent is positive, and $f(E) < \frac{1}{2}$. The shape depends on the ratio E_F/kT. At $T \ll E_F/k$ this ratio is very large. Then for $E < E_F$ the curve very quickly approaches 1, and for $E > E_F$ it quickly approaches zero. When T is larger, the changes are more gradual. When T is zero, all the states up to the Fermi level E_{F0} are filled, and all states above that level are empty (Fig. 42.24).

42.25 Graphs of the Fermi-Dirac distribution function for various values of kT, assuming that the Fermi energy E_F is independent of the temperature T.



As T increases, more and more of the electrons are excited to states with energy $E > E_F$.

Example 42.7 Probabilities in the free-electron model

For free electrons in a solid, at what energy is the probability that a particular state is occupied equal to (a) 0.01 and (b) 0.99?

SOLUTION

IDENTIFY: This problem asks us to explore how the Fermi-Dirac distribution depends on temperature.

SET UP: Equation (42.17) tells us the occupation probability $f(E)$ for a given energy E. If we solve this equation for E, we get an expression for the energy that corresponds to a given occupation probability—which is just what we need to solve this problem.

EXECUTE: Solving Eq. (42.17) for E, we get

$$E = E_F + kT\ln\left(\frac{1}{f(E)} - 1\right)$$

Continued

(a) When $f(E) = 0.01$,

$$E = E_F + kT \ln\left(\frac{1}{0.01} - 1\right) = E_F + 4.6kT$$

A state $4.6kT$ above the Fermi level is occupied only 1% of the time.

(b) When $f(E) = 0.99$,

$$E = E_F + kT \ln\left(\frac{1}{0.99} - 1\right) = E_F - 4.6kT$$

A state $4.6kT$ below the Fermi level is occupied 99% of the time.

EVALUATE: At very low temperatures, $4.6kT$ becomes very small. Then levels even slightly below E_F are nearly always full, and levels even slightly above E_F are nearly always empty (see Fig. 42.25). In general, if the probability is P that a state with an energy ΔE *above* E_F is occupied, then the probability is $1 - P$ that a state ΔE *below* E_F is occupied. We leave the proof as a problem (Problem 42.48).

Electron Concentration and Fermi Energy

Equation (42.17) gives the probability that any specific state with energy E is occupied at a temperature T. To get the actual number of electrons in any energy range dE, we have to multiply this probability by the number dn of states in that range $g(E)\,dE$. Thus the number dN of electrons with energies in the range dE is

$$dN = g(E)f(E)\,dE = \frac{(2m)^{3/2}VE^{1/2}}{2\pi^2\hbar^3}\,\frac{1}{e^{(E-E_F)/kT} + 1}\,dE \qquad (42.18)$$

The Fermi energy E_F is determined by the total number N of electrons; at any temperature the electron states are filled up to a point at which all electrons are accommodated. At absolute zero there is a simple relationship between E_{F0} and N. *All* states below E_{F0} are filled; in Eq. (42.14) we set n equal to the total number of electrons N and E to the Fermi energy at absolute zero E_{F0}:

$$N = \frac{(2m)^{3/2}VE_{F0}^{\;3/2}}{3\pi^2\hbar^3} \qquad (42.19)$$

Solving for E_{F0}, we get

$$E_{F0} = \frac{3^{2/3}\pi^{4/3}\hbar^2}{2m}\left(\frac{N}{V}\right)^{2/3} \qquad (42.20)$$

The quantity N/V is the number of free electrons per unit volume. It is called the *electron concentration* and is usually denoted by n.

If we replace N/V with n, Eq. (42.20) becomes

$$E_{F0} = \frac{3^{2/3}\pi^{4/3}\hbar^2 n^{2/3}}{2m} \qquad (42.21)$$

CAUTION **Electron concentration and number of electrons** Don't confuse the electron concentration n with any quantum number n. Furthermore, the number of states is *not* in general the same as the total number of electrons N. ▮

Example 42.8 The Fermi energy in copper

At low temperatures, copper has a free-electron concentration of $8.45 \times 10^{28}\ \text{m}^{-3}$. Using the free-electron model, find the Fermi energy for solid copper, and find the speed of an electron with a kinetic energy equal to the Fermi energy.

SOLUTION

IDENTIFY: This problem uses the relationship between Fermi energy and free-electron concentration.

SET UP: Because copper is a solid conductor, its Fermi energy changes very little with temperature and we can safely use the expression for the Fermi energy at absolute zero, Eq. (42.21). We determine the speed v_F that corresponds to kinetic energy E_F using the familiar nonrelativistic formula for kinetic energy.

EXECUTE: Using the given value of n,

$$E_F = \frac{3^{2/3}\pi^{4/3}(1.055 \times 10^{-34}\ \text{J}\cdot\text{s})^2(8.45 \times 10^{28}\ \text{m}^{-3})^{2/3}}{2(9.11 \times 10^{-31}\ \text{kg})}$$
$$= 1.126 \times 10^{-18}\ \text{J} = 7.03\ \text{eV}$$

To find the corresponding speed v_F, we use $E_F = \frac{1}{2}mv_F^{\,2}$:

$$v_F = \sqrt{\frac{2E_F}{m}} = \sqrt{\frac{2(1.126 \times 10^{-18}\ \text{J})}{9.11 \times 10^{-31}\ \text{kg}}} = 1.57 \times 10^6\ \text{m/s}$$

EVALUATE: Typical Fermi energies for metals range from 1.6 to 14 eV; our value is within this range, as it should be.

The quantity v_F is called the *Fermi speed*. The calculated value of v_F is far less than the speed of light $c = 3.00 \times 10^8\ \text{m/s}$, which justifies our use of nonrelativistic formulas. Typical Fermi speeds for metals range from 0.8 to $2.2 \times 10^6\ \text{m/s}$.

Our results show that the Fermi energy is much *larger* than kT at ordinary temperatures, so it is a good approximation to take almost all the states below E_F as completely full and almost all those above E_F as completely empty (see Fig. 42.24).

We can also use Eq. (42.16) to find $g(E)$ if E and V are known. You can show that if $E = 7$ eV and $V = 1\ \text{cm}^3$, $g(E)$ is about 2×10^{22} states/eV. This huge number shows why we were justified in treating n and E as continuous variables in our density-of-states derivation.

Average Free-Electron Energy

We can calculate the *average* free-electron energy in a metal at absolute zero by using the same ideas that we used to find E_{F0}. From Eq. (42.18) the number dN of electrons with energies in the range dE is $g(E)f(E)\,dE$. The energy of these electrons is $E\,dN = Eg(E)f(E)\,dE$. At absolute zero we substitute $f(E) = 1$ from $E = 0$ to $E = E_{F0}$ and $f(E) = 0$ for all other energies. Therefore the total energy E_{tot} of all the N electrons is

$$E_{\text{tot}} = \int_0^{E_{F0}} Eg(E)(1)\,dE + \int_{E_{F0}}^{\infty} Eg(E)(0)\,dE = \int_0^{E_{F0}} Eg(E)\,dE$$

The simplest way to evaluate this expression is to compare Eqs. (42.16) and (42.20), noting that

$$g(E) = \frac{3NE^{1/2}}{2E_{F0}^{\;3/2}}$$

Substituting this expression into the integral and using $E_{\text{av}} = E_{\text{tot}}/N$, we get

$$E_{\text{av}} = \frac{3}{2E_{F0}^{\;3/2}}\int_0^{E_{F0}} E^{3/2}\,dE = \frac{3}{5}E_{F0} \qquad (42.22)$$

That is, at absolute zero the average free-electron energy equals $\frac{3}{5}$ of the corresponding Fermi energy.

Example 42.9 Free-electron gas versus ideal gas

(a) Find the average energy of the free electrons in copper at absolute zero (Example 42.8). (b) If the electrons behaved like an ideal gas (see Section 18.3) at room temperature, what would be their average kinetic energy? What would be the speed of an electron with this kinetic energy?

SOLUTION

IDENTIFY: Free electrons in a metal behave like a type of gas. In this example we're asked to compare this gas to the ideal gas that we examined in Chapter 18.

SET UP: We use Eq. (42.22) to determine the average kinetic energy of free electrons. If the electrons behaved like a classic ideal gas with temperature T, from Eq. (18.16) the average kinetic energy per electron would be $E_{\text{av}} = \frac{3}{2}kT$; we use this relationship to determine the energy and the speed asked for in part (b).

EXECUTE: (a) From Example 42.8, the Fermi energy in copper is $1.126 \times 10^{-18}\ \text{J} = 7.03$ eV. According to Eq. (42.22), the average energy is $\frac{3}{5}$ of this, or $6.76 \times 10^{-19}\ \text{J} = 4.22$ eV.

(b) If the electrons behaved like an ideal gas at room temperature ($T = 20°\text{C} = 293\ \text{K}$), the average kinetic energy per electron would be

$$E_{\text{av}} = \frac{3}{2}kT = \frac{3}{2}(1.381 \times 10^{-23}\ \text{J/K})(293\ \text{K})$$
$$= 6.07 \times 10^{-21}\ \text{J} = 0.0379\ \text{eV}$$

The speed of an electron with this kinetic energy would be

$$v = \sqrt{\frac{2E_{\text{av}}}{m}} = \sqrt{\frac{2(6.07 \times 10^{-21}\ \text{J})}{9.11 \times 10^{-31}\ \text{kg}}} = 1.15 \times 10^5\ \text{m/s}$$

EVALUATE: The average energy predicted by the ideal-gas model is less than 1% of the value given (correctly) by the free-electron model, and the corresponding speed in the ideal-gas model is only a small fraction of the characteristic Fermi speed given by the free-electron model (see Example 42.8). Thus temperature plays a *very* small role in determining the properties of electrons in metals; instead, their average energies are determined almost entirely by the exclusion principle.

Continued

A similar analysis allows us to determine the contributions of electrons to the heat capacities of a solid metal. If there is one conduction electron per atom, the principle of equipartition of energy (see Section 18.4) would predict that the kinetic energies of these electrons contribute $3R/2$ to the molar heat capacity at constant volume C_V. But when kT is much smaller than E_F, which is usually the situation in metals, only those few electrons near the Fermi level can find empty states and change energy appreciably when the temperature changes. The number of such electrons is proportional to kT/E_F, so we expect that the electron molar heat capacity at constant volume is proportional to $(kT/E_F)(3R/2) = (3kT/2E_F)R$. A more detailed analysis shows that the actual electron contribution to C_V for a solid metal is $(\pi^2 kT/2E_F)R$, not far from our prediction. You can verify that if $T = 293$ K and $E_F = 7.03$ eV, the electron contribution to C_V is $0.018R$, which is only 1.2% of the (incorrect) $3R/2$ prediction of the equipartition principle. Because the electronic contribution is so small, the overall heat capacity of most solid metals is due primarily to vibration of the atoms in the crystal structure (see Fig. 18.18 in Section 18.4).

Test Your Understanding of Section 42.5 An ideal gas obeys the relationship $pV = nRT$ (see Section 18.1). That is, for a given volume V and a number of moles n, as the temperature T decreases, the pressure p decreases proportionally and tends to zero as T approaches absolute zero. Is this also true of the free-electron gas in a solid metal?

42.6 Semiconductors

A **semiconductor** has an electrical resistivity that is intermediate between those of good conductors and of good insulators. The tremendous importance of semiconductors in present-day electronics stems in part from the fact that their electrical properties are very sensitive to very small concentrations of impurities. We'll discuss the basic concepts using the semiconductor elements silicon (Si) and germanium (Ge) as examples.

Silicon and germanium are in Group IV of the periodic table. Both have four electrons in the outermost atomic subshells ($3s^2 3p^2$ for silicon, $4s^2 4p^2$ for germanium), and both crystallize in the covalently bonded diamond structure discussed in Section 42.3 (Fig. 42.16). Because all four of the outer electrons are involved in the bonding, at absolute zero the band structure (see Section 42.4) has a completely empty conduction band (Fig. 42.21b). As we discussed in Section 42.4, at very low temperatures electrons cannot jump from the filled valence band into the conduction band. This property makes these materials insulators at very low temperatures; their electrons have no nearby states available into which they can move in response to an applied electric field.

However, the energy gap E_g between the valence and conduction bands is small in comparison to the gap of 5 eV or more for many insulators; room temperature values are 1.12 eV for silicon and only 0.67 eV for germanium. Thus even at room temperature a substantial number of electrons can gain enough energy to jump the gap to the conduction band, where they are dissociated from their parent atoms and are free to move about the crystal. The number of these electrons increases rapidly with temperature.

Example 42.10 Jumping the energy gap

Consider a material with the band structure described above, with its Fermi energy in the middle of the gap (Fig. 42.26). Find the probability that a state at the bottom of the conduction band is occupied at a temperature of 300 K if the band gap is (a) 0.200 eV; (b) 1.00 eV; (c) 5.00 eV. Repeat the calculations for a temperature of 310 K.

SOLUTION

IDENTIFY: Figure 42.25 shows that the higher the temperature, the larger the fraction of electrons that have energies greater than the Fermi energy E_F. We use this idea to carry out the desired calculations.

SET UP: The Fermi-Dirac distribution function gives us the probability that a state of energy E is occupied at temperature T. Figure 42.26 shows that the state of interest at the bottom of the conduction band has energy $E = E_F + E_g/2$, so $E - E_F = E_g/2$.

EXECUTE: (a) When $E_g = 0.200$ eV,

$$\frac{E - E_F}{kT} = \frac{0.100\text{ eV}}{(8.617 \times 10^{-5}\text{ eV/K})(300\text{ K})} = 3.87$$

$$f(E) = \frac{1}{e^{3.87} + 1} = 0.0205$$

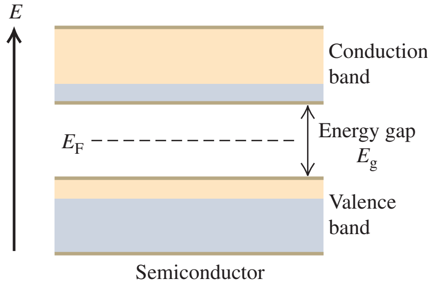
With $E_g = 0.200$ eV and $T = 310$ K, the exponent is 3.74 and $f(E) = 0.0231$, a 13% increase for a temperature rise of only 10K.

(b) When $E_g = 1.00$ eV, both exponents are five times as large as before, 19.3 and 18.7; the values of $f(E)$ are 4.0×10^{-9} and 7.4×10^{-9}. In this case the probability nearly doubles with a temperature rise of 10 K.

(c) When $E_g = 5.0$ eV, the exponents are 96.7 and 93.6; the values of $f(E)$ are 1.0×10^{-42} and 2.3×10^{-41}. The probability increases by a factor of 23 for a 10-K temperature rise, but it is still extremely small. Pure diamond, with a 5.47-eV band gap, has essentially no electrons in the conduction band and is an excellent insulator.

EVALUATE: This example illustrates two important points. First, the probability of finding an electron in a state at the bottom of the conduction band is extremely sensitive to the width of the band gap. When the gap is 0.20 eV, the chance is about 2%, but when it is 1.00 eV, the chance is a few in a thousand million, and for a band gap of 5.0 eV, it is essentially zero. Second, for any given band gap the probability is very temperature dependent, more so for large gaps than for small.

42.26 Band structure of a semiconductor. At absolute zero a completely filled valence band is separated by a narrow energy gap E_g of 1 eV or so from a completely empty conduction band. At ordinary temperatures, a number of electrons are excited to the conduction band.

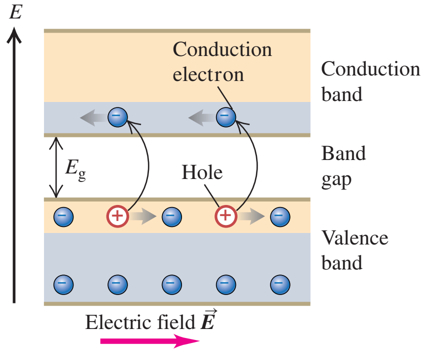


In principle, we could continue the calculation in Example 42.10 to find the actual density $n = N/V$ of electrons in the conduction band at any temperature. To do this, we would have to evaluate the integral $\int g(E) f(E)\, dE$ from the bottom of the conduction band to its top. First we would need to know the density of states function $g(E)$. It wouldn't be correct to use Eq. (42.16) because the energy-level structure and the density of states for real solids are more complex than those for the simple free-electron model. However, there are theoretical methods for predicting what $g(E)$ should be near the bottom of the conduction band, and such calculations have been carried out. Once we know n, we can *begin* to determine the resistivity of the material (and its temperature dependence) using the analysis of Section 25.2, which you may want to review. But next we'll see that the electrons in the conduction band don't tell the whole story about conduction in semiconductors.

Holes

When an electron is removed from a covalent bond, it leaves a vacancy behind. An electron from a neighboring atom can move into this vacancy, leaving the neighbor with the vacancy. In this way the vacancy, called a **hole,** can travel through the material and serve as an additional current carrier. It's like describing the motion of a bubble in a liquid. In a pure, or *intrinsic,* semiconductor, valence-band holes and conduction-band electrons are always present in equal numbers. When an electric field is applied, they move in opposite directions (Fig. 42.27). Thus a hole in the valence band behaves like a positively charged particle, even though the moving charges in that band are electrons. The conductivity that we just described for a pure semiconductor is called *intrinsic conductivity.* Another kind of conductivity, to be discussed in the next subsection, is due to impurities.

42.27 Motion of electrons in the conduction band and of holes in the valence band of a semiconductor under the action of an applied electric field $\vec{E}$.



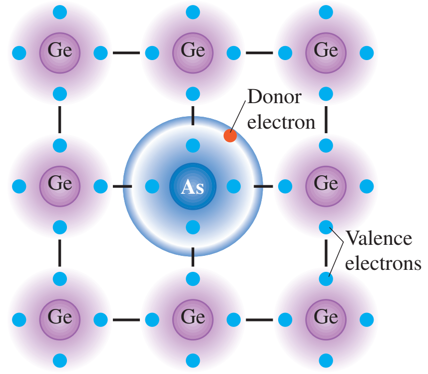
An analogy helps to picture conduction in an intrinsic semiconductor. The valence band at absolute zero is like a floor of a parking garage that's filled bumper to bumper with cars (which represent electrons). No cars can move because there is nowhere for them to go. But if one car is moved to the vacant floor above, it can move freely, just as electrons can move freely in the conduction band. Also, the empty space that it leaves permits cars to move on the nearly filled floor, thereby moving the empty space just as holes move in the normally filled valence band.

Impurities

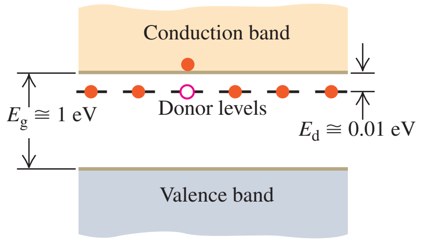
Suppose we mix into melted germanium $(Z = 32)$ a small amount of arsenic $(Z = 33)$, the next element after germanium in the periodic table. This deliberate addition of impurity elements is called *doping.* Arsenic is in Group V; it has

42.28 An n-type semiconductor.

(a) A donor (n-type) impurity atom has a fifth valence electron that does not participate in the covalent bonding and is very loosely bound.



(b) Energy-band diagram for an n-type semiconductor at a low temperature. One donor electron has been excited from the donor levels into the conduction band.



five valence electrons. When one of these electrons is removed, the remaining electron structure is essentially identical to that of germanium. The only difference is that it is smaller; the arsenic nucleus has a charge of $+33e$ rather than $+32e$, and it pulls the electrons in a little more. An arsenic atom can comfortably take the place of a germanium atom as a substitutional impurity. Four of its five valence electrons form the necessary nearest-neighbor covalent bonds.

The fifth valence electron is very loosely bound (Fig. 42.28a); it doesn't participate in the covalent bonds, and it is screened from the nuclear charge of $+33e$ by the 32 electrons, leaving a net effective charge of about $+e$. We might guess that the binding energy would be of the same order of magnitude as the energy of the $n = 4$ level in hydrogen—that is, $\left(\frac{1}{4}\right)^2(13.6\ \text{eV}) = 0.85\ \text{eV}$. In fact, it is much smaller than this, only about 0.01 eV, because the electron probability distribution actually extends over many atomic diameters and the polarization of intervening atoms provides additional screening.

The energy level of this fifth electron corresponds in the band picture to an isolated energy level lying in the gap, about 0.01 eV below the bottom of the conduction band (Fig. 42.28b). This level is called a *donor level,* and the impurity atom that is responsible for it is simply called a *donor.* All Group V elements, including N, P, As, Sb, and Bi, can serve as donors. At room temperature, kT is about 0.025 eV. This is substantially greater than 0.01 eV, so at ordinary temperatures, most electrons can gain enough energy to jump from donor levels into the conduction band, where they are free to wander through the material. The remaining ionized donor stays at its site in the structure and does not participate in conduction.

Example 42.10 shows that at ordinary temperatures and with a band gap of 1.0 eV, only a very small fraction (of the order of 10^{-9}) of the states at the bottom of the conduction band in a pure semiconductor contain electrons to participate in intrinsic conductivity. Thus we expect the conductivity of such a semiconductor to be about 10^{-9} as great as that of good metallic conductors, and measurements bear out this prediction. However, a concentration of donors as small as one part in 10^8 can increase the conductivity so drastically that conduction due to impurities becomes by far the dominant mechanism. In this case the conductivity is due almost entirely to *negative* charge (electron) motion. We call the material an ***n*-type semiconductor,** with n-type impurities.

Adding atoms of an element in Group III (B, Al, Ga, In, Tl), with only *three* valence electrons, has an analogous effect. An example is gallium $(Z = 31)$; as a substitutional impurity in germanium, the gallium atom would like to form four covalent bonds, but it has only three outer electrons. It can, however, steal an electron from a neighboring germanium atom to complete the required four covalent bonds (Fig. 42.29a). The resulting atom has the same electron configuration as Ge but is somewhat larger because gallium's nuclear charge is smaller, $+31e$ instead of $+32e$.

This theft leaves the neighboring atom with a *hole,* or missing electron. The hole acts as a positive charge that can move through the crystal just as with intrinsic conductivity. The stolen electron is bound to the gallium atom in a level called an *acceptor level* about 0.01 eV above the top of the valence band (Fig. 42.29b). The gallium atom, called an *acceptor,* thus accepts an electron to complete its desire for four covalent bonds. This extra electron gives the previously neutral gallium atom a net charge of $-e$. The resulting gallium ion is *not* free to move. In a semiconductor that is doped with acceptors, we consider the conductivity to be almost entirely due to *positive* charge (hole) motion. We call the material a ***p*-type semiconductor,** with p-type impurities. Some semiconductors are doped with *both* n- and p-type impurities. Such materials are called *compensated* semiconductors.

CAUTION **The meaning of "*p*-type" and "*n*-type"** Saying that a material is a p-type semiconductor does *not* mean that the material has a positive charge; ordinarily, it would be neutral. Rather, it means that its *majority carriers* of current are positive holes (and therefore its *minority carriers* are negative electrons). The same idea holds for an n-type semiconductor; ordinarily, it will *not* have a negative charge, but its majority carriers are negative electrons.

We can verify the assertion that the current in n- and p-type semiconductors really *is* carried by electrons and holes, respectively, by using the Hall effect (see optional Section 27.9). The sign of the Hall emf is opposite in the two cases. Hall-effect devices constructed from semiconductor materials are used in probes to measure magnetic fields and the currents that cause those fields.

Test Your Understanding of Section 42.6 Would there be any advantage to adding n-type or p-type impurities to copper?

42.7 Semiconductor Devices

Semiconductor devices play an indispensable role in contemporary electronics. In the early days of radio and television, transmitting and receiving equipment relied on vacuum tubes, but these have been almost completely replaced in the last four decades by solid-state devices, including transistors, diodes, integrated circuits, and other semiconductor devices. The only surviving vacuum tubes in consumer electronics are the picture tubes in older TV receivers and computer monitors; these are gradually being replaced by flat-screen displays.

One simple semiconductor device is the *photocell* (Fig. 42.30). When a thin slab of semiconductor is irradiated with an electromagnetic wave whose photons have at least as much energy as the band gap between the valence and conduction bands, an electron in the valence band can absorb a photon and jump to the conduction band, where it and the hole it left behind contribute to the conductivity (see Example 42.6 in Section 42.4). The conductivity therefore increases with wave intensity, thus increasing the current I in the photocell circuit of Fig. 42.30. Hence the ammeter reading indicates the intensity of the light.

Detectors for charged particles operate on the same principle. An external circuit applies a voltage across a semiconductor. An energetic charged particle passing through the semiconductor collides inelastically with valence electrons, exciting them from the valence to the conduction band and creating pairs of holes and conduction electrons. The conductivity increases momentarily, causing a pulse of current in the external circuit. Solid-state detectors are widely used in nuclear and high-energy physics research; without them, many important discoveries could not have been made.

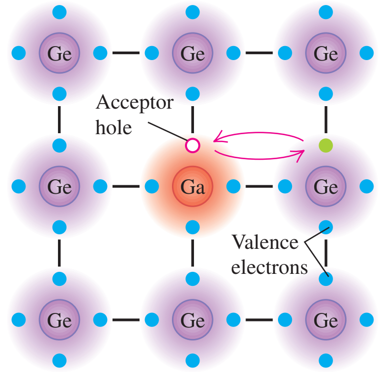
The *p*-*n* Junction

In many semiconductor devices the essential principle is the fact that the conductivity of the material is controlled by impurity concentrations, which can be varied within wide limits from one region of a device to another. An example is the ***p*-*n* junction** at the boundary between one region of a semiconductor with p-type impurities and another region containing n-type impurities. One way of fabricating a p-n junction is to deposit some n-type material on the *very* clean surface of some p-type material. (We can't just stick p- and n-type pieces together and expect the junction to work properly because of the impossibility of matching their surfaces at the atomic level.)

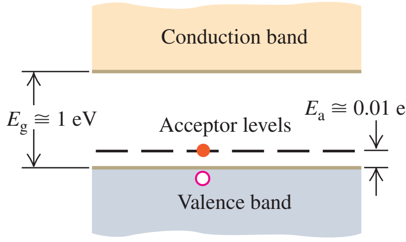
When a p-n junction is connected to an external circuit, as in Fig. 42.31a, and the potential difference $V_p - V_n = V$ across the junction is varied, the current I varies as shown in Fig. 42.31b. In striking contrast to the symmetrical behavior of resistors that obey Ohm's law and give a straight line on an I-V graph, a p-n junction conducts much more readily in the direction from p to n than the reverse.

42.29 A p-type semiconductor.

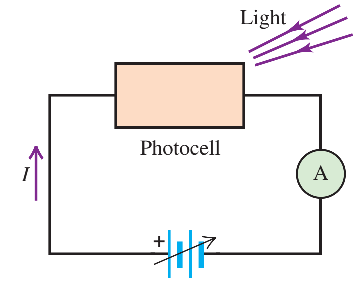
(a) An acceptor (p-type) impurity atom has only three valence electrons, so it can borrow an electron from a neighboring atom. The resulting hole is free to move about the crystal.

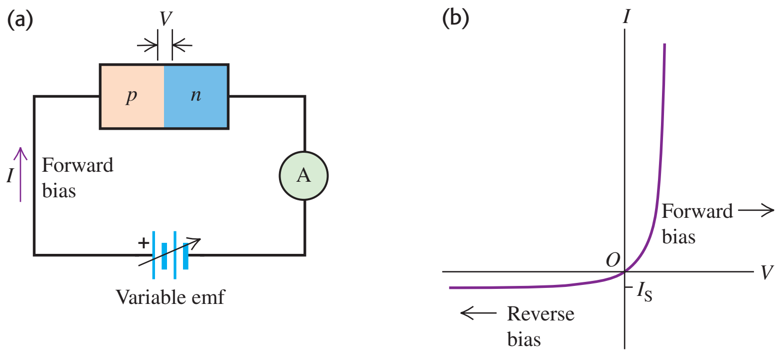


(b) Energy-band diagram for a p-type semiconductor at a low temperature. One acceptor level has accepted an electron from the valence band, leaving a hole behind.



42.30 A semiconductor photocell in a circuit. The more intense the light falling on the photocell, the greater the conductivity of the photocell and the greater the current measured by the ammeter (A).





42.31 (a) A semiconductor *p-n* junction in a circuit. (b) Graph showing the asymmetrical current–voltage relationship. The curve is described by Eq. (42.23).

Such a (mostly) one-way device is called a **diode rectifier.** Later we'll discuss a simple model of *p-n* junction behavior that predicts a current–voltage relationship in the form

$$I = I_S\left(e^{eV/kT} - 1\right) \qquad \text{(current through a } p\text{-}n \text{ junction)} \qquad (42.23)$$

In the exponent, $e = 1.602 \times 10^{-19}$ C is the quantum of charge, k is Boltzmann's constant, and T is absolute temperature.

CAUTION **Two different Uses of e** In $e^{eV/kT}$ the base of the exponent also uses the symbol e, standing for the base of the natural logarithms, 2.71828 . . . . This e is quite different from $e = 1.602 \times 10^{-19}$ C in the exponent.

Equation (42.23) is valid for both positive and negative values of V; note that V and I always have the same sign. As V becomes very negative, I approaches the value $-I_S$. The magnitude I_S (always positive) is called the *saturation current.*

Example 42.11 Is a *p-n* junction diode always a one-way device?

At a temperature of 290 K, a certain *p-n* junction diode has a saturation current $I_S = 0.500$ mA. Find the current at this temperature when the voltage is 1.00 mV, −1.00 mV, 100 mV, and −100 mV.

SOLUTION

IDENTIFY: This problem uses the relationship among current, saturation current, voltage, and temperature for a semiconductor diode.

SET UP: We are given the values of the saturation current I_S and the temperature T, so we can use Eq. (42.23) to determine the current I for various values of the voltage V.

EXECUTE: At $T = 290$ K, $kT = 0.0250$ eV $= 25.0$ meV. When $V = 1.00$ mV, $eV/kT = e(1.00 \text{ mV})/(25.0 \text{ meV}) = 0.0400$. From Eq. (42.23) the current is

$$I = (0.500 \text{ mA})\left(e^{0.0400} - 1\right) = 0.0204 \text{ mA}$$

When $V = -1.00$ mV,

$$I = (0.500 \text{ mA})\left(e^{-0.0400} - 1\right) = -0.0196 \text{ mA}$$

The values of I for the other two voltages are obtained in the same way; when $V = 100$ mV, $I = 26.8$ mA; and when $V = -100$ mV, $I = -0.491$ mA. We summarize the data in the following table, also calculating the resistance $R = V/I$.

V (mV)	I (mA)	R (Ω)
+1.00	+0.0204	49.0
−1.00	−0.0196	51.0
+100	+26.8	3.73
−100	−0.491	204

EVALUATE: Note that at $|V| = 1.00$ mV the current has nearly the same magnitude for both directions. That is, when $|V| \ll kT/e$ (near the origin of Fig. 42.31b), the curve approaches a straight line, and this junction diode acts more like a 50.0-Ω resistor than like a rectifier. However, as the voltage increases, the directional asymmetry becomes more and more pronounced. At $|V| = 100$ V the negative current is nearly equal to the saturation value and has a magnitude that is less than 2% of the positive current.

Currents Through a *p-n* Junction

We can understand the behavior of a *p-n* junction diode qualitatively on the basis of the mechanisms for conductivity in the two regions. Suppose, as in Fig. 42.31a, you connect the positive terminal of the battery to the *p* region and the negative terminal to the *n* region. Then the *p* region is at higher potential than the *n* region, corresponding to positive V in Eq. (42.23), and the resulting electric field is in the direction *p* to *n*. This is called the *forward* direction, and the positive potential difference is called *forward bias.* Holes, plentiful in the *p* region, flow easily across the junction into the *n* region, and free electrons, plentiful in the *n* region, easily flow into the *p* region; these movements of charge constitute a *forward* current. Connecting the battery with the opposite polarity gives *reverse bias,* and the field tends to push electrons from *p* to *n* and holes from *n* to *p*. But there are very few free electrons in the *p* region and very few holes in the *n* region. As a result, the current in the *reverse* direction is much smaller than that with the same potential difference in the forward direction.

Suppose you have a box with a barrier separating the left and right sides: You fill the left side with oxygen gas and the right side with nitrogen gas. What happens if the barrier leaks? Oxygen diffuses to the right, and nitrogen diffuses to the left. A similar diffusion occurs across a *p-n* junction. First consider the equilibrium situation with no applied voltage (Fig. 42.32). The many holes in the *p* region act like a hole gas that diffuses across the junction into the *n* region. Once there, the holes recombine with some of the many free electrons. Similarly, electrons diffuse from the *n* region to the *p* region and fall into some of the many holes there. The hole and electron diffusion currents lead to a net positive charge in the *n* region and a net negative charge in the *p* region, causing an electric field in the direction from *n* to *p* at the junction. The potential energy associated with this field raises the electron energy levels in the *p* region relative to the same levels in the *n* region.

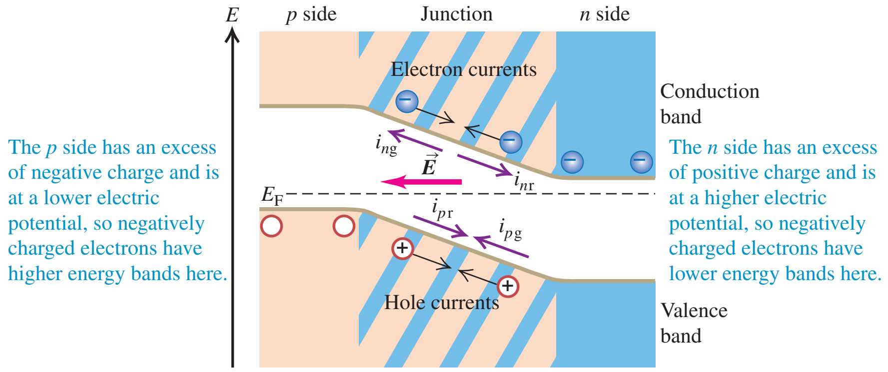
There are four currents across the junction, as shown. The diffusion processes lead to *recombination currents* of holes and electrons, labeled i_{pr} and i_{nr} in Fig. 42.32. At the same time, electron–hole pairs are generated in the junction region by thermal excitation. The electric field described above sweeps these electrons and holes out of the junction; electrons are swept opposite the field to the *n* side, and holes are swept in the same direction as the field to the *p* side. The corresponding currents, called *generation currents,* are labeled i_{pg} and i_{ng}. At equilibrium the magnitudes of the generation and recombination currents are equal:

$$|i_{pg}| = |i_{pr}| \quad \text{and} \quad |i_{ng}| = |i_{nr}| \qquad (42.24)$$

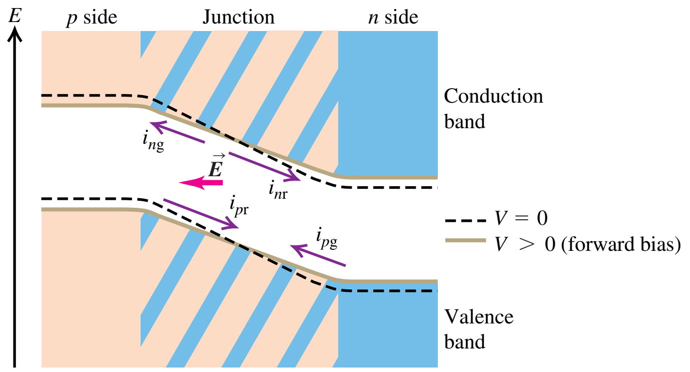
At thermal equilibrium the Fermi energy is the same at each point across the junction.

Now we apply a forward bias—that is, a positive potential difference V across the junction. A forward bias *decreases* the electric field in the junction region. It also decreases the difference between the energy levels on the *p* and *n* sides (Fig. 42.33, next page) by an amount $\Delta E = -eV$. It becomes easier for the electrons in the *n* region to climb the potential-energy hill and diffuse into the *p* region and for the holes in the *p* region to diffuse into the *n* region. This effect increases both recombination currents by the Maxwell-Boltzmann factor $e^{-\Delta E/kT} = e^{eV/kT}$. (We don't have

42.32 A *p-n* junction in equilibrium, with no externally applied field or potential difference. The generation and recombination currents exactly balance. The Fermi energy E_F is the same on both sides of the junction. The excess positive and negative charges on the *n* and *p* sides produce an electric field $\vec{E}$ in the direction shown.



42.33 A *p*-*n* junction under forward-bias conditions. The potential difference between *p* and *n* regions is reduced, as is the electric field within the junction. The recombination currents increase but the generation currents are nearly constant, causing a net current from left to right. (Compare Fig. 42.32.)



to use the Fermi-Dirac distribution because most of the available states for the diffusing electrons and holes are empty, so the exclusion principle has little effect.) The generation currents don't change appreciably, so the net hole current is

$$\begin{aligned} i_{p\text{tot}} &= i_{p\text{r}} - \lvert i_{p\text{g}} \rvert \\ &= \lvert i_{p\text{g}} \rvert e^{eV/kT} - \lvert i_{p\text{g}} \rvert \\ &= \lvert i_{p\text{g}} \rvert \left(e^{eV/kT} - 1 \right) \end{aligned} \tag{42.25}$$

The net electron current $i_{n\text{tot}}$ is given by a similar expression, so the total current $I = i_{p\text{tot}} + i_{n\text{tot}}$ is

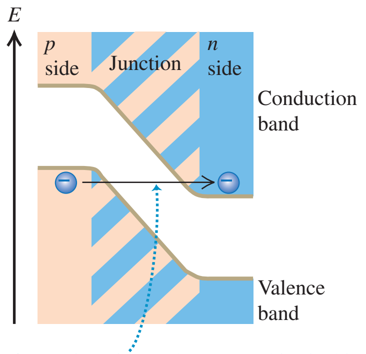
$$I = I_\text{S}\left(e^{eV/kT} - 1 \right) \tag{42.26}$$

in agreement with Eq. (42.23). This entire discussion can be repeated for reverse bias (negative V and I) with the same result. Therefore Eq. (42.23) is valid for both positive and negative values.

Several effects make the behavior of practical *p*-*n* junction diodes more complex than this simple analysis predicts. One effect, *avalanche breakdown,* occurs under large reverse bias. The electric field in the junction is so great that the carriers can gain enough energy between collisions to create electron–hole pairs during inelastic collisions. The electrons and holes then gain energy and collide to form more pairs, and so on. (A similar effect occurs in dielectric breakdown in insulators, discussed in Section 42.4.)

A second type of breakdown begins when the reverse bias becomes large enough that the top of the valence band in the *p* region is just higher in energy than the bottom of the conduction band in the *n* region (Fig. 42.34). If the junction region is thin enough, the probability becomes large that electrons can *tunnel* from the valence band of the *p* region to the conduction band of the *n* region. This process is called *Zener breakdown.* It occurs in Zener diodes, which are widely used for voltage regulation and protection against voltage surges.

42.34 Under reverse-bias conditions the potential-energy difference between the *p* and *n* sides of a junction is greater than at equilibrium. If this difference is great enough, the bottom of the conduction band on the *n* side may actually be below the top of the valence band on the *p* side.



If a *p*-*n* junction under reverse bias is thin enough, electrons can tunnel from the valence band to the conduction band (a process called Zener breakdown).

Semiconductor Devices and Light

A *light-emitting diode (LED)* is a *p*-*n* junction diode that emits light. When the junction is forward biased, many holes are pushed from their *p* region to the junction region, and many electrons are pushed from their *n* region to the junction region. In the junction region the electrons fall into holes (recombine). In recombining, the electron can emit a photon with energy approximately equal to the band gap. This energy (and therefore the photon wavelength and the color of the light) can be varied by using materials with different band gaps. Light-emitting diodes are widely used for digital displays in clocks, electronic equipment, automobile instrument panels, and many other applications.

The reverse process is called the *photovoltaic effect.* Here the material absorbs photons, and electron–hole pairs are created. Pairs that are created in the *p*-*n* junction, or close enough to migrate to it without recombining, are separated by the electric field we described above that sweeps the electrons to the *n* side and the holes to the *p* side. We can connect this device to an external circuit, where it becomes a source of emf and power. Such a device is often called a *solar cell,* although sunlight isn't required. *Any* light with photon energies greater than the band gap will do. You might have a calculator powered by such cells. Production of low-cost photovoltaic cells for large-scale solar energy conversion is a very active field of research. The same basic physics is used in charge-coupled device (CCD) image detectors, digital cameras, and camcorders.

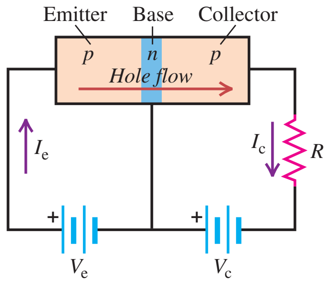
Transistors

A *bipolar junction transistor* includes two *p*-*n* junctions in a "sandwich" configuration, which may be either *p*-*n*-*p* or *n*-*p*-*n*. Such a *p*-*n*-*p* transistor is shown in Fig. 42.35. The three regions are called the emitter, base, and collector, as shown. When there is no current in the left loop of the circuit, there is only a very small current through the resistor R because the voltage across the base–collector junction is in the reverse direction. But when a forward bias is applied between emitter and base, as shown, most of the holes traveling from emitter to base travel *through* the base (which is typically both narrow and lightly doped) to the second junction, where they come under the influence of the collector-to-base potential difference and flow on through the collector to give an increased current to the resistor.

In this way the current in the collector circuit is *controlled* by the current in the emitter circuit. Furthermore, V_c may be considerably larger than V_e, so the *power* dissipated in R may be much larger than the power supplied to the emitter circuit by the battery V_e. Thus the device functions as a *power amplifier.* If the potential drop across R is greater than V_e, it may also be a voltage amplifier.

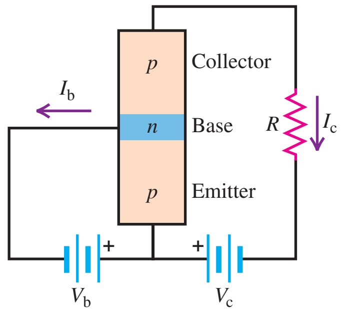
In this configuration the *base* is the common element between the "input" and "output" sides of the circuit. Another widely used arrangement is the *common-emitter* circuit, shown in Fig. 42.36. In this circuit the current in the collector side of the circuit is much larger than that in the base side, and the result is current amplification.

42.35 Schematic diagram of a *p*-*n*-*p* transistor and circuit.



- When $V_\text{e} = 0$, the current is very small.
- When a potential V_e is applied between emitter and base, holes travel from the emitter to the base.
- When V_c is sufficiently large, most of the holes continue into the collector.

42.36 A common-emitter circuit.

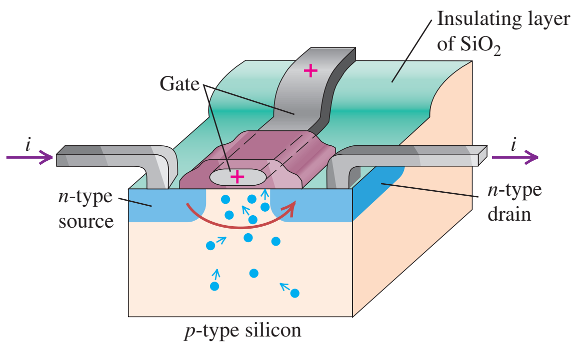


- When $V_\text{b} = 0$, I_c is very small, and most of the voltage V_c appears across the base–collector junction.
- As V_b increases, the base–collector potential decreases, and more holes can diffuse into the collector; thus, I_c increases. Ordinarily, I_c is much larger than I_b.

The *field-effect transistor* (Fig. 42.37) is an important type. In one variation a slab of *p*-type silicon is made with two *n*-type regions on the top, called the *source* and the *drain;* a metallic conductor is fastened to each. A third electrode called the *gate* is separated from the slab, source, and drain by an insulating layer of SiO_2. When there is no charge on the gate and a potential difference of either polarity is applied between the source and the drain, there is very little current because one of the *p*-*n* junctions is reverse biased.

Now we place a positive charge on the gate. With dimensions of the order of 10^{-6} m, it takes little charge to provide a substantial electric field. Thus there is very little current into or out of the gate. There aren't many free electrons in the *p*-type material, but there are some, and the effect of the field is to attract them toward the positive gate. The resulting greatly enhanced concentration of electrons near the gate (and between the two junctions) permits current to flow between the source and the drain. The current is very sensitive to the gate charge and potential,

42.37 A field-effect transistor. The current from source to drain is controlled by the potential difference between the source and the drain and by the charge on the gate; no current flows through the gate.

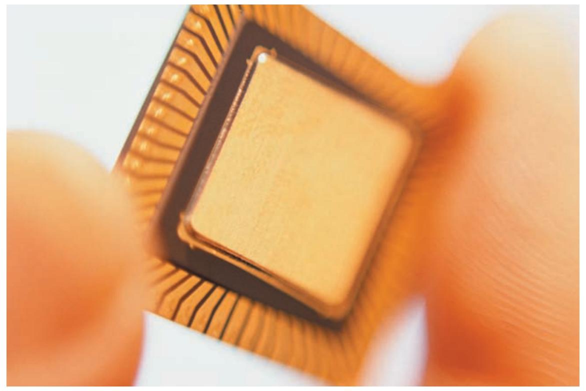


and the device functions as an amplifier. The device just described is called an *enhancement-type MOSFET* (metal-oxide-semiconductor field-effect transistor).

Integrated Circuits

A further refinement in semiconductor technology is the *integrated circuit.* By successively depositing layers of material and etching patterns to define current paths, we can combine the functions of several MOSFETs, capacitors, and resistors on a single square of semiconductor material that may be only a few millimeters on a side. An elaboration of this idea leads to *large-scale integrated circuits* and *very-large-scale integration* (VLSI). The resulting integrated circuit chips are the heart of all pocket calculators and present-day computers, large and small. An example is shown in Fig. 42.38.

42.38 An integrated circuit chip the size of your thumb can contain millions of transistors.



The first semiconductor devices were invented in 1947. Since then, they have completely revolutionized the electronics industry through miniaturization, reliability, speed, energy usage, and cost. They have found applications in communications, computer systems, control systems, and many other areas. In transforming these areas, they have changed, and continue to change, human civilization itself.

Test Your Understanding of Section 42.7 Suppose a negative charge is placed on the gate of the MOSFET shown in Fig. 42.37. Will a substantial current flow between the source and the drain?

42.8 Superconductivity

Superconductivity is the complete disappearance of all electrical resistance at low temperatures. We described this property at the end of Section 25.2 and the magnetic properties of type-I and type-II superconductors in Section 29.8. In this section we'll relate superconductivity to the structure and energy-band model of a solid.

Although superconductivity was discovered in 1911, it was not well understood on a theoretical basis until 1957. In that year, the American physicists John Bardeen, Leon Cooper, and Robert Schrieffer published the theory of superconductivity, now called the BCS theory, that was to earn them the Nobel Prize in physics in 1972. (It was Bardeen's second Nobel Prize; he shared his first for his work on the development of the transistor.) The key to the BCS theory is an interaction between *pairs* of conduction electrons, called *Cooper pairs,* caused by an interaction with the positive ions of the crystal. Here's a rough qualitative picture of what happens. A free electron exerts attractive forces on nearby positive ions, pulling them slightly closer together. The resulting slight concentration of positive charge then exerts an attractive force on another free electron with momentum opposite to the first. At ordinary temperatures this electron-pair interaction is very small in comparison to energies of thermal motion, but at very low temperatures it becomes significant.

Bound together this way, the pairs of electrons cannot *individually* gain or lose very small amounts of energy, as they would ordinarily be able to do in a partly filled conduction band. Their pairing gives an energy gap in the allowed electron quantum levels, and at low temperatures there is not enough collision energy to jump this gap. Therefore the electrons can move freely through the crystal without any energy exchange through collisions—that is, with zero resistance.

Researchers have not yet reached a consensus on whether some modification of the BCS theory can explain the properties of the high-T_C superconductors that have been discovered since 1986. There *is* evidence for pairing, but possibly of holes rather than electrons. Furthermore, the original pairing mechanism of the BCS theory seems too weak to explain the high transition temperatures and critical fields of these new superconductors.

CHAPTER 42 SUMMARY

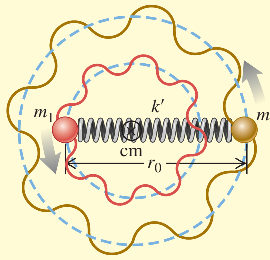
Molecular bonds and molecular spectra: The principal types of molecular bonds are ionic, covalent, van der Waals, and hydrogen bonds. In a diatomic molecule the rotational energy levels are given by Eq. (42.3), where I is the moment of inertia of the molecule, m_r is its reduced mass, and r_0 is the distance between the two atoms. The vibrational energy levels are given by Eq. (42.7), where k' is the effective force constant of the interatomic force. (See Examples 42.1–42.4.)

$$E_l = l(l+1)\frac{\hbar^2}{2I} \quad (l = 0, 1, 2, \ldots) \tag{42.3}$$

$$I = m_r r_0^2 \tag{42.6}$$

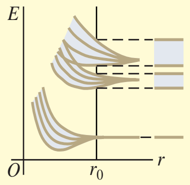
$$m_r = \frac{m_1 m_2}{m_1 + m_2} \tag{42.4}$$

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{m_r}} \quad (n = 0, 1, 2, \ldots) \tag{42.7}$$



Solids and energy bands: Interatomic bonds in solids are of the same types as in molecules plus one additional type, the metallic bond. Associating the basis with each lattice point gives the crystal structure. (See Example 42.5.)

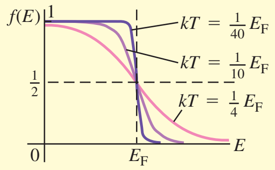
When atoms are bound together in condensed matter, their outer energy levels spread out into bands. At absolute zero, insulators and conductors have a completely filled valence band separated by an energy gap from an empty conduction band. Conductors, including metals, have partially filled conduction bands. (See Example 42.6.)



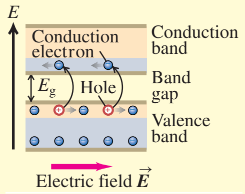
Free-electron model of metals: In the free-electron model of the behavior of conductors, the electrons are treated as completely free particles within the conductor. In this model the density of states is given by Eq. (42.16). The probability that an energy state of energy E is occupied is given by the Fermi-Dirac distribution, Eq. (42.17), which is a consequence of the exclusion principle. In Eq. (42.17), E_F is the Fermi energy. (See Examples 42.7–42.9.)

$$g(E) = \frac{(2m)^{3/2}V}{2\pi^2\hbar^3}E^{1/2} \tag{42.16}$$

$$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1} \tag{42.17}$$

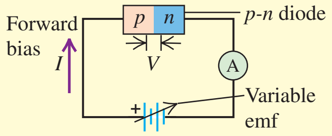


Semiconductors: A semiconductor has an energy gap of about 1 eV between its valence and conduction bands. Its electrical properties may be drastically changed by the addition of small concentrations of donor impurities, giving an n-type semiconductor, or acceptor impurities, giving a p-type semiconductor. (See Example 42.10.)



Semiconductor devices: Many semiconductor devices, including diodes, transistors, and integrated circuits, use one or more p-n junctions. The current–voltage relationship for an ideal p-n junction diode is given by Eq. (42.23). (See Example 42.11.)

$$I = I_S\left(e^{eV/kT} - 1\right) \tag{42.23}$$



Key Terms

ionic bond, *1433*
covalent bond, *1434*
van der Waals bond, *1435*
hydrogen bond, *1435*
metallic crystal, *1444*
energy band, *1445*
valence band, *1446*
conduction band, *1446*
free-electron model, *1447*
density of states, *1448*
Fermi-Dirac distribution, *1449*
Fermi energy, *1449*
semiconductor, *1452*
hole, *1453*
n-type semiconductor, *1454*
p-type semiconductor, *1454*
p-n junction, *1455*
diode rectifier, *1456*

Answer to Chapter Opening Question

The earth must radiate energy into space at the same rate that it receives energy in the form of sunlight. However, carbon dioxide (CO_2) molecules in the atmosphere absorb infrared radiation emitted by the earth's surface and re-emit it toward the ground. To compensate for this and to maintain the balance between emitted and received energy, the earth's surface temperature and hence the rate of blackbody radiation from the surface both increase.

Answers to Test Your Understanding Questions

42.1 Answer: (i) The exclusion principle states that only one electron can be in a given state. Real electrons have spin, so two electrons (one spin-up, one spin-down) can be in a given *spatial* state and hence two can participate in a given covalent bond between two atoms. If electrons obeyed the exclusion principle but did not have spin, that state of an electron would be completely described by its spatial distribution and only *one* electron could participate in a covalent bond. (We will learn in Chapter 44 that this situation is wholly imaginary: There are subatomic particles without spin, but they do *not* obey the exclusion principle.)

42.2 Answer: (ii) Figure 42.5 shows that the difference in energy between adjacent rotational levels increases with increasing l. Hence, as l increases, the energy E of the emitted photon increases and the wavelength $\lambda = hc/E$ decreases.

42.3 Answer (ii) In Fig. 42.14 let a be the distance between adjacent Na^+ and Cl^- ions. This figure shows that the Cl^- ion that is the next nearest neighbor to a Na^+ ion is on the opposite corner of a cube of side a. The distance between these two ions is $\sqrt{a^2 + a^2 + a^2} = \sqrt{3a^2} = a\sqrt{3}$.

42.4 Answer (ii) A small temperature change causes a substantial increase in the population of electrons in a semiconductor's conduction band and a comparably substantial increase in conductivity. The conductivity of conductors and insulators varies more gradually with temperature.

42.5 Answer: no The kinetic-molecular model of an ideal gas (see Section 18.3) shows that the gas pressure is proportional to the average translational kinetic energy E_{av} of the particles that make up the gas. In a classical ideal gas, E_{av} is directly proportional to the average temperature T, so the pressure decreases as T decreases. In a free-electron gas, the average kinetic energy per electron is *not* related simply to T; as Example 42.9 shows, for the free-electron gas in a metal, E_{av} is almost completely a consequence of the exclusion principle at room temperature and colder. Hence the pressure of a free-electron gas in a solid metal does *not* change appreciably between room temperature and absolute zero.

42.6 Answer: no Pure copper is already an excellent conductor since it has a partially filled conduction band (Fig. 42.21c). Furthermore, copper forms a metallic crystal (Fig. 42.17) as opposed to the covalent crystals of silicon or germanium, so the scheme of using an impurity to donate or accept an electron does not work for copper. In fact, adding impurities to copper *decreases* the conductivity because an impurity tends to scatter electrons, impeding the flow of current.

42.7 Answer: no A negative charge on the gate will repel, not attract, electrons in the *p*-type silicon. Hence the electron concentration in the region between the two *p-n* junctions will be made even smaller. With so few charge carriers present in this region, very little current will flow between the source and the drain.

PROBLEMS

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

Discussion Questions

Q42.1. Ionic bonds result from the electrical attraction of oppositely charged particles. Are other types of molecular bonds also electrical in nature, or is some other interaction involved? Explain.

Q42.2. In ionic bonds, an electron is transferred from one atom to another and thus no longer "belongs" to the atom from which it came. Are there similar transfers of ownership of electrons with other types of molecular bonds? Explain.

Q42.3. Van der Waals bonds occur in many molecules, but hydrogen bonds occur only with materials that contain hydrogen. Why is this type of bond unique to hydrogen?

Q42.4. The bonding of gallium arsenide (GaAs) is said to be 31% ionic and 69% covalent. Explain.

Q42.5. The H_2^+ molecule consists of two hydrogen nuclei and a single electron. What kind of molecular bond do you think holds this molecule together? Explain.

Q42.6. The moment of inertia for an axis through the center of mass of a diatomic molecule calculated from the wavelength emitted in an $l = 19 \rightarrow l = 18$ transition is different from the moment of inertia calculated from the wavelength of the photon emitted in an $l = 1 \rightarrow l = 0$ transition. Explain this difference. Which transition corresponds to the larger moment of inertia?

Q42.7. Analysis of the photon absorption spectrum of a diatomic molecule shows that the vibrational energy levels for small values of n are very nearly equally spaced but the levels for large n are not equally spaced. Discuss the reason for this observation. Do you expect the adjacent levels to move closer together or farther apart as n increases? Explain.

Q42.8. Discuss the differences between the rotational and vibrational energy levels of the deuterium ("heavy hydrogen") molecule D_2 and those of the ordinary hydrogen molecule H_2. A deuterium atom has twice the mass of an ordinary hydrogen atom.

Q42.9. Various organic molecules have been discovered in interstellar space. Why were these discoveries made with radio telescopes rather than optical telescopes?

Q42.10. The air you are breathing contains primarily nitrogen (N_2) and oxygen (O_2). Many of these molecules are in excited rotational energy levels $(l = 1, 2, 3, \ldots)$, but almost all of them are in the vibrational ground level $(n = 0)$. Explain this difference between the rotational and vibrational behaviors of the molecules.

Q42.11. In what ways do atoms in a diatomic molecule behave as though they were held together by a spring? In what ways is this a poor description of the interaction between the atoms?

Q42.12. Individual atoms have discrete energy levels, but certain solids (which are made up of only individual atoms) show energy bands and gaps. What causes the solids to behave so differently from the atoms of which they are composed?

Q42.13. What factors determine whether a material is a conductor of electricity or an insulator? Explain.

Q42.14. Ionic crystals are often transparent, whereas metallic crystals are always opaque. Why?

Q42.15. Speeds of molecules in a gas vary with temperature, whereas speeds of electrons in the conduction band of a metal are nearly independent of temperature. Why are these behaviors so different?

Q42.16. Use the band model to explain how it is possible for some materials to undergo a semiconductor-to-metal transition as the temperature or pressure varies.

Q42.17. An isolated zinc atom has a ground-state electron configuration of filled 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, and 4*s* subshells. How can zinc be a conductor if its valence subshell is full?

Q42.18. The assumptions of the *free-electron model* of metals may seem contrary to reason, since electrons exert powerful electrical forces on each other. Give some reasons why these assumptions actually make physical sense.

Q42.19. Why are materials that are good thermal conductors also good electrical conductors? What kinds of problems does this pose for the design of appliances such as clothes irons and electric heaters? Are there materials that do not follow this general rule?

Q42.20. What is the essential characteristic for an element to serve as a donor impurity in a semiconductor such as Si or Ge? For it to serve as an acceptor impurity? Explain.

Q42.21. There are several methods for removing electrons from the surface of a semiconductor. Can holes be removed from the surface? Explain.

Q42.22. A student asserts that silicon and germanium become good insulators at very low temperatures and good conductors at very high temperatures. Do you agree? Explain your reasoning.

Q42.23. The electrical conductivities of most metals decrease gradually with increasing temperature, but the intrinsic conductivity of semiconductors always *increases* rapidly with increasing temperature. What causes the difference?

Q42.24. How could you make compensated silicon that has twice as many acceptors as donors?

Q42.25. For electronic devices such as amplifiers, what are some advantages of transistors compared to vacuum tubes? What are some disadvantages? Are there any situations in which vacuum tubes *cannot* be replaced by solid-state devices? Explain your reasoning.

Q42.26. Why does tunneling limit the miniaturization of MOSFETs?

Q42.27. The saturation current I_S for a *p-n* junction, Eq. (42.23), depends strongly on temperature. Explain why.

Exercises

Section 42.1 Types of Molecular Bonds

42.1. We know from Chapter 18 that the average kinetic energy of an ideal gas atom or molecule at Kelvin temperature T is $\frac{3}{2}kT$. For what value of T does this energy correspond to (a) the bond energy of the van der Waals bond in He_2 $(7.9 \times 10^{-4}\ \text{eV})$ and (b) the bond energy of the covalent bond in H_2 (4.48 eV)? (c) The kinetic energy in a collision between molecules can go into dissociating one or both molecules, provided the kinetic energy is higher than the bond energy. At room temperature (300 K), is it likely that He_2 molecules will remain intact after a collision? What about H_2 molecules? Explain.

42.2. An Ionic Bond. (a) Calculate the electric potential energy for a K^+ ion and a Br^- ion separated by a distance of 0.29 nm, the equilibrium separation in the KBr molecule. Treat the ions as point charges. (b) The ionization energy of the potassium atom is 4.3 eV. Atomic bromine has an electron affinity of 3.5 eV. Use these data and the results of part (a) to estimate the binding energy of the KBr molecule. Do you expect the actual binding energy to be higher or lower than your estimate? Explain your reasoning.

Section 42.2 Molecular Spectra

42.3. A hypothetical NH molecule makes a rotational-level transition from $l = 3$ to $l = 1$ and gives off a photon of wavelength 1.780 nm in doing so. What is the separation between the two atoms in this molecule if we model them as point masses? The mass of hydrogen is 1.67×10^{-27} kg, and the mass of nitrogen is 2.33×10^{-26} kg.

42.4. The water molecule has an $l = 1$ rotational level 1.01×10^{-5} eV above the $l = 0$ ground level. Calculate the wavelength and frequency of the photon absorbed by water when it undergoes a rotational-level transition from $l = 0$ to $l = 1$. The magnetron oscillator in a microwave oven generates microwaves with a frequency of 2450 MHz. Does this make sense, in view of the frequency you calculated in this problem? Explain.

42.5. In Example 42.2 the moment of inertia for CO was calculated using Eq. (42.6). (a) In CO, how far is each atom from the center of mass of the molecule? (b) Use $I = m_1 r_1^2 + m_2 r_2^2$ to calculate the moment of inertia of CO about an axis through the center of mass and perpendicular to the line joining the centers of the two atoms. Does your result agree with the value obtained in Example 42.2?

42.6. Two atoms of cesium (Cs) can form a Cs_2 molecule. The equilibrium distance between the nuclei in a Cs_2 molecule is 0.447 nm. Calculate the moment of inertia about an axis through the center of mass of the two nuclei and perpendicular to the line joining them. The mass of a cesium atom is 2.21×10^{-25} kg.

42.7. The rotational energy levels of CO are calculated in Example 42.2. If the energy of the rotating molecule is described by the classical expression $K = \frac{1}{2}I\omega^2$, for the $l = 1$ level what are (a) the angular speed of the rotating molecule; (b) the linear speed of each atom (use the result of Exercise 42.5); (c) the rotational period (the time for one rotation)?

42.8. If a sodium chloride (NaCl) molecule could undergo an $n \rightarrow n - 1$ vibrational transition with no change in rotational quantum number, a photon with wavelength 20.0 μm would be emitted. The mass of a sodium atom is 3.82×10^{-26} kg, and the mass of a chlorine atom is 5.81×10^{-26} kg. Calculate the force constant k' for the interatomic force in NaCl.

42.9. A lithium atom has mass 1.17×10^{-26} kg, and a hydrogen atom has mass 1.67×10^{-27} kg. The equilibrium separation between the two nuclei in the LiH molecule is 0.159 nm. (a) What is the difference in energy between the $l = 3$ and $l = 4$ rotational levels? (b) What is the wavelength of the photon emitted in a transition from the $l = 4$ to the $l = 3$ level?

42.10. When a hypothetical diatomic molecule having atoms 0.8860 nm apart undergoes a rotational transition from the $l = 2$ state to the next lower state, it gives up a photon having energy 8.841×10^{-4} eV. When the molecule undergoes a vibrational transition from one energy state to the next lower energy state, it gives up 0.2560 eV. Find the force constant of this molecule.

42.11. (a) Show that the energy difference between rotational levels with angular-momentum quantum numbers l and $l - 1$ is $l\hbar^2/I$. (b) In terms of l, $\hbar$, and I, what is the frequency of the photon emitted in the pure rotation transition $l \rightarrow l - 1$?

42.12. The rotational energy levels of the CO molecule are calculated in Example 42.2 and the vibrational-level energy differences are given in Example 42.3. The vibrational and rotational energies are given by Eq. (42.9). Calculate the wavelength of the photon absorbed by CO in each of the following vibration–rotation transitions: (a) $n = 0,\ l = 1 \rightarrow n = 1,\ l = 2$; (b) $n = 0,\ l = 2 \rightarrow n = 1,\ l = 1$; (c) $n = 0,\ l = 3 \rightarrow n = 1,\ l = 2$.

42.13. The vibration frequency for the molecule HF is 1.24×10^{14} Hz. The mass of a hydrogen atom is 1.67×10^{-27} kg, and the mass of a fluorine atom is 3.15×10^{-26} kg. (a) What is the force constant k' for the interatomic force? (b) What is the spacing between adjacent vibrational energy levels in joules and in electron volts? (c) What is the wavelength of a photon of energy equal to the energy difference between two adjacent vibrational levels? In what region of the spectrum does it lie?

Section 42.3 Structure of Solids

42.14. Potassium bromide (KBr) has a density of $2.75 \times 10^3\ \mathrm{kg/m^3}$ and the same crystal structure as NaCl. The mass of a potassium atom is 6.49×10^{-26} kg, and the mass of a bromine atom is 1.33×10^{-25} kg. (a) Calculate the average spacing between adjacent atoms in a KBr crystal. (b) How does the value calculated in part (a) compare with the spacing in NaCl (see Exercise 42.15)? Is the relationship between the two values qualitatively what you would expect? Explain.

42.15. Density of NaCl. The spacing of adjacent atoms in a crystal of sodium chloride is 0.282 nm. The mass of a sodium atom is 3.82×10^{-26} kg, and the mass of a chlorine atom is 5.89×10^{-26} kg. Calculate the density of sodium chloride.

42.16. Calculate the wavelengths of (a) a 6.20-keV x ray; (b) a 37.6-eV electron; (c) a 0.0205-eV neutron.

Section 42.4 Energy Bands

42.17. The maximum wavelength of light that a certain silicon photocell can detect is 1.11 μm. (a) What is the energy gap (in electron volts) between the valence and conduction bands for this photocell? (b) Explain why pure silicon is opaque.

42.18. The gap between valence and conduction bands in diamond is 5.47 eV. (a) What is the maximum wavelength of a photon that can excite an electron from the top of the valence band into the conduction band? In what region of the electromagnetic spectrum does this photon lie? (b) Explain why pure diamond is transparent and colorless. (c) Most gem diamonds have a yellow color. Explain how impurities in the diamond can cause this color.

42.19. The gap between valence and conduction bands in silicon is 1.12 eV. A nickel nucleus in an excited state emits a gamma-ray photon with wavelength 9.31×10^{-4} nm. How many electrons can be excited from the top of the valence band to the bottom of the conduction band by the absorption of this gamma ray?

Section 42.5 Free-Electron Model of Metals

42.20. What is the value of the constant A in Eq. (42.10) that makes $\psi(x, y, z)$ normalized?

42.21. Calculate the density of states $g(E)$ for the free-electron model of a metal if $E = 7.0$ eV and $V = 1.0\ \mathrm{cm^3}$. Express your answer in units of states per electron volt.

42.22. Calculate v_{rms} for free electrons with average kinetic energy $\frac{3}{2}kT$ at a temperature of 300 K. How does your result compare to the speed of an electron with a kinetic energy equal to the Fermi energy of copper, calculated in Example 42.9? Why is there such a difference between these speeds?

42.23. (a) Show that the wave function ψ given in Eq. (42.10) is a solution of the three-dimensional Schrödinger equation, Eq. (40.29), with the energy as given by Eq. (42.11). (b) What are the energies of the ground level and the lowest two excited levels? What is the degeneracy of each of these levels? (Include the factor of 2 in the degeneracy that is due to the two possible spin states.)

42.24. Supply the details in the derivation of Eq. (42.14) from Eqs. (42.13) and (42.12).

42.25. Silver has a Fermi energy of 5.48 eV. Calculate the electron contribution to the molar heat capacity at constant volume of silver, C_V, at 300 K. Express your result (a) as a multiple of R and (b) as a fraction of the actual value for silver, $C_V = 25.3\ \mathrm{J/mol \cdot K}$. (c) Is the value of C_V due principally to the electrons? If not, to what is it due? (*Hint:* See Section 18.4.)

42.26. The Fermi energy of sodium is 3.23 eV. (a) Find the average energy E_{av} of the electrons at absolute zero. (b) What is the speed of an electron that has energy E_{av}? (c) At what Kelvin temperature T is kT equal to E_{F}? (This is called the *Fermi temperature* for the metal. It is approximately the temperature at which molecules in a classical ideal gas would have the same kinetic energy as the fastest-moving electron in the metal.)

42.27. For a solid metal having a Fermi energy of 8.500 eV, what is the probability, at room temperature, that a state having an energy of 8.520 eV is occupied by an electron?

Section 42.6 Semiconductors

42.28. Pure germanium has a band gap of 0.67 eV. The Fermi energy is in the middle of the gap. (a) For temperatures of 250 K, 300 K, and 350 K, calculate the probability $f(E)$ that a state at the bottom of the conduction band is occupied. (b) For each temperature in part (a), calculate the probability that a state at the top of the valence band is empty.

42.29. Germanium has a band gap of 0.67 eV. Doping with arsenic adds donor levels in the gap 0.01 eV below the bottom of the conduction band. At a temperature of 300 K, the probability is 4.4×10^{-4} that an electron state is occupied at the bottom of the conduction band. Where is the Fermi level relative to the conduction band in this case?

Section 42.7 Semiconductor Devices

42.30. For a certain *p-n* junction diode, the saturation current at room temperature $(20°\mathrm{C})$ is 0.750 mA. What is the resistance of this diode when the voltage across it is (a) 85.0 mV (b) -50.0 mV?

42.31. (a) A forward-bias voltage of 15.0 mV produces a positive current of 9.25 mA through a *p-n* junction at 300 K. What does the positive current become if the forward-bias voltage is reduced to 10.0 mV? (b) For reverse-bias voltages of -15.0 mV and -10.0 mV, what is the reverse-bias negative current?

42.32. A *p-n* junction has a saturation current of 3.60 mA. (a) At a temperature of 300 K, what voltage is needed to produce a positive current of 40.0 mA? (b) For a voltage equal to the negative of the value calculated in part (a), what is the negative current?

Problems

42.33. A hypothetical diatomic molecule of oxygen $(\text{mass} = 2.656 \times 10^{-26}\ \text{kg})$ and hydrogen $(\text{mass} = 1.67 \times 10^{-27}\ \text{kg})$ emits a photon of wavelength 2.39 μm when it makes a transition from one vibrational state to the next lower state. If we model this molecule as two point masses at opposite ends of a massless spring, (a) what is the force constant of this spring, and (b) how many vibrations per second is the molecule making?

42.34. When a diatomic molecule undergoes a transition from the $l = 2$ to the $l = 1$ rotational state, a photon with wavelength 63.8 μm is emitted. What is the moment of inertia of the molecule for an axis through its center of mass and perpendicular to the line connecting the nuclei?

42.35. (a) The equilibrium separation of the two nuclei in an NaCl molecule is 0.24 nm If the molecule is modeled as charges $+e$ and $-e$ separated by 0.24 nm, what is the electric dipole moment of the molecule (see Section 21.7)? (b) The measured electric dipole moment of an NaCl molecule is $3.0 \times 10^{-29}\ \mathrm{C \cdot m}$. If this dipole moment arises from point charges $+q$ and $-q$ separated by 0.24 nm, what is q? (c) A definition of the *fractional ionic character* of the bond is q/e. If the sodium atom has charge $+e$ and the chlorine atom has charge $-e$, the fractional ionic character would be equal to 1. What is the actual fractional ionic character for the bond in NaCl? (d) The equilibrium distance between nuclei in the hydrogen iodide (HI) molecule is 0.16 nm, and the measured electric dipole moment of the molecule is $1.5 \times 10^{-30}\ \mathrm{C \cdot m}$. What is the fractional ionic character for the bond in HI? How does your answer compare to that for NaCl calculated in part (c)? Discuss reasons for the difference in these results.

42.36. The binding energy of a potassium chloride molecule (KCl) is 4.43 eV. The ionization energy of a potassium atom is 4.3 eV, and the electron affinity of chlorine is 3.6 eV. Use these data to estimate the equilibrium separation between the two atoms in the KCl molecule. Explain why your result is only an estimate and not a precise value.

42.37. (a) For the sodium chloride molecule (NaCl) discussed at the beginning of Section 42.1, what is the maximum separation of the ions for stability if they may be regarded as point charges? That is, what is the largest separation for which the energy of an $\mathrm{Na^+}$ ion and a $\mathrm{Cl^-}$ ion, calculated in this model, is lower than the energy of the two separate atoms Na and Cl? (b) Calculate this distance for the potassium bromide molecule, described in Exercise 42.2.

42.38. The rotational spectrum of HCl contains the following wavelengths (among others): 60.4 μm, 69.0 μm, 80.4 μm, 96.4 μm, and 120.4 μm. Use this spectrum to find the moment of inertia of the HCl molecule about an axis through the center of mass and perpendicular to the line joining the two nuclei.

42.39. (a) Use the result of Problem 42.38 to calculate the equilibrium separation of the atoms in HCl molecule. The mass of a chlorine atom is 5.81×10^{-26} kg, and the mass of a hydrogen atom is 1.67×10^{-27} kg. (b) The value of l changes by ± 1 in rotational transitions. What is the value of l for the upper level of the transition that gives rise to each of the wavelengths listed in Problem 42.38? (c) What is the longest-wavelength line in the rotational spectrum of HCl? (d) Calculate the wavelengths of the emitted light for the corresponding transitions in the deuterium chloride (DCl) molecule. In this molecule the hydrogen atom in HCl is replaced by an atom of deuterium, an isotope of hydrogen with a mass of 3.34×10^{-27} kg. Assume that the equilibrium separation between the atoms is the same as for HCl.

42.40. When a NaF molecule makes a transition from the $l = 3$ to the $l = 2$ rotational level with no change in vibrational quantum number or electronic state, a photon with wavelength 3.83 mm is emitted. A sodium atom has mass 3.82×10^{-26} kg, and a fluorine atom has mass 3.15×10^{-26} kg. Calculate the equilibrium separation between the nuclei in a NaF molecule. How does your answer compare with the value for NaCl given in Section 42.1? Is this result reasonable? Explain.

42.41. Consider a gas of diatomic molecules (moment of inertia I) at an absolute temperature T. If E_{g} is a ground-state energy and E_{ex} is the energy of an excited state, then the Maxwell-Boltzmann distribution (see Section 38.6) predicts that the ratio of the numbers of molecules in the two states is

$$\frac{n_{\mathrm{ex}}}{n_{\mathrm{g}}} = e^{-(E_{\mathrm{ex}} - E_{\mathrm{g}})/kT}$$

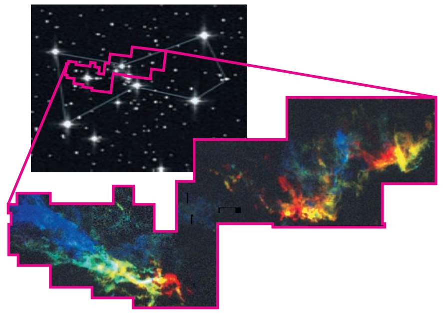
(a) Explain why the ratio of the number of molecules in the lth rotational energy *level* to the number of molecules in the ground $(l = 0)$ rotational level is

$$\frac{n_l}{n_0} = (2l + 1)e^{-[l(l+1)\hbar^2]/2IkT}$$

(*Hint:* For each value of l, how many states are there with different values of m_l?) (b) Determine the ratio n_l/n_0 for a gas of CO molecules at 300 K for the cases (i) $l = 1$; (ii) $l = 2$; (iii) $l = 10$; (iv) $l = 20$; (v) $l = 50$. The moment of inertia of the CO molecule is given in Example 42.2 (Section 42.2). (c) Your results in part (b) show that as l is increased, the ratio n_l/n_0 first increases and then decreases. Explain why.

42.42. Our galaxy contains numerous *molecular clouds,* regions many light-years in extent in which the density is high enough and the temperature low enough for atoms to form into molecules. Most of the molecules are H_2, but a small fraction of the molecules are carbon monoxide (CO). Such a molecular cloud in the constellation Orion is shown in Fig. 42.39. The left-hand image was made with an ordinary visible-light telescope; the right-hand image shows the molecular cloud in Orion as imaged with a radio tele-

Figure **42.39** Problem 42.42.



scope tuned to a wavelength emitted by CO in a rotational transition. The different colors in the radio image indicate regions of the cloud that are moving either toward us (blue) or away from us (red) relative to the motion of the cloud as a whole, as determined by the Doppler shift of the radiation. (Since a molecular cloud has about 10,000 hydrogen molecules for each CO molecule, it might seem more reasonable to tune a radio telescope to emissions from H_2 than to emissions from CO. Unfortunately, it turns out that the H_2 molecules in molecular clouds do not radiate in either the radio or visible portions of the electromagnetic spectrum.) (a) Using the data in Example 42.2 (Section 42.2), calculate the energy and wavelength of the photon emitted by a CO molecule in an $l = 1 \rightarrow l = 0$ rotational transition. (b) As a rule, molecules in a gas at temperature T will be found in a certain excited rotational energy level provided the energy of that level is no higher than kT (see Problem 42.41). Use this rule to explain why astronomers can detect radiation from CO in molecular clouds even though the typical temperature of a molecular cloud is a very low 20 K.

42.43. Spectral Lines from Isotopes. The equilibrium separation for NaCl is 0.2361 nm. The mass of a sodium atom is 3.8176×10^{-26} kg. Chlorine has two stable isotopes, ^{35}Cl and ^{37}Cl, that have different masses but identical chemical properties. The atomic mass of ^{35}Cl is 5.8068×10^{-26} kg, and the atomic mass of ^{37}Cl is 6.1384×10^{-26} kg. (a) Calculate the wavelength of the photon emitted in the $l = 2 \rightarrow l = 1$ and $l = 1 \rightarrow l = 0$ transitions for Na^{35}Cl. (b) Repeat part (a) for Na^{37}Cl. What are the differences in the wavelengths for the two isotopes?

42.44. When an OH molecule undergoes a transition from the $n = 0$ to the $n = 1$ vibrational level, its internal vibrational energy increases by 0.463 eV. Calculate the frequency of vibration and the force constant for the interatomic force. (The mass of an oxygen atom is 2.66×10^{-26} kg, and the mass of a hydrogen atom is 1.67×10^{-27} kg.)

42.45. The force constant for the internuclear force in a hydrogen molecule (H_2) is $k' = 576$ N/m. A hydrogen atom has mass 1.67×10^{-27} kg. Calculate the zero-point vibrational energy for H_2 (that is, the vibrational energy the molecule has in the $n = 0$ ground vibrational level). How does this energy compare in magnitude with the H_2 bond energy of -4.48 eV?

42.46. Suppose the hydrogen atom in HF (see Exercise 42.13) is replaced by an atom of deuterium, an isotope of hydrogen with a mass of 3.34×10^{-27} kg. The force constant is determined by the electron configuration, so it is the same as for the normal HF molecule. (a) What is the vibrational frequency of this molecule? (b) What wavelength of light corresponds to the energy difference between the $n = 1$ and $n = 0$ levels? In what region of the spectrum does this wavelength lie?

42.47. The hydrogen iodide (HI) molecule has equilibrium separation 0.160 nm and vibrational frequency 6.93×10^{13} Hz. The mass of a hydrogen atom is 1.67×10^{-27} kg, and the mass of an iodine atom is 2.11×10^{-25} kg. (a) Calculate the moment of inertia of HI about a perpendicular axis through its center of mass. (b) Calculate the wavelength of the photon emitted in each of the following vibration–rotation transitions: (i) $n = 1$, $l = 1 \rightarrow n = 0$, $l = 0$; (ii) $n = 1$, $l = 2 \rightarrow n = 0$, $l = 1$; (iii) $n = 2$, $l = 2 \rightarrow n = 1$, $l = 3$.

42.48. Prove this statement: For free electrons in a solid, if a state that is at an energy ΔE above E_F has probability P of being occupied, then the probability is $1 - P$ that a state at an energy ΔE below E_F is occupied.

42.49. Compute the Fermi energy of potassium by making the simple approximation that each atom contributes one free electron. The density of potassium is 851 kg/m^3, and the mass of a single potassium atom is 6.49×10^{-26} kg.

42.50. Hydrogen is found in two naturally occurring isotopes; normal hydrogen (containing a single proton in its nucleus) and deuterium (having a proton and a neutron). Assuming that both molecules are the same size and that the proton and neutron have the same mass (which is almost the case), find the ratio of (a) the energy of any given rotational state in a diatomic hydrogen molecule to the energy of the same state in a diatomic deuterium molecule and (b) the energy of any given vibrational state in hydrogen to the same state in deuterium (assuming that the force constant is the same for both molecules). Why is it physically reasonable that the force constant would be the same for hydrogen and deuterium molecules?

42.51. Metallic lithium has a bcc crystal structure. Each unit cell is a cube of side length $a = 0.35$ nm. (a) For a bcc lattice, what is the number of atoms per unit volume? Give your answer in terms of a. (*Hint:* How many atoms are there per unit cell?) (b) Use the result of part (a) to calculate the zero-temperature Fermi energy E_{F0} for metallic lithium. Assume there is one free electron per atom.

42.52. The one-dimensional calculation of Example 42.5 (Section 42.3) can be extended to three dimensions. For the three-dimensional fcc NaCl lattice, the result for the potential energy of a pair of Na$^+$ and Cl$^-$ ions due to the electrostatic interaction with all of the ions in the crystal is $U = -\alpha e^2/4\pi\epsilon_0 r$, where $\alpha = 1.75$ is the *Madelung constant.* Another contribution to the potential energy is a repulsive interaction at small ionic separation r due to overlap of the electron clouds. This contribution can be represented by A/r^8, where A is a positive constant, so the expression for the total potential energy is

$$U_{\text{tot}} = -\frac{\alpha e^2}{4\pi\epsilon_0 r} + \frac{A}{r^8}$$

(a) Let r_0 be the value of the ionic separation r for which U_{tot} is a minimum. Use this definition to find an equation that relates r_0 and A, and use this to write U_{tot} in terms of r_0. For NaCl, $r_0 = 0.281$ nm. Obtain a numerical value (in electron volts) of U_{tot} for NaCl. (b) The quantity $-U_{\text{tot}}$ is the energy required to remove a Na$^+$ ion and a Cl$^-$ ion from the crystal. Forming a pair of neutral atoms from this pair of ions involves the release of 5.14 eV (the ionization energy of Na) and the expenditure of 3.61 eV (the electron affinity of Cl). Use the result of part (a) to calculate the energy required to remove a pair of neutral Na and Cl atoms from the crystal. The experimental value for this quantity is 6.39 eV; how well does your calculation agree?

42.53. Consider a system of N free electrons within a volume V. Even at absolute zero, such a system exerts a pressure p on its surroundings due to the motion of the electrons. To calculate this pressure, imagine that the volume increases by a small amount dV. The electrons will do an amount of work pdV on their surroundings, which means that the total energy E_{tot} of the electrons will change by an amount $dE_{\text{tot}} = -pdV$. Hence $p = -dE_{\text{tot}}/dV$. (a) Show that the pressure of the electrons at absolute zero is

$$p = \frac{3^{2/3}\pi^{4/3}\hbar^2}{5m}\left(\frac{N}{V}\right)^{5/3}$$

(b) Evaluate this pressure for copper, which has a free-electron concentration of 8.45×10^{28} m^{-3}. Express your result in pascals and in atmospheres. (c) The pressure you found in part (b) is extremely high. Why, then, don't the electrons in a piece of copper simply explode out of the metal?

42.54. When the pressure p on a material increases by an amount Δp, the volume of the material will change from V to $V + \Delta V$, where ΔV is negative. The *bulk modulus B* of the material is defined to be the ratio of the pressure change Δp to the absolute value $|\Delta V/V|$ of the fractional volume change. The greater the bulk modulus, the greater the pressure increase required for a given fractional volume change, and the more incompressible the material (see Section 11.4). Since $\Delta V < 0$, the bulk modulus can be written as $B = -\Delta p/(\Delta V/V_0)$. In the limit that the pressure and volume changes are very small, this becomes

$$B = -V\frac{dp}{dV}$$

(a) Use the result of Problem 42.53 to show that the bulk modulus for a system of N free electrons in a volume V at low temperatures is $B = \frac{5}{3}p$. (*Hint:* The quantity p in the expression $B = -V(dp/dV)$ is the *external* pressure on the system. Can you explain why this is equal to the *internal* pressure of the system itself, as found in Problem 42.53?) (b) Evaluate the bulk modulus for the electrons in copper, which has a free-electron concentration of 8.45×10^{28} m^{-3}. Express your result in pascals. (c) The actual bulk modulus of copper is 1.4×10^{11} Pa. Based on your result in part (b), what fraction of this is due to the free electrons in copper? (This result shows that the free electrons in a metal play a major role in making the metal resistant to compression.) What do you think is responsible for the remaining fraction of the bulk modulus?

42.55. In the discussion of free electrons in Section 42.5, we assumed that we could ignore the effects of relativity. This is not a safe assumption if the Fermi energy is greater than about $\frac{1}{100}mc^2$ (that is, more than about 1% of the rest energy of an electron). (a) Assume that the Fermi energy at absolute zero, as given by Eq. (42.20), is equal to $\frac{1}{100}mc^2$. Show that the electron concentration is

$$\frac{N}{V} = \frac{2^{3/2}m^3c^3}{3000\pi^2\hbar^3}$$

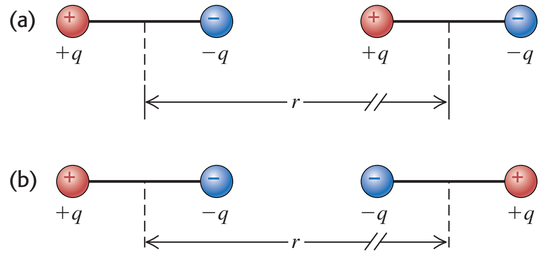
and determine the numerical value of N/V. (b) Is it a good approximation to ignore relativistic effects for electrons in a metal such as copper, for which the electron concentration is 8.45×10^{28} m^{-3}? Explain. (c) A *white dwarf star* is what is left behind by a star like the sun after it has ceased to produce energy by nuclear reactions. (Our own sun will become a white dwarf star in another 6×10^9 years or so.) A typical white dwarf has mass 2×10^{30} kg (comparable to the sun) and radius 6000 km (comparable to that of the earth). The gravitational attraction of different parts of the white dwarf for each other tends to compress the star; what prevents it from compressing is the pressure of free electrons within the star (see Problem 42.53). Estimate the electron concentration within a typical white dwarf star using the following assumptions: (i) the white dwarf star is made of carbon, which has a mass per atom of 1.99×10^{-26} kg; and (ii) all six of the electrons from each carbon atom are able to move freely throughout the star. (d) Is it a good approximation to ignore relativistic effects in the structure of a white dwarf star? Explain.

42.56. A variable DC battery is connected in series with a 125-Ω resistor and a *p-n* junction diode that has a saturation current of 0.625 mA at room temperature (20°C). When a voltmeter across the 125-Ω resistor reads 35.0 V, what are (a) the voltage across the diode and (b) the resistance of the diode?

Challenge Problems

42.57. Van der Waals bonds arise from the interaction between two permanent or induced electric dipole moments in a pair of atoms or molecules. (a) Consider two identical dipoles, each consisting of charges $+q$ and $-q$ separated by a distance d and oriented as shown in Fig. 42.40a. Calculate the electric potential energy, expressed in terms of the electric dipole moment $p = qd$, for the situation where $r \gg d$. Is the interaction attractive or repulsive, and how does this potential energy vary with r, the separation between the centers of the two dipoles? (b) Repeat part (a) for the orientation of the dipoles shown in Fig. 42.40b. The dipole interaction is more complicated when we have to average over the relative orientations of the two dipoles due to thermal motion or when the dipoles are induced rather than permanent.

Figure 42.40 Challenge Problem 42.57.



42.58. (a) Consider the hydrogen molecule (H_2) to be a simple harmonic oscillator with an equilibrium spacing of 0.074 nm, and estimate the vibrational energy-level spacing for H_2. The mass of a hydrogen atom is 1.67×10^{-27} kg. (*Hint:* Estimate the force constant by equating the change in Coulomb repulsion of the protons, when the atoms move slightly closer together than r_0, to the "spring" force. That is, assume that the chemical binding force remains approximately constant as r is decreased slightly from r_0.) (b) Use the results of part (a) to calculate the vibrational energy-level spacing for the deuterium molecule, D_2. Assume that the spring constant is the same for D_2 as for H_2. The mass of a deuterium atom is 3.34×10^{-27} kg.