

# CHAPTER 42 MOLECULAR AND SOLID-STATE PHYSICS

## Section 42-2: Molecular Energy Levels

### Problem

1. Find the energies of the first four rotational states of the HCl molecules described in Example 42-1.

### Solution

The energies of rotational states (above the  $j = 0$  state) are given by Equation 42-2, where for the HCl molecule,  $2I = 2.63 \text{ meV}$  (from Example 42-1). Thus,  $E_{\text{rot}} = j(j+1)I = \frac{1}{2}j(j+1)2.63 \text{ meV}$ . For  $j = 0, 1, 2,$  and  $3$ ,  $E_{\text{rot}} = 0, 2.63 \text{ meV}, 7.89 \text{ meV},$  and  $15.78 \text{ meV}$ .

### Problem

2. Find the wavelength of electromagnetic radiation needed to excite oxygen molecules ( $\text{O}_2$ ) to their first rotational excited state. The rotational inertia of an oxygen molecule is  $1.95 \times 10^{-46} \text{ kg} \cdot \text{m}^2$ .

### Solution

The difference in energy between the  $j = 1$  and  $j = 0$  states is  $\Delta E = 1(1+1)I - 0 = 2I$ . The photon wavelength corresponding to this transition is  $\lambda = hc/\Delta E = hc/2I = 2pcI = 2p(3 \times 10^8 \text{ m/s})(1.95 \times 10^{-46} \text{ kg} \cdot \text{m}^2)/(1.055 \times 10^{-34} \text{ J} \cdot \text{s}) = 3.48 \text{ mm}$ .

### Problem

3. A molecule drops from the  $j = 2$  to the  $j = 1$  rotational level, emitting a 2.50-meV photon. If the molecule then drops to the rotational ground state, what energy photon will be emitted?

### Solution

The energy of a photon emitted in a transition between rotational levels with  $\Delta j = -1$  is shown in Example 42-1 to be  $\Delta E_{j \rightarrow (j-1)} = j^2 I$ . Using the given data for the first transition,  $j = 2$  to  $j = 1$ , we find  $2^2 I = 2.50 \times 10^{-3} \text{ eV} = 1.25 \times 10^{-3} \text{ eV}$ . This is also equal to the energy of a photon in the  $j = 1$  to  $j = 0$  transition.

### Problem

4. Calculate the wavelength of a photon emitted in the  $j = 5$  to  $j = 4$  transition of a molecule whose rotational inertia is  $1.75 \times 10^{-47} \text{ kg} \cdot \text{m}^2$ .

### Solution

The energy difference between adjacent rotational levels is proportional to the upper  $j$ -value (see Example 42-1 and the solution to Problem 6 below), so  $\lambda = hc/\Delta E = 2pcI/j = 2p(3 \times 10^8 \text{ m/s})(1.75 \times 10^{-47} \text{ kg} \cdot \text{m}^2)/(5(1.055 \times 10^{-34} \text{ J} \cdot \text{s})) = 62.5 \text{ nm}$ .

### Problem

5. Photons of wavelength 1.68 cm excite transitions from the rotational ground state to the first rotational excited state in a gas. What is the rotational inertia of the gas molecules?

### Solution

The energy of the absorbed photon equals the difference in energy between the  $j = 1$  and  $j = 0$  rotational levels, which is (see Example 42-1)  $2I = \Delta E_{1 \rightarrow 0} = hc/\lambda = 1240 \text{ eV} \cdot \text{nm}/1.68 \text{ cm} = 7.38 \times 10^{-5} \text{ eV} = 1.18 \times 10^{-23} \text{ J}$ . Therefore,  $I = (1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2/(1.18 \times 10^{-23} \text{ J}) = 9.41 \times 10^{-46} \text{ kg} \cdot \text{m}^2$ .

**Problem**

6. A molecule absorbs a photon and jumps to the next higher rotational state. If the photon energy is three times what would be needed for a transition from the rotational ground state to the first rotational excited state, between what two levels is the transition?

**Solution**

From Equation 42-2, the photon energy in a  $\Delta j = 1$  transition is  $\Delta E_{j \rightarrow (j+1)} = [(j+1)(j+2) - j(j+1)] \hbar^2 = 2I = (j+1)^2 \hbar^2$ . Given that  $\Delta E_{j \rightarrow (j+1)} = 3 \Delta E_{0 \rightarrow 1}$ , we have  $(j+1)^2 \hbar^2 = 3 \hbar^2$ , or  $j = 2$ . The  $j$ -levels of the transition were  $2 \rightarrow 3$ .

**Problem**

7. Find an expression for the energy of a photon required for a transition from the  $(j-1)$ th level to the  $j$ th level in a molecule with rotational inertia  $I$ .

**Solution**

This energy difference is calculated in Example 42-1. The energy difference between two adjacent rotational levels is proportional to the upper  $j$ -value.

**Problem**

8. A molecule of rotational inertia  $I$  undergoes a transition from the  $j$ th rotational level to the  $(j-1)$ th level. Show that the wavelength of the emitted photon is  $\lambda = 4\pi^2 I c / \hbar j$ .

**Solution**

From the previous problem,  $\Delta E_{j,j-1} = j^2 \hbar^2$ , so  $\lambda = hc / \Delta E_{j,j-1} = 2\pi^2 I c / \hbar j$ . (See also Problem 4.)

**Problem**

9. The rotational spectrum of diatomic oxygen ( $O_2$ ) shows spectral lines spaced 0.356 meV apart in energy. Find the atomic separation in this molecule. *Hint:* See Example 42-1, but remember that the oxygen atoms have equal mass.

**Solution**

The separation of the rotational spectral lines in energy is  $\Delta(\Delta E) = \hbar^2$  (see Example 42-1), or  $\hbar^2 = 0.356$  meV for  $O_2$ . In a diatomic molecule, with equal-mass atoms and atomic separation  $R$ , each atom rotates about the center of mass at a distance of  $R/2$ , so  $I = 2(m_O)(R/2)^2 = (m_O)R^2$ , where the mass of an oxygen atom is about  $m_O = 16$  u. Then  $R^2 = I/m_O = (0.356 \text{ meV}) / (8 \text{ u})$ , or  $R = \sqrt{(0.356 \text{ meV}) / (8 \text{ u})} = \sqrt{(0.356 \times 10^{-3} \text{ eV}) / (8 \times 1.66 \times 10^{-27} \text{ kg})} = 1.13 \text{ \AA}$ .

**Problem**

10. Use the result given in Problem 52 to find the bond length in carbon monoxide (CO), using the fact that excitation of the first rotational state requires photons of wavelength 2.59 mm.

**Solution**

The energy of the first excited rotational state ( $j = 1$ ) of the CO molecule is  $\hbar^2 = \Delta E_{0 \rightarrow 1} = hc / \lambda$  (see Equation 42-2 and Example 42-1). Thus,  $I = \hbar^2 / 2\pi^2 c = (1.054 \times 10^{-34} \text{ J} \cdot \text{s})^2 / (2\pi^2)(3 \times 10^8 \text{ m/s}) = 1.45 \times 10^{-46} \text{ kg} \cdot \text{m}^2$ . From the result of Problem 52, with  $m_C = 12$  u and  $m_O = 16$  u,  $I = (m_C m_O / (m_C + m_O)) R^2 = (12 \times 16 / (12 + 16)) R^2 = (48/28) R^2$ ; thus  $R = \sqrt{(1.45 \times 10^{-46} \text{ kg} \cdot \text{m}^2) \times (28/48)} = 1.13 \text{ \AA}$  (most chemists still prefer angstrom units).

**Problem**

11. For the HCl molecule of Example 42-2, determine (a) the energy of the vibrational ground state and (b) the energy of a photon emitted in a transition between adjacent vibrational levels. Assume the rotational quantum number does not change.

**Solution**

(a) The vibrational ground-state energy is  $\frac{1}{2} \hbar \omega = \frac{1}{2} h f = \frac{1}{2} (4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(8.66 \times 10^{13} \text{ Hz}) = 0.179 \text{ eV}$  (see Equation 42-3 with  $n = 0$ ). (b) The photon energy for allowed transitions ( $\Delta n = 1$ ) is  $\hbar \omega$ , which is twice the zero point energy, or 0.358 eV.

**Problem**

12. The classical vibration frequency for diatomic hydrogen ( $\text{H}_2$ ) is  $1.32 \times 10^{14} \text{ Hz}$ . What is the spacing between its vibrational energy levels?

**Solution**

The spacing between adjacent vibrational energy levels is  $\hbar \omega = h f = (4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(1.32 \times 10^{14} \text{ Hz}) = 0.546 \text{ eV}$ .

**Problem**

13. The energy between adjacent vibrational levels in diatomic nitrogen is 0.293 eV. What is the classical vibration frequency of this molecule?

**Solution**

From  $\Delta E_{\text{vib}} = \hbar \omega = h f$ , for adjacent levels, we find  $f = 0.293 \text{ eV} / 4.136 \times 10^{-15} \text{ eV} \cdot \text{s} = 7.08 \times 10^{13} \text{ Hz}$  for the  $\text{N}_2$ -molecule.

**Problem**

14. Diatomic deuterium ( $\text{D}_2$ ) has classical vibration frequency  $9.35 \times 10^{13} \text{ Hz}$  and rotational inertia  $9.17 \times 10^{-48} \text{ kg} \cdot \text{m}^2$ . Find (a) the energy and (b) the wavelength of a photon emitted in a transition between the  $n = 1, j = 1$  state and the  $n = 0, j = 2$  state.

**Solution**

(a) The transition energy (Equations 42-2 and 3) is  $\Delta E_{\text{vib}} + \Delta E_{\text{rot}} = \hbar \omega (1 + \frac{1}{2} - \frac{1}{2}) + (\frac{\hbar^2}{2I})(1 \times 2 - 2 \times 3) = h f - 2 \frac{\hbar^2}{2I} = (4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(9.35 \times 10^{13} \text{ Hz}) - 2(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2 / (9.17 \times 10^{-48} \text{ kg} \cdot \text{m}^2)(1.602 \times 10^{-19} \text{ J/eV}) = 0.387 \text{ eV} - 0.0152 \text{ eV} = 0.372 \text{ eV}$ . (b) The corresponding photon wavelength is  $\lambda = hc / \Delta E = 1.240 \text{ eV} \cdot \text{nm} / 0.372 \text{ eV} = 3.34 \text{ nm}$ .

**Problem**

15. An oxygen molecule is in its vibrational and rotational ground states. It absorbs a photon of energy 0.19653 eV and jumps to the  $n = 1, j = 1$  state. It then drops to the  $n = 0, j = 2$  level, emitting a 0.19546-eV photon. Find (a) the classical vibration frequency and (b) the rotational inertia of the molecule.

**Solution**

For the  $n = 0, j = 0$  to  $n = 1, j = 1$  transition, the energy difference is  $0.19653 \text{ eV} = \Delta E_{\text{vib}} + \Delta E_{\text{rot}} = h f + (\frac{\hbar^2}{2I})$ , and for the  $n = 1, j = 1$  to  $n = 0, j = 2$  transition,  $0.19546 \text{ eV} = h f - 2(\frac{\hbar^2}{2I})$  (see Equations 42-2 and 3). We can solve these

equations simultaneously for  $hf$  and  $\hbar^2 = I$  to find  $f$  and  $I$ . (a)  $2(0.19653 \text{ eV}) + (0.19546 \text{ eV}) = 3hf$ , or  $f = 4.74 \times 10^{13} \text{ Hz}$ .  
 (b)  $(0.19653 - 0.19546) \text{ eV} = 3(\hbar^2 = I)$ , or  $I = 1.95 \times 10^{-46} \text{ kg} \cdot \text{m}^2$ .

### Section 42-3: Solids

#### Problem

16. Use the  $2.16 \text{ g/cm}^3$  density of NaCl to calculate the ionic spacing  $r_0$  in the NaCl crystal. *Hint:* Consult Appendix D for atomic weights.

#### Solution

The atomic weights of Na and Cl are 22.99 and 35.45, so the average masses of these ions are  $22.99 \text{ g} = 6.022 \times 10^{23} = 3.82 \times 10^{-23} \text{ g}$  and  $35.45 \text{ g} = 5.89 \times 10^{-23} \text{ g}$ , respectively. If each ion occupies the same cubic volume  $r_0^3$ , then the density of the crystal is  $(3.82 + 5.89) \times 10^{-23} \text{ g} = 2r_0^3 = 2.16 \text{ g/cm}^3$ . Therefore, the ionic separation is  $r_0 = [(9.70 \times 10^{-23} \text{ g} \div (2 \times 2.16 \text{ g/cm}^3))]^{1/3} = 2.82 \times 10^{-8} \text{ cm} = 2.82 \text{ \AA}$ . (Actually, the ionic radii of Na and Cl are different, but each cubic cell of NaCl crystal contains half Na and half Cl atoms, so the above estimate is the same, that is,  $r_{\text{NaCl}} = \frac{1}{2}(m_{\text{Na}} + m_{\text{Cl}})r_0^3$ .)

#### Problem

17. Express the 7.84-eV ionic cohesive energy of NaCl in kilocalories per mole of ions.

#### Solution

Using conversion factors from Appendix C, we find:  $(7.84 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV})(1 \text{ kcal} = 4184 \text{ J})(6.022 \times 10^{23} / \text{mol}) = 181 \text{ kcal/mol}$ .

#### Problem

18. Lithium fluoride, LiF, has the same crystal structure as NaCl and therefore essentially the same Madelung constant  $a$ . Its ionic cohesive energy is  $-10.5 \text{ eV}$ , and the value of  $n$  in Equation 42-4 is 6.25. What is the equilibrium ionic separation in LiF?

#### Solution

From the definition of the ionic cohesive energy and the potential energy function in Equation 42-4 with the given data,  $r_0 = -(a ke^2 = U_0)(1 - 1/n) = (1.748)(1.44 \text{ eV} \cdot \text{nm} = 10.5 \text{ eV})(1 - 1/6.25) = 0.201 \text{ nm}$ . (See the next solution for  $ke^2$  in atomic units.)

#### Problem

19. Determine the constant  $n$  in Equation 42-4 for potassium chloride (KCl), for which  $r_0 = 0.315 \text{ nm}$  and  $U_0 = -7.21 \text{ eV}$ . The crystal structure is the same as for NaCl.

#### Solution

As shown in Example 42-3,  $n = (1 + U_0 r_0 = a ke^2)^{-1}$ . Since the crystal structures of KCl and NaCl are the same,  $a = 1.748$ . Therefore:

$$n = \frac{1}{1 + \frac{(-7.21 \text{ eV})(0.315 \text{ nm})}{(1.748)(1.44 \text{ eV} \cdot \text{nm})}} = 10.2,$$

where we used a convenient value of  $ke^2$  in atomic units:

$$ke^2 = (9 \times 10^9 \text{ N} \cdot \text{m}^2 = \text{C}^2)(1.6 \times 10^{-19} \text{ C})^2 (1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}) = 1.44 \text{ eV} \cdot \text{nm}.$$

**Problem**

20. A salt crystal contains  $10^{21}$  sodium-chlorine pairs. How much energy would it take to compress the crystal to 90% of its normal size?

**Solution**

The energy per ion pair would increase, under compression, to  $U(0.9r_0) = (-ake^2/r_0)(0.9^{-1} - 0.9^{-n})$  from its normal value of  $U_0 = -7.84$  eV, where  $n = 8.22$  for NaCl. Thus, the constant  $(ake^2/r_0)$  equals  $(7.84 \text{ eV})(1 - 8.22^{-1}) = 8.93$  eV, and the extra energy for compressing  $10^{21}$  ion pairs is  $10^{21}(U(0.9r_0) - U_0) = 10^{21}[(-8.93 \text{ eV})(0.9^{-1} - 0.9^{-8.22}) + 7.84 \text{ eV}] = 5.01 \times 10^{20} \text{ eV} = 80.2 \text{ J}$ . (Use of the numerical value of  $r_0$  quoted in Example 42-3 gives  $\Delta U = 5.04 \times 10^{20} \text{ eV} = 80.7 \text{ J}$ .)

**Problem**

21. (a) Differentiate Equation 42-4 to obtain an expression for the force on an ion in an ionic crystal. (b) Use your result to find the force on an ion in NaCl if the crystal could be compressed to half its equilibrium spacing (see Example 42-3 for relevant parameters). Compare with the electrostatic attraction between the ions at a separation of  $\frac{1}{2} r_0$ . Your result shows how very “stiff” this ionic crystal is.

**Solution**

(a) The force in the  $r$  direction (positive is repulsive) is:

$$F_r = -\frac{dU}{dr} = a \frac{ke^2}{r_0} \frac{d}{dr} \left[ \frac{1}{r} - \frac{1}{n} \left( \frac{r_0}{r} \right)^n \right] = a \frac{ke^2}{r_0} \left[ -\frac{1}{r^2} + \frac{n}{n} \left( \frac{r_0}{r} \right)^{n-1} \frac{r_0}{r^2} \right] = a \frac{ke^2}{r_0^2} \left[ -\frac{1}{r^2} + \left( \frac{r_0}{r} \right)^{n-1} \right]$$

(b) If  $r = \frac{1}{2} r_0$ ,  $F_r = (ake^2/r_0^2)(2^{n+1} - 2^2) = a(2^{n-1} - 1)F_{el}$ , where  $F_{el} = 4ke^2/r_0^2$  is the magnitude of the electrostatic attraction between a  $\text{Na}^+$  and  $\text{Cl}^-$  ion at a distance of  $\frac{1}{2} r_0$ . If we use values from Example 42-3 ( $a = 1.748$ ,  $r_0 = 0.282$  nm, and  $n = 8.22$ ), the repulsive force is  $(1.748)(2^{7.22} - 1) = 259$  times the electrostatic attractive force. Since  $F_{el} = 4(9 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2)(1.6 \times 10^{-19} \text{ C})^2/(0.282 \text{ nm})^2 = 1.16 \times 10^{-8} \text{ N}$ ,  $F_r = 259(1.16 \times 10^{-8} \text{ N}) = 3.00 \times 10^{-6} \text{ N}$ .

**Problem**

22. The Fermi energy in aluminum is 11.6 eV. What is the density of conduction electrons in aluminum?

**Solution**

A relation between the electron number density and the Fermi energy is derived in Example 42-4. For aluminum, we get:

$$n_e = \frac{8\pi^{3/2} p m^{3/2} E_F^{3/2}}{3h^3} = 8.61 \times 10^{28} \text{ m}^{-3} \left( \frac{11.6}{7.13} \right)^{3/2} = 1.79 \times 10^{29} \text{ m}^{-3}.$$

(Since the nature of the metal enters into  $E_F$  only, we could appropriately modify the numerical result in Example 42-4 by multiplying by the  $\frac{3}{2}$ -power of the ratio of the Fermi energies of Al and Mg.)

An alternative calculation in atomic units yields:

$$n_e = \frac{2^{9/2} p (mc^2 E_F)^{3/2}}{3(hc)^3} = \frac{2^{9/2} p (0.511 \text{ MeV})^{3/2} (11.6 \text{ eV})^{3/2}}{3(1240 \text{ eV} \cdot \text{nm})^3} = 179 \text{ nm}^{-3}.$$

**Problem**

23. Determine the Fermi energy for calcium, which has  $4.60 \times 10^{28}$  conduction electrons per cubic meter.

**Solution**

The equation for  $n$  in Example 42-4 can be solved for the Fermi energy. With the aid of constants expressed in atomic units, the result for Ca is:

$$E_F = \frac{(hc)^2}{8mc^2} \left( \frac{3n}{\pi} \right)^{2/3} = \frac{(1240 \text{ eV} \cdot \text{nm})^2}{8(0.511 \text{ MeV})} \left( \frac{3 \times 4.60 \times 10^{28} \text{ m}^{-3}}{\pi} \right)^{2/3} = 4.68 \text{ eV}.$$

**Problem**

24. Metal A has twice the Fermi energy of metal B. How do their conduction electron densities compare?

**Solution**

Example 42-4 shows that  $n \propto E_F^{3/2}$ ; hence  $(n_A/n_B) = (E_{FA}/E_{FB})^{3/2} = 2^{3/2} = 2.83$ .

**Problem**

25. Suppose the charge carriers in a material were protons, with density  $10^{28} \text{ m}^{-3}$ —comparable to that of electrons in a metal. What would be the order of magnitude of the Fermi energy?

**Solution**

Since the Fermi energy is proportional to the reciprocal of the charge carrier's mass (see solution to Problem 23), we expect the magnitude for protons to be  $\approx 1836$  times the Fermi energy for electrons (with comparable density), or about three orders of magnitude smaller (i.e.,  $\approx \text{meV}$ ). In fact, if one uses  $n = 10^{28} \text{ m}^{-3}$  and  $mc^2 = 938 \text{ MeV}$  (for protons) in the expression for  $E_F$  in Example 42-4, one finds  $E_F = (3n/\pi)^{2/3} (hc)^2 / (8mc^2) = (3 \times 10^{28} \text{ m}^{-3})^{2/3} (1.24 \times 10^{-6} \text{ eV} \cdot \text{m})^2 / 8(938 \times 10^6 \text{ eV}) = 9.22 \times 10^{-4} \text{ eV} \approx 1 \text{ meV}$ .

**Problem**

26. The Fermi energy for copper is 7.0 eV. Compare the electron speed associated with this energy with the classical thermal speed for an electron at room temperature (300 K). Your result shows how the quantum and classical descriptions of metallic conduction differ.

**Solution**

Classically, the average thermal energy at 300 K is  $\frac{3}{2} k_B T = \frac{3}{2} (8.617 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1})(300 \text{ K}) = 0.0388 \text{ eV}$ , much smaller than the Fermi energy for Cu, 7.0 eV. The classical thermal speed,  $v_{\text{th}} = c \sqrt{2E_{\text{th}}/mc^2} = (3 \times 10^8 \text{ m/s}) \sqrt{2(0.0388 \text{ eV})/(511 \text{ keV})} = 1.17 \times 10^5 \text{ m/s}$ , is about  $\sqrt{E_F/E_{\text{th}}} = 13.4$  times smaller than the Fermi speed,  $v_F = 1.57 \times 10^6 \text{ m/s}$ .

**Problem**

27. The *Fermi temperature* is defined by equating the thermal energy  $kT$  to the Fermi energy, where  $k$  is Boltzmann's constant. Calculate the Fermi temperature for silver ( $E_F = 5.48 \text{ eV}$ ), and compare with room temperature.

**Solution**

$T_F = E_F/k_B = 5.48 \text{ eV} / (8.617 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}) = 6.36 \times 10^4 \text{ K}$ , about 212 times room temperature (300 K).

**Problem**

28. What is the wavelength of light emitted by a gallium phosphide (GaP) light-emitting diode? *Hint:* See Table 42-1.

**Solution**

A photon of energy corresponding to the band gap would have a wavelength of  $\lambda = hc/E = 1240 \text{ eV} \cdot \text{nm} / 2.26 \text{ eV} = 548.7 \text{ nm}$ , which is green in color. (The mercury green line has wavelength 546.0 nm, for comparison.)

**Problem**

29. What is the shortest wavelength of light that could be produced by electrons jumping the band gap in a material from Table 42-1? What is the material?

**Solution**

The wavelength emitted depends on the energy gap, since  $\lambda = hc/E_{\text{gap}}$ . The maximum wavelength for the materials in Table 42-1 (corresponding to the smallest gap) is for InAs,  $\lambda = 1240 \text{ eV} \cdot \text{nm} / 0.35 \text{ eV} = 3.54 \text{ } \mu\text{m}$  (in the infrared). The minimum is for ZnS,  $\lambda = 1240 \text{ eV} \cdot \text{nm} / 3.6 \text{ eV} = 344 \text{ nm}$  (in the ultraviolet).

**Problem**

30. Which material in Table 42-1 would provide the longest wavelength of light in a light-emitting diode? What is the wavelength?

**Solution**

See previous solution.

**Problem**

31. A common light-emitting diode is made from a combination of gallium, arsenic, and phosphorous (GaAsP) and emits red light at 650 nm. What is its band gap?

**Solution**

The band gap corresponding to this wavelength is  $E_{\text{gap}} = hc/\lambda = 1240 \text{ eV} \cdot \text{nm} / 650 \text{ nm} = 1.91 \text{ eV}$ .

**Problem**

32. Photons with energy less than a semiconductor's band gap are not readily absorbed by the material, so measurement of light absorption versus wavelength gives the band gap. An absorption spectrum for silicon shows no absorption for wavelengths greater than 1090 nm. Use this information to calculate the band gap in silicon, and verify its entry in Table 42-1.

**Solution**

As stated in the problem, the band gap corresponds to the energy of a photon of wavelength 1090 nm, hence  $E_{\text{gap}} = hc/\lambda = 1240 \text{ eV} \cdot \text{nm} / 1090 \text{ nm} = 1.14 \text{ eV}$ . This agrees with the entry in Table 42-1 for Si.

**Problem**

33. The Sun radiates most strongly at about 500 nm, the peak of its Planck curve. The semiconductor zinc sulfide has a band gap of 3.6 eV. (a) What is the maximum wavelength absorbed by ZnS? (b) Would ZnS make a good photovoltaic cell? Why or why not?

**Solution**

(a) The photon wavelength corresponding to the band gap in ZnS is 344 nm (see solution to Problem 29), so photons with greater wavelengths (less energy) would not be readily absorbed (see statement of Problem 32). (b) ZnS would be a poor photovoltaic material since most of the energy in the solar spectrum is near the peak wavelength at 500 nm, and would not be absorbed.

**Problem**

34. Light-emitting diodes are available commercially with output wavelengths in the range from about 550 nm to 1300 nm. What is the corresponding range of band-gap energies?

**Solution**

The band gaps correspond to the photon energies produced in the LED's. The range is  $hc/\lambda = 1240 \text{ eV} \cdot \text{nm}/\lambda$ . For  $\lambda = 1300 \text{ nm}$ ,  $E = 0.954 \text{ eV}$ . For  $\lambda = 550 \text{ nm}$ ,  $E = 2.25 \text{ eV}$ .

**Problem**

35. A blue-green semiconductor laser being developed for long-playing compact discs emits at 447 nm (see Application: From CD to DVD, in Chapter 37). What is the band gap in this laser?

**Solution**

The band gap corresponding to photons of the given wavelength is  $E_{\text{gap}} = hc/\lambda = 1240 \text{ eV} \cdot \text{nm}/447 \text{ nm} = 2.77 \text{ eV}$ .

**Section 42-4: Superconductivity****Problem**

36. Pure aluminum, which superconducts below 1.20 K, exhibits a critical field of 9.57 mT. What is the maximum current that can be carried in a 30-gauge (0.255 mm diameter) aluminum superconducting wire without the field from that current exceeding the critical field? *Hint:* Where is the field greatest? Consult Example 30-4.

**Solution**

The maximum magnetic field is at the wire's surface,  $B_{\text{max}} = \mu_0 I/2\pi R$ , which is less than the critical field if  $I \leq (0.255 \text{ mm})(9.57 \text{ mT})(4 \times 10^{-7} \text{ T} \cdot \text{m/A}) = 6.10 \text{ A}$ .

**Problem**

37. The critical magnetic field in niobium-titanium superconductor is 15 T. What current is required in a 5000-turn solenoid 75 cm long to produce a field of this strength?

**Solution**

The magnetic field inside a long thin solenoid is  $B = \mu_0 n I$  (see Equation 30-11), so  $I = 15 \text{ T}/(5000/0.75 \text{ m}) \times (4\pi \times 10^{-7} \text{ T} \cdot \text{m/A}) = 1.79 \text{ kA}$ .

**Problem**

38. A danger in superconducting magnet systems is "quenching"—a sudden loss of superconductivity associated with rapid resistive heating and loss of coolant. If the solenoid of the preceding example has a diameter of 5.0 cm, (a) how much magnetic energy will be released if it quenches? (b) What volume of liquid helium could be vaporized? The heat of vaporization is 2.6 kJ per liter of liquid helium.

**Solution**

(a) If approximately all the magnetic energy stored in the solenoid of Problem 37 is quenched, the amount is  $U = u_B \frac{1}{4} \pi D^2 L = (B^2/2\mu_0)(\frac{1}{4} \pi D^2 L) = (15 \text{ T})^2 (5 \text{ cm})^2 (0.75 \text{ m}) / (4 \times 10^{-7} \text{ T} \cdot \text{m/A}) = 132 \text{ kJ}$ . ( $U = \frac{1}{2} LI^2$  gives the same result.) (b) If this amount of energy were supplied to liquid helium at its normal boiling point,  $132 \text{ kJ}/(2.6 \text{ kJ/L}) = 50.7 \text{ L}$  would be vaporized.

## Paired Problems

### Problem

39. The atomic spacing in diatomic hydrogen ( $H_2$ ) is 74 pm. Find the energy of a photon emitted in a transition from the first rotational excited state to the ground state.

### Solution

The rotational inertia of an  $H_2$ -molecule is  $I = 2m_H(R/2)^2 = \frac{1}{2}m_H R^2$ , since both atoms rotate about the center-of-mass, a distance  $R/2$  from each atom, where  $R$  is the interatomic spacing (see Problems 9 and 52). The energy of the first rotational state  $j = 1$  (above the ground state  $j = 0$  and  $E_0 = 0$ ) is  $\Delta E_{1,0} = j(j+1) \frac{2I}{\hbar^2} = 2 \frac{2I}{\hbar^2} = 2 \frac{m_H R^2}{\hbar^2} = 2(197.3 \text{ eV} \cdot \text{nm} = 74 \text{ pm})^2 = (938 \text{ MeV}) = 15.2 \text{ meV}$ , which equals the photon energy released in this transition. (We took the mass of a hydrogen atom approximately equal to a proton's mass.)

### Problem

40. Find the wavelength of electromagnetic radiation needed to excite a transition from the rotational ground state to the first rotational excited state in  $N_2$ , whose atomic spacing is 109 pm.

### Solution

The mass of a nitrogen atom is about 14 u, so the reasoning in the preceding solution gives  $\Delta E_{1,0} = 2(197.3 \cdot 0.109)^2 \text{ eV} = (14 \times 931.5 \times 10^6) = 0.502 \text{ meV}$ , corresponding to a photon wavelength of  $\lambda = hc/\Delta E_{1,0} = 2.47 \text{ mm}$ .

### Problem

41. What wavelength of infrared radiation is needed to excite a transition between the  $n = 0, j = 3$  state and the  $n = 1, j = 2$  state in KCl, for which the rotational inertia is  $2.43 \times 10^{-45} \text{ kg} \cdot \text{m}^2$  and the classical vibration frequency is  $8.40 \times 10^{12} \text{ Hz}$ ?

### Solution

The difference in energy between these vibrational-rotational levels is  $\Delta E = \Delta E_{\text{vib}} + \Delta E_{\text{rot}} = hf - 3 \frac{2I}{\hbar^2} = (4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(8.40 \times 10^{12} \text{ Hz}) - 3(6.582 \times 10^{-16} \text{ eV} \cdot \text{s})^2(1.602 \times 10^{-19} \text{ J/eV})/(2.43 \times 10^{-45} \text{ J} \cdot \text{s}^2) = 34.7 \text{ meV}$ , corresponding to a photon wavelength of  $\lambda = hc/\Delta E = 35.8 \text{ nm}$ . (See Example 42-2 for  $\Delta E_{\text{rot}}$  between the  $j = 2$  and  $j = 3$  levels, and Equation 42-3 for  $\Delta E_{\text{vib}}$  between the  $n = 1$  and  $n = 0$  levels. Note that  $\Delta n = -\Delta j$  in this transition.)

### Problem

42. Find the wavelengths emitted in all possible allowed transitions between the first three rotational states in the  $n = 1$  level to any states in the  $n = 0$  level in diatomic hydrogen. The rotational inertia of the hydrogen molecule is  $4.60 \times 10^{-48} \text{ kg} \cdot \text{m}^2$ , and its classical vibration frequency is  $3.69 \times 10^{14} \text{ Hz}$ .

### Solution

The vibrational-rotational energy levels are  $E_{nj} = (n + \frac{1}{2})hf + j(j+1) \frac{2I}{\hbar^2}$ , and the allowed transitions ( $\Delta n = \pm 1$  and  $\Delta j = \pm 1$ ) from the first three rotational levels with  $n = 1$ , to  $n = 0$  levels, are  $(1, 2) \rightarrow (0, 3)$ ,  $(1, 1) \rightarrow (0, 2)$ ,  $(1, 0) \rightarrow (0, 1)$ ,  $(1, 1) \rightarrow (0, 0)$ , and  $(1, 2) \rightarrow (0, 1)$ . The energy differences for these transitions are  $hf - 3 \frac{2I}{\hbar^2}$ ,  $hf - 2 \frac{2I}{\hbar^2}$ ,  $hf - \frac{2I}{\hbar^2}$ ,  $hf + \frac{2I}{\hbar^2}$ , and  $hf + 2 \frac{2I}{\hbar^2}$ , respectively. (Note that these energies are equally spaced,  $\Delta(\Delta E) = \frac{2I}{\hbar^2}$ , except that in the center of the spectrum the spacing is  $2 \frac{2I}{\hbar^2}$ , because  $\Delta E = hf$  is not allowed; see

Fig 42-12.) From the given data for the H<sub>2</sub>-molecule,  $hf = (4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.69 \times 10^{14} \text{ Hz}) = 1.53 \text{ eV}$  and  $I = (6.582 \times 10^{-16} \text{ eV} \cdot \text{s})^2(1.602 \times 10^{-19} \text{ J/eV})(4.60 \times 10^{-48} \text{ kg} \cdot \text{m}^2) = 15.1 \text{ meV}$ , so the transition energies are 1.48 eV, 1.50 eV, 1.51 eV, 1.54 eV, and 1.56 eV, corresponding to wavelengths of 837 nm, 829 nm, 821 nm, 805 nm, and 797 nm, respectively.

**Problem**

43. Lithium chloride, LiCl, has the same structure and therefore the same Madelung constant as NaCl. The equilibrium separation in LiCl is 0.257 nm, and  $n = 7$  in Equation 42-4. Find the ionic cohesive energy of the LiCl crystal.

**Solution**

As calculated in Example 42-3, the ionic cohesive energy for LiCl is  $U_0 = -(ake^2/r_0)(1 - 1/n) = -(1.748)(1.44 \text{ eV} \cdot \text{nm} / 0.257 \text{ nm})(1 - 1/7) = -8.40 \text{ eV}$ .

**Problem**

44 Find the energy per unit cell needed to decrease the ionic separation in NaCl by 15%.

**Solution**

This problem asks for essentially the same calculation as done in the solution to Problem 20. Here, we need  $U(0.85r_0) - U_0 = (-8.93 \text{ eV})(0.85^{-1} - 0.85^{-8.22}) - (-7.84 \text{ eV}) = 1.47 \text{ eV}$ , which is the energy per ion pair needed for a 15% compression.

**Supplementary Problems**

**Problem**

45. What would be the Fermi energy in a one-dimensional infinite square well 10 nm wide and holding 100 electrons? Assume two electrons (with opposite spins) per energy level.

**Solution**

With two electrons of opposite spin in each level (which is non-degenerate for the one-dimensional infinite square well), the highest filled level for 100 electrons is  $n = 50$ . Thus, the Fermi energy is  $E_F = n^2 (hc/L)^2 / 8mc^2 = (50 \times 1240 \text{ eV} \cdot \text{nm} / 10 \text{ nm})^2 / 8(511 \text{ keV}) = 9.40 \text{ eV}$  (see Equation 40-6).

**Problem**

46. Find the fraction of conduction electrons in a metal at absolute zero that have energies less than half the Fermi energy.

**Solution**

The number of electrons with  $E \leq \frac{1}{2} E_F$ , at  $T = 0$  kelvin, is

$$n \int_0^{\frac{1}{2} E_F} g(E) dE = \frac{2^{9/2} \pi m^{3/2} E_F^{3/2}}{3h^3} \int_0^{\frac{1}{2} E_F} E^{1/2} dE = \frac{1}{2} n(E \leq E_F),$$

where the integral is done in Example 42-4, and  $n(E \leq E_F)$  is the density of conduction electrons. Thus, the fraction is  $2^{-3/2} =$

**Problem**

Figure 21-23 shows that diatomic hydrogen acts like a monatomic gas at temperatures below about 100 K. Use the fact that the rotational inertia of H<sub>2</sub> is  $4.6 \times 10^{-48} \text{ kg} \cdot \text{m}^2$  to show that this low-temperature behavior makes sense. *Hint:* Compare the thermal energy  $kT$  with the minimum energy needed to excite molecular rotation.

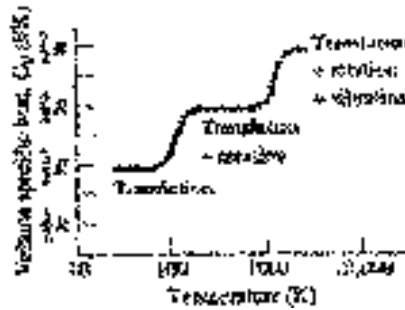


FIGURE 21-23 For reference.

**Solution**

The minimum energy needed to excite the first non-zero rotational level ( $\Delta E$  for  $j = 0$  to  $j = 1$ ) in the  $H_2$ -molecule is  $^2=I = (6.582 \times 10^{-16} \text{ eV} \cdot \text{s})(1.055 \times 10^{-34} \text{ J} \cdot \text{s})(4.6 \times 10^{-48} \text{ kg} \cdot \text{m}^2) = 15.1 \text{ meV}$ . A typical thermal energy at a temperature of 100 K is  $k_B T = (8.617 \times 10^{-5} \text{ eV/K})(100 \text{ K}) = 8.62 \text{ meV}$ , which is enough smaller than 15.1 meV so that one would not expect any rotational levels to be occupied. Thus, the specific heat of  $H_2$  (and all gases which don't first liquify) should approach the monatomic value at sufficiently low temperatures, as shown in Fig. 21-23.

**Problem**

48. Repeat the preceding problem, now considering vibrational energy levels. The classical vibration frequency for  $H_2$  is about  $4.4 \times 10^{13} \text{ Hz}$ , and Fig. 21-23 shows that vibrational effects on the specific heat become important at about 2000 K.

**Solution**

The excitation energy for the first non-zero vibrational state in the  $H_2$ -molecule is  $hf = (4.136 \times 10^{-15} \text{ eV} \cdot \text{s}) \times (4.4 \times 10^{13} \text{ Hz}) = 0.182 \text{ eV}$ , whereas the average thermal energy (for a classical vibrational state) is nearly equal to this at  $T = 2000 \text{ K}$  ( $k_B T = (8.617 \times 10^{-5} \text{ eV/K}) \times 2000 \text{ K} = 0.172 \text{ eV}$ ). Thus, thermal excitation of molecular vibrational states in  $H_2$  should affect the specific heat above about 2000 K (provided the molecule doesn't first dissociate), as shown in Fig. 21-23.

**Problem**

49. The transition from the ground state to the first rotational excited state in diatomic oxygen ( $O_2$ ) requires about 356 meV. At what temperature would the thermal energy  $kT$  be sufficient to set diatomic oxygen into rotation? Would you ever find diatomic oxygen exhibiting the specific heat of a monatomic gas at normal pressure?

**Solution**

With reference to the solution of Problem 47,  $O_2$  would behave like a monatomic gas if there were insufficient thermal energy to excite rotational states. This implies that  $k_B T < 356 \text{ meV}$ , or  $T < 356 \text{ meV} / (86.17 \text{ meV/K}) = 4.1 \text{ K}$ . Such behavior is not observed, however, since the normal boiling point of oxygen (below which  $O_2$  liquifies) is 90.2 K (see Table 20-1).

**Problem**

50. The density of rubidium iodide (RbI) is  $3.55 \text{ g/cm}^3$ , and its ionic cohesive energy is  $-145 \text{ kcal/mol}$ . Determine (a) the equilibrium separation and (b) the exponent  $n$  in Equation 42-2 for RbI.

**Solution**

(a) The equilibrium ionic separation,  $r_0$ , can be estimated from the density,  $\rho$ , as in the solution to Problem 16. If we assume that the crystal structure of RbI is cubic, like NaCl in Example 42-3, then each cubic volume,  $r_0^3$ , contains one ion of average mass  $\frac{1}{2}(m_{Rb} + m_I)$ . Thus,  $r_0 = [(m_{Rb} + m_I)/2\rho]^{1/3} = [(85.47 \text{ g} + 126.9 \text{ g})/2(6.022 \times 10^{23})(3.55 \text{ g/cm}^3)]^{1/3} = 0.368 \text{ nm}$ , where we used Appendix D for the atomic weights. (b) The ionic cohesive energy per ion pair is:  $(-145 \text{ kcal/mol})(4184 \text{ J/kcal})(1 \text{ eV}=1.602 \times 10^{-19} \text{ J})(1 \text{ mol}=6.022 \times 10^{23}) = -6.29 \text{ eV}$  (see Appendix C for the conversion factors). Equation 42-4 evaluated at  $r = r_0$ , can be solved for  $n$  (as in Example 42-3 or the solution to Problem 19) with the following result:

$$n = \frac{U_0 r_0}{a k e^2} = \frac{(-6.29 \text{ eV})(0.368 \text{ nm})}{(1.748)(1.44 \text{ eV} \cdot \text{nm})} = 12.3.$$

**Problem**

51. The HCl bond-length calculation of Example 42-1 assumed the molecule was not vibrating. But because the ground-state vibrational energy is not zero, the bond is actually stretched slightly by its vibration. To estimate this stretching (a) use the classical vibration frequency of  $8.66 \times 10^{13} \text{ Hz}$  to find the ground-state vibrational energy. (b) Use the result of part (a) and the fact that the effective “spring constant” for HCl is about  $480 \text{ N/m}$  to estimate the stretching of the molecular bond due to ground-state vibration. Assume that half the energy is potential energy of the stretched “spring.” (c) Compare your result with the bond length found in Example 42-1.

**Solution**

(a) The ground-state vibrational energy corresponding to the given frequency is  $E_0 = \frac{1}{2} h f = \frac{1}{2} (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) \times (8.66 \times 10^{13} \text{ Hz}) = 2.87 \times 10^{-20} \text{ J} = 0.179 \text{ eV}$ . (b) If half of this energy is associated with the potential energy of stretching the bond, then  $\frac{1}{2} E_0 = \frac{1}{2} k \Delta x^2$ , or  $\Delta x = \sqrt{2.87 \times 10^{-20} \text{ J}/480 \text{ N/m}} = 7.73 \times 10^{-12} \text{ m} \approx 8 \text{ pm}$ . (c) In this case,  $\Delta x$  is about 6% of the bond length found in Example 42-1, which is a small correction.

**Problem**

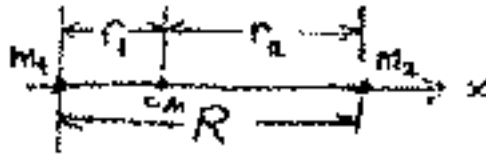
52. Consider a diatomic molecule consisting of different atoms with masses  $m_1$  and  $m_2$ , separated by a distance  $R$ . (a) Find the molecule’s center of mass. (b) Use your result to show that the rotational inertia about the center of mass is

$$I = \frac{m_1 m_2}{m_1 + m_2} R^2.$$

The quantity  $m_1 m_2 / (m_1 + m_2)$  is called the reduced mass. (c) Use this result to compute a more accurate value for the HCl bond length of Example 42-1.

**Solution**

(a) With origin at  $m_1$  and the molecule along the  $x$ -axis,  $x_{\text{CM}} = (m_1 \times 0 + m_2 \times R)/(m_1 + m_2) = m_2 R / (m_1 + m_2)$ . In part (b), it is convenient to choose the origin at the center of mass, so  $m_1$  is at a distance  $r_1 = |-m_2 R / (m_1 + m_2)|$ , and  $m_2$  is at  $r_2 = R - r_1 = m_1 R / (m_1 + m_2)$ . (b) Using the distances found in part (a), we get  $I_{\text{CM}} = m_1 r_1^2 + m_2 r_2^2 = (m_1 m_2^2 + m_2 m_1^2) R^2 / (m_1 + m_2)^2 = m_r R^2$ , where  $m_r = m_1 m_2 / (m_1 + m_2)$  is the reduced mass. (The two-body problem, for  $m_1$  and  $m_2$  is equivalent to a one-body problem, for  $m_r$  in the CM-system, plus the center of mass motion, for  $m_1 + m_2$ .) (c) For the HCl-molecule,  $m_H \approx 1 \text{ u}$  and  $m_{Cl} \approx 35.5 \text{ u}$ , so  $m_r = 0.973 \text{ u} = 1.61 \times 10^{-27} \text{ kg}$ . Using the reduced mass in the final equation of Example 42-1, one finds  $R = \sqrt{2.65 \times 10^{-47} \text{ kg} \cdot \text{m}^2 / 1.61 \times 10^{-27} \text{ kg}} = 0.128 \text{ nm}$ .



Problem 52 Solution.

**Problem**

53. The Madelung constant (Section 42-3) is notoriously difficult to calculate because it is the sum of an alternating series of nearly equal terms. But it can be calculated for a hypothetical one-dimensional crystal consisting of a line of alternating positive and negative ions, evenly spaced (Fig. 42-39). Show that the potential energy of an ion in this “crystal” can be written

$$U = -a \frac{ke^2}{r_0},$$

where the Madelung constant  $a$  has the value  $2 \ln 2$ . *Hint:* Study the series expansions listed in Appendix A.

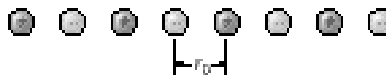


FIGURE 42-39 Problem 53.

**Solution**

For any ion in Fig. 42-39, there are two oppositely charged ions at distances of  $r_0$ , two similarly charged ions at distances of  $2r_0$ , two opposite ions at  $3r_0$ , etc. Thus, the electrostatic potential energy of any ion is

$$U = -\frac{2ke^2}{r_0} + \frac{2ke^2}{2r_0} - \frac{2ke^2}{3r_0} + \dots = -\frac{2ke^2}{r_0} \left[ \frac{1}{2} - \frac{1}{3} + \dots \right] = -a \frac{ke^2}{r_0}.$$

Comparison of this with the series expansion of  $\ln(1 + x)$  in Appendix A shows that  $a = 2 \ln 2$  for this “crystal”. (Note: The convergence of this series, which needs special consideration for  $x = 1$ , is discussed in many first-year calculus textbooks.)