

BRIDGING PROBLEM

Detecting Infrared Photons

At 80 K, the band gap in the semiconductor indium antimonide (InSb) is 0.230 eV. A photon emitted by a hydrogen fluoride (HF) molecule undergoing a vibration-rotation transition from $(n = 1, l = 0)$ to $(n = 0, l = 1)$ is absorbed by an electron at the top of the valence band of InSb. (a) How far above the top of the band gap (in eV) is the final state of the electron? (b) What is the probability that the final state was already occupied? The vibration frequency for HF is 1.24×10^{14} Hz, the mass of a hydrogen atom is 1.67×10^{-27} kg, the mass of a fluorine atom is 3.15×10^{-26} kg, and the equilibrium distance between the two nuclei is 0.092 nm. Assume that the Fermi energy for InSb is in the middle of the gap.

SOLUTION GUIDE

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IDENTIFY and SET UP

1. This problem involves what you learned about molecular transitions in Section 42.2, about the Fermi-Dirac distribution in Section 42.5, and about semiconductors in Section 42.6.
2. Equation (42.9) gives the combined vibrational-rotational energy in the initial and final molecular states. The difference between the initial and final molecular energies equals the energy E of the emitted photon, which is in turn equal to the energy gained by the InSb valence electron when it absorbs that

photon. The probability that the final state is occupied is given by the Fermi-Dirac distribution, Eq. (42.16).

EXECUTE

3. Before you can use Eq. (42.9), you'll first need to use the data given to calculate the moment of inertia I and the quantity $\hbar\omega$ for the HF molecule. (*Hint:* Be careful not to confuse frequency f and angular frequency ω .)
4. Use your results from step 3 to calculate the initial and final energies of the HF molecule. (*Hint:* Does the vibrational energy increase or decrease? What about the rotational energy?)
5. Use your result from step 4 to find the energy imparted to the InSb electron. Determine the final energy of this electron relative to the bottom of the conduction band.
6. Use your result from step 5 to determine the probability that the InSb final state is already occupied.

EVALUATE

7. Is the molecular transition of the HF molecule allowed? Which is larger: the vibrational energy change or the rotational energy change?
8. Is it likely that the excited InSb electron will be blocked from entering a state in the conduction band?

Problems

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•, ••, •••: Problems of increasing difficulty. CP: Cumulative problems incorporating material from earlier chapters. CALC: Problems requiring calculus. BIO: Biosciences problems.

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 ($l = 1, 2, 3, \dots$), 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 $1s$, $2s$, $2p$, $3s$, $3p$, and $4s$ 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. (42.22), depends strongly on temperature. Explain why.
- 42.3** • 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 (7.9×10^{-4} 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.
- 42.4** •• Light of wavelength 3.10 mm strikes and is absorbed by a molecule. Is this process most likely to alter the rotational, vibrational, or atomic energy levels of the molecule? Explain your reasoning. (b) If the light in part (a) had a wavelength of 207 nm, which energy levels would it most likely affect? Explain.
- 42.5** • For the H_2 molecule the equilibrium spacing of the two protons is 0.074 nm. The mass of a hydrogen atom is 1.67×10^{-27} kg. Calculate the wavelength of the photon emitted in the rotational transition $l = 2$ to $l = 1$.
- 42.6** • (a) A molecule decreases its vibrational energy by 0.250 eV by giving up a photon of light. What wavelength of light does it give up during this process, and in what part of the electromagnetic spectrum does that wavelength of light lie? (b) An atom decreases its energy by 8.50 eV by giving up a photon of light. What wavelength of light does it give up during this process, and in what part of the electromagnetic spectrum does that wavelength of light lie? (c) A molecule decreases its rotational energy by 3.20×10^{-3} eV by giving up a photon of light. What wavelength of light does it give up during this process, and in what part of the electromagnetic spectrum does that wavelength of light lie?

Section 42.2 Molecular Spectra

- 42.7** • 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.
- 42.8** • 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.
- 42.9** • 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?
- 42.10** • 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.
- 42.11** •• CP 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

EXERCISES

Section 42.1 Types of Molecular Bonds

- 42.1** • If the energy of the H_2 covalent bond is -4.48 eV, what wavelength of light is needed to break that molecule apart? In what part of the electromagnetic spectrum does this light lie?
- 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.

of each atom (use the result of Exercise 42.9); (c) the rotational period (the time for one rotation)?

42.12 • 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 $20.0 \mu\text{m}$ would be emitted. The mass of a sodium atom is $3.82 \times 10^{-26} \text{ kg}$, and the mass of a chlorine atom is $5.81 \times 10^{-26} \text{ kg}$. Calculate the force constant k' for the interatomic force in NaCl.

42.13 • A lithium atom has mass $1.17 \times 10^{-26} \text{ kg}$, and a hydrogen atom has mass $1.67 \times 10^{-27} \text{ kg}$. 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?

42.14 • 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 $8.841 \times 10^{-4} \text{ eV}$. 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.

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

42.16 • The vibrational and rotational energies of the CO molecule 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) $n = 0, l = 3 \rightarrow n = 1, l = 2$.

Section 42.3 Structure of Solids

42.17 • **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 $3.82 \times 10^{-26} \text{ kg}$, and the mass of a chlorine atom is $5.89 \times 10^{-26} \text{ kg}$. Calculate the density of sodium chloride.

42.18 • Potassium bromide (KBr) has a density of $2.75 \times 10^3 \text{ kg/m}^3$ and the same crystal structure as NaCl. The mass of a potassium atom is $6.49 \times 10^{-26} \text{ kg}$, and the mass of a bromine atom is $1.33 \times 10^{-25} \text{ kg}$. (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 42.17)? Is the relationship between the two values qualitatively what you would expect? Explain.

Section 42.4 Energy Bands

42.19 • The maximum wavelength of light that a certain silicon photocell can detect is $1.11 \mu\text{m}$. (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.

42.20 • 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.

42.21 • 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 $9.31 \times 10^{-4} \text{ nm}$. 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

42.22 • 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 42.7? Why is there such a difference between these speeds?

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

42.24 • Supply the details in the derivation of Eq. (42.13) from Eqs. (42.11) and (42.12).

42.25 • **CP** 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, $C_V = 25.3 \text{ J/mol} \cdot \text{K}$. (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 • (a) Suppose a piece of very pure germanium is to be used as a light detector by observing, through the absorption of photons, the increase in conductivity resulting from generation of electron-hole pairs. If each pair requires 0.67 eV of energy, what is the maximum wavelength that can be detected? In what portion of the spectrum does it lie? (b) What are the answers to part (a) if the material is silicon, with an energy requirement of 1.14 eV per pair, corresponding to the gap between valence and conduction bands in that element?

42.31 • **CP** At a temperature of 290 K , a certain p - n junction has a saturation current $I_S = 0.500 \text{ mA}$. (a) Find the current at this temperature when the voltage is (i) 1.00 mV , (ii) -1.00 mV , (iii) 100 mV , and (iv) -100 mV . (b) Is there a region of applied voltage where the diode obeys Ohm's law?

42.32 • For a certain p - n junction diode, the saturation current at room temperature (20°C) is 0.750 mA . What is the resistance of this diode when the voltage across it is (a) 85.0 mV and (b) -50.0 mV ?

42.33 •• (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?

42.34 •• 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

42.35 •• A hypothetical diatomic molecule of oxygen (mass = 2.656×10^{-26} kg) and hydrogen (mass = 1.67×10^{-27} kg) emits a photon of wavelength $2.39 \mu\text{m}$ 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?

42.36 • When a diatomic molecule undergoes a transition from the $l = 2$ to the $l = 1$ rotational state, a photon with wavelength $63.8 \mu\text{m}$ 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?

42.37 •• **CP** (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 3.0×10^{-29} C·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 1.5×10^{-30} C·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.

42.38 • The binding energy of a potassium chloride molecule (KCl) is 4.43 eV. The ionization energy of a potassium atom is 4.18 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 give a precise value.

42.39 • (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 Na^+ ion and a 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 42.38.

42.40 • The rotational spectrum of HCl contains the following wavelengths (among others): $60.4 \mu\text{m}$, $69.0 \mu\text{m}$, $80.4 \mu\text{m}$, $94.0 \mu\text{m}$, and $120.4 \mu\text{m}$. 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.

(a) Use the result of Problem 42.40 to calculate the equilibrium separation of the atoms in an HCl molecule. The mass of a hydrogen atom is 1.67×10^{-27} kg, and the mass of a chlorine

atom is 35.5×10^{-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 42.40? (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 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.

42.42 • When a NaF molecule makes a transition from the $l = 2$ to the $l = 1$ rotational level with no change in vibrational quantum number or electronic state, a photon with wavelength $3.83 \text{ m}\mu\text{m}$ 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 the result reasonable? Explain.

42.43 •• **CP** 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 39.4) predicts that the ratio of the numbers of molecules in the two states is

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

(a) Explain why the ratio of the number of molecules in the l th 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.

42.44 •• Our galaxy contains numerous *molecular clouds*, regions of space 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. P42.44. 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 telescope 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

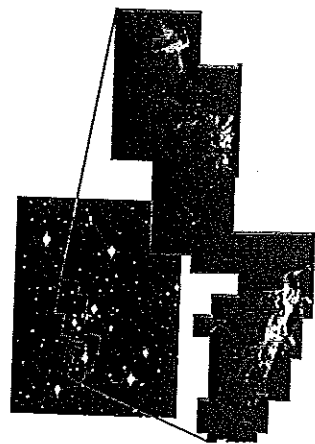


Figure P42.44

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 42.43). 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.

42.45 • 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?

42.46 • 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.)

42.47 • 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?

42.48 • Suppose the hydrogen atom in HF (see the Bridging Problem for this chapter) 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?

42.49 • 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) $n = 2, l = 2 \rightarrow n = 1, l = 3$.

42.50 •• 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.

42.51 •• 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/m³, and the mass of a single potassium atom is 6.49×10^{-26} kg.

42.52 •• Hydrogen is found in two naturally occurring isotopes; normal hydrogen (containing a single proton in its nucleus) and deu-

terium (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?

42.53 ••• 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.

42.54 •• CALC The one-dimensional calculation of Example 42.4 (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?

42.55 •• CALC 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 $p dV$ on their surroundings, which means that the total energy E_{tot} of the electrons will change by an amount $dE_{\text{tot}} = -p dV$. 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?

42.56 •• CALC 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

rial 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 42.55 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 42.55?) (b) Evaluate the bulk modulus for the electrons in copper, which has a free-electron concentration of $8.45 \times 10^{28} \text{ m}^{-3}$. Express your result in pascals. (c) The actual bulk modulus of copper is $1.4 \times 10^{11} \text{ Pa}$. 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?

42.57 •• 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. (42.19), is equal to $\frac{1}{100}mc^2$. Show that the electron concentration is

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

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 $8.45 \times 10^{28} \text{ m}^{-3}$? 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 $2 \times 10^{30} \text{ kg}$ (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 42.55). 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

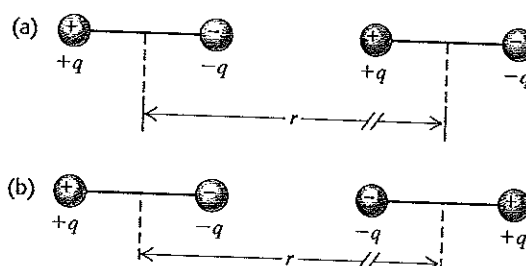
$1.99 \times 10^{-26} \text{ kg}$; and (ii) all six of the electrons from each carbon atom are able to move freely throughout the star. (d) Is it a good approximation to ignore relativistic effects in the structure of a white dwarf star? Explain.

42.58 •• CP A variable DC battery is connected in series with a $125\text{-}\Omega$ 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 $125\text{-}\Omega$ resistor reads 35.0 V , what are (a) the voltage across the diode and (b) the resistance of the diode?

CHALLENGE PROBLEMS

42.59 ••• CP 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. P42.59a. 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. P42.59b. 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 P42.59



42.60 ••• CP CALC (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 $1.67 \times 10^{-27} \text{ kg}$. (Hint: Estimate the force constant by equating the change in Coulomb repulsion 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 $3.34 \times 10^{-27} \text{ kg}$.

Answers

Chapter Opening Question ?

Venus 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 surface of Venus and re-emit it toward the ground. To compensate for this and to maintain the balance between emitted and received energy, the surface temperature of Venus and hence the rate of blackbody radiation from the surface both increase.