

MOLECULES AND CONDENSED MATTER

42.1. (a) $K = \frac{3}{2}kT \Rightarrow T = \frac{2K}{3k} = \frac{2(7.9 \times 10^{-4} \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{3(1.38 \times 10^{-23} \text{ J/K})} = 6.1 \text{ K}$

(b) $T = \frac{2(4.48 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{3(1.38 \times 10^{-23} \text{ J/K})} = 34,600 \text{ K}$.

(c) The thermal energy associated with room temperature (300 K) is much greater than the bond energy of He_2 (calculated in part (a)), so the typical collision at room temperature will be more than enough to break up He_2 . However, the thermal energy at 300 K is much less than the bond energy of H_2 , so we would expect it to remain intact at room temperature.

42.2. (a) $U = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} = -5.0 \text{ eV}$.

(b) $-5.0 \text{ eV} + (4.3 \text{ eV} - 3.5 \text{ eV}) = -4.2 \text{ eV}$.

42.3. **IDENTIFY:** The energy given to the photon comes from a transition between rotational states.

SET UP: The rotational energy of a molecule is $E = l(l+1)\frac{\hbar^2}{2I}$ and the energy of the photon is $E = hc/\lambda$.

EXECUTE: Use the energy formula, the energy difference between the $l = 3$ and $l = 1$ rotational levels of the molecule is $\Delta E = \frac{\hbar^2}{2I}[3(3+1) - 1(1+1)] = \frac{5\hbar^2}{I}$. Since $\Delta E = hc/\lambda$, we get $hc/\lambda = 5\hbar^2/I$. Solving for I gives

$$I = \frac{5\hbar\lambda}{2\pi c} = \frac{5(1.055 \times 10^{-34} \text{ J}\cdot\text{s})(1.780 \text{ nm})}{2\pi(3.00 \times 10^8 \text{ m/s})} = 4.981 \times 10^{-52} \text{ kg}\cdot\text{m}^2.$$

Using $I = m_r r_0^2$, we can solve for r_0 : $r_0 = \sqrt{\frac{I(m_N + m_H)}{m_N m_H}} = \sqrt{\frac{(4.981 \times 10^{-52} \text{ kg}\cdot\text{m}^2)(2.33 \times 10^{-26} \text{ kg} + 1.67 \times 10^{-27} \text{ kg})}{(2.33 \times 10^{-26} \text{ kg})(1.67 \times 10^{-27} \text{ kg})}}$

$$r_0 = 5.65 \times 10^{-13} \text{ m}$$

EVALUATE: This separation is much smaller than the diameter of a typical atom and is not very realistic. But we are treating a *hypothetical* NH molecule.

42.4. The energy of the emitted photon is $1.01 \times 10^{-5} \text{ eV}$, and so its frequency and wavelength are

$$f = \frac{E}{h} = \frac{(1.01 \times 10^{-5} \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})} = 2.44 \text{ GHz} \quad \text{and} \quad \lambda = \frac{c}{f} = \frac{(3.00 \times 10^8 \text{ m/s})}{(2.44 \times 10^9 \text{ Hz})} = 0.123 \text{ m}.$$
 This frequency

corresponds to that given for a microwave oven.

42.5. Let 1 refer to C and 2 to O. $m_1 = 1.993 \times 10^{-26} \text{ kg}$, $m_2 = 2.656 \times 10^{-26} \text{ kg}$, $r_0 = 0.1128 \text{ nm}$.

$$r_1 = \left(\frac{m_2}{m_1 + m_2}\right)r_0 = 0.0644 \text{ nm (carbon)}; \quad r_2 = \left(\frac{m_1}{m_1 + m_2}\right)r_0 = 0.0484 \text{ nm (oxygen)}$$

(b) $I = m_1 r_1^2 + m_2 r_2^2 = 1.45 \times 10^{-46} \text{ kg}\cdot\text{m}^2$; yes, this agrees with Example 42.2.

42.6. Each atom has a mass m and is at a distance $L/2$ from the center, so the moment of inertia is

$$2(m)(L/2)^2 = mL^2/2 = 2.21 \times 10^{-44} \text{ kg}\cdot\text{m}^2.$$

42.7. **IDENTIFY and SET UP:** Set $K = E_1$ from Example 42.2. Use $K = \frac{1}{2}I\omega^2$ to solve for ω and $v = r\omega$ to solve for v .

EXECUTE: (a) From Example 42.2, $E_1 = 0.479 \text{ meV} = 7.674 \times 10^{-23} \text{ J}$ and $I = 1.449 \times 10^{-46} \text{ kg}\cdot\text{m}^2$

$$K = \frac{1}{2}I\omega^2 \quad \text{and} \quad K = E \quad \text{gives} \quad \omega = \sqrt{2E_1/I} = 1.03 \times 10^{12} \text{ rad/s}$$

$$(b) v_1 = r_1 \omega_1 = (0.0644 \times 10^{-9} \text{ m})(1.03 \times 10^{12} \text{ rad/s}) = 66.3 \text{ m/s (carbon)}$$

$$v_2 = r_2 \omega_2 = (0.0484 \times 10^{-9} \text{ m})(1.03 \times 10^{12} \text{ rad/s}) = 49.8 \text{ m/s (oxygen)}$$

$$(c) T = 2\pi / \omega = 6.10 \times 10^{-12} \text{ s}$$

EVALUATE: From the information in Example 42.3 we can calculate the vibrational period to be $T = 2\pi / \omega = 2\pi \sqrt{m_r / k'} = 1.5 \times 10^{-14} \text{ s}$. The rotational motion is over an order of magnitude slower than the vibrational motion.

$$42.8. \quad \Delta E = \frac{hc}{\lambda} = \hbar \sqrt{k' / m_r}, \text{ and solving for } k', k' = \left(\frac{2\pi c}{\lambda} \right)^2 m_r = 205 \text{ N/m.}$$

42.9. IDENTIFY and SET UP: The energy of a rotational level with quantum number l is $E_l = l(l+1)\hbar^2 / 2I$ (Eq.(42.3)). $I = m_r r^2$, with the reduced mass m_r given by Eq.(42.4). Calculate I and ΔE and then use $\Delta E = hc / \lambda$ to find λ .

$$\text{EXECUTE: (a) } m_r = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_{\text{Li}} m_{\text{H}}}{m_{\text{Li}} + m_{\text{H}}} = \frac{(1.17 \times 10^{-26} \text{ kg})(1.67 \times 10^{-27} \text{ kg})}{1.17 \times 10^{-26} \text{ kg} + 1.67 \times 10^{-27} \text{ kg}} = 1.461 \times 10^{-27} \text{ kg}$$

$$I = m_r r^2 = (1.461 \times 10^{-27} \text{ kg})(0.159 \times 10^{-9} \text{ m})^2 = 3.694 \times 10^{-47} \text{ kg} \cdot \text{m}^2$$

$$l = 3: E = 3(4) \left(\frac{\hbar^2}{2I} \right) = 6 \left(\frac{\hbar^2}{I} \right)$$

$$l = 4: E = 4(5) \left(\frac{\hbar^2}{2I} \right) = 10 \left(\frac{\hbar^2}{I} \right)$$

$$\Delta E = E_4 - E_3 = 4 \left(\frac{\hbar^2}{I} \right) = 4 \left(\frac{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{3.694 \times 10^{-47} \text{ kg} \cdot \text{m}^2} \right) = 1.20 \times 10^{-21} \text{ J} = 7.49 \times 10^{-3} \text{ eV}$$

$$(b) \Delta E = hc / \lambda \text{ so } \lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV})(2.998 \times 10^8 \text{ m/s})}{7.49 \times 10^{-3} \text{ eV}} = 166 \mu\text{m}$$

EVALUATE: LiH has a smaller reduced mass than CO and λ is somewhat smaller here than the λ calculated for CO in Example 42.2

42.10. IDENTIFY: The vibrational energy of the molecule is related to its force constant and reduced mass, while the rotational energy depends on its moment of inertia, which in turn depends on the reduced mass.

$$\text{SET UP: The vibrational energy is } E_n = \left(n + \frac{1}{2} \right) \hbar \omega = \left(n + \frac{1}{2} \right) \hbar \sqrt{\frac{k'}{m_r}} \text{ and the rotational energy is } E_l = l(l+1) \frac{\hbar^2}{2I}.$$

EXECUTE: For a vibrational transition, we have $\Delta E_v = \hbar \sqrt{\frac{k'}{m_r}}$, so we first need to find m_r . The energy for a

rotational transition is $\Delta E_r = \frac{\hbar^2}{2I} [2(2+1) - 1(1+1)] = \frac{2\hbar^2}{I}$. Solving for I and using the fact that $I = m_r r_0^2$, we have

$$m_r r_0^2 = \frac{2\hbar^2}{\Delta E_r}, \text{ which gives}$$

$$m_r = \frac{2\hbar^2}{r_0^2 \Delta E_r} = \frac{2(1.055 \times 10^{-34} \text{ J} \cdot \text{s}) (6.583 \times 10^{-16} \text{ eV} \cdot \text{s})}{(0.8860 \times 10^{-9} \text{ m})^2 (8.841 \times 10^{-4} \text{ eV})} = 2.0014 \times 10^{-28} \text{ kg}$$

Now look at the vibrational transition to find the force constant.

$$\Delta E_v = \hbar \sqrt{\frac{k'}{m_r}} \Rightarrow k' = \frac{m_r (\Delta E_v)^2}{\hbar^2} = \frac{(2.0014 \times 10^{-28} \text{ kg})(0.2560 \text{ eV})^2}{(6.583 \times 10^{-16} \text{ eV} \cdot \text{s})^2} = 30.27 \text{ N/m}$$

EVALUATE: This would be a rather weak spring in the laboratory.

$$42.11. (a) E_l = \frac{l(l+1)\hbar^2}{2I}, E_{l-1} = \frac{l(l-1)\hbar^2}{2I} \Rightarrow \Delta E = \frac{\hbar^2}{2I} (l^2 + l - l^2 + l) = \frac{l\hbar^2}{I}$$

$$(b) f = \frac{\Delta E}{h} = \frac{\Delta E}{2\pi\hbar} = \frac{l\hbar}{2\pi I}$$

42.12. IDENTIFY: Find ΔE for the transition and compute λ from $\Delta E = hc/\lambda$.

SET UP: From Example 42.2, $E_l = l(l+1)\frac{\hbar^2}{2I}$, with $\frac{\hbar^2}{2I} = 0.2395 \times 10^{-3}$ eV. From Example 42.3, $\Delta E = 0.2690$ eV is the spacing between vibrational levels. Thus $E_n = (n + \frac{1}{2})\hbar\omega$, with $\hbar\omega = 0.2690$ eV. By Eq.(42.9),

$$E = E_n + E_l = (n + \frac{1}{2})\hbar\omega + l(l+1)\frac{\hbar^2}{2I}.$$

EXECUTE: (a) $n = 0 \rightarrow n = 1$ and $l = 1 \rightarrow l = 2$

$$\text{For } n = 0, l = 1, E_i = \frac{1}{2}\hbar\omega + 2\left(\frac{\hbar^2}{2I}\right).$$

$$\text{For } n = 1, l = 2, E_f = \frac{3}{2}\hbar\omega + 6\left(\frac{\hbar^2}{2I}\right).$$

$$\Delta E = E_f - E_i = \hbar\omega + 4\left(\frac{\hbar^2}{2I}\right) = 0.2690 \text{ eV} + 4(0.2395 \times 10^{-3} \text{ eV}) = 0.2700 \text{ eV}$$

$$\frac{hc}{\lambda} = \Delta E \text{ so } \lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{0.2700 \text{ eV}} = 4.592 \times 10^{-6} \text{ m} = 4.592 \mu\text{m}$$

(b) $n = 0 \rightarrow n = 1$ and $l = 2 \rightarrow l = 1$

$$\text{For } n = 0, l = 2, E_i = \frac{1}{2}\hbar\omega + 6\left(\frac{\hbar^2}{2I}\right).$$

$$\text{For } n = 1, l = 1, E_f = \frac{3}{2}\hbar\omega + 2\left(\frac{\hbar^2}{2I}\right).$$

$$\Delta E = E_f - E_i = \hbar\omega - 4\left(\frac{\hbar^2}{2I}\right) = 0.2690 \text{ eV} - 4(0.2395 \times 10^{-3} \text{ eV}) = 0.2680 \text{ eV}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{0.2680 \text{ eV}} = 4.627 \times 10^{-6} \text{ m} = 4.627 \mu\text{m}$$

(c) $n = 0 \rightarrow n = 1$ and $l = 3 \rightarrow l = 2$

$$\text{For } n = 0, l = 3, E_i = \frac{1}{2}\hbar\omega + 12\left(\frac{\hbar^2}{2I}\right).$$

$$\text{For } n = 1, l = 2, E_f = \frac{3}{2}\hbar\omega + 6\left(\frac{\hbar^2}{2I}\right).$$

$$\Delta E = E_f - E_i = \hbar\omega - 6\left(\frac{\hbar^2}{2I}\right) = 0.2690 \text{ eV} - 6(0.2395 \times 10^{-3} \text{ eV}) = 0.2676 \text{ eV}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{0.2676 \text{ eV}} = 4.634 \times 10^{-6} \text{ m} = 4.634 \mu\text{m}$$

EVALUATE: All three transitions are for $n = 0 \rightarrow n = 1$. The spacing between vibrational levels is larger than the spacing between rotational levels, so the difference in λ for the various rotational transitions is small. When the transition is to a larger l , $\Delta E > \hbar\omega$ and when the transition is to a smaller l , $\Delta E < \hbar\omega$.

42.13. (a) IDENTIFY and SET UP: Use $\omega = \sqrt{k'/m_r}$ and $\omega = 2\pi f$ to calculate k' . The atomic masses are used in Eq.(42.4) to calculate m_r .

$$\text{EXECUTE: } f = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k'}{m_r}}, \text{ so } k' = m_r(2\pi f)^2$$

$$m_r = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_H m_F}{m_H + m_F} = \frac{(1.67 \times 10^{-27} \text{ kg})(3.15 \times 10^{-26} \text{ kg})}{1.67 \times 10^{-27} \text{ kg} + 3.15 \times 10^{-26} \text{ kg}} = 1.586 \times 10^{-27} \text{ kg}$$

$$k' = m_r(2\pi f)^2 = (1.586 \times 10^{-27} \text{ kg})(2\pi[1.24 \times 10^{14} \text{ Hz}])^2 = 963 \text{ N/m}$$

(b) IDENTIFY and SET UP: The energy levels are given by Eq.(42.7). $E_n = (n + \frac{1}{2})\hbar\omega = (n + \frac{1}{2})hf$, since $\hbar\omega = (h/2\pi)\omega$ and $(\omega/2\pi) = f$. The energy spacing between adjacent levels is

$$\Delta E = E_{n+1} - E_n = (n+1 + \frac{1}{2} - n - \frac{1}{2})hf = hf, \text{ independent of } n.$$

EXECUTE: $\Delta E = hf = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(1.24 \times 10^{14} \text{ Hz}) = 8.22 \times 10^{-20} \text{ J} = 0.513 \text{ eV}$

(c) IDENTIFY and SET UP: The photon energy equals the transition energy so $\Delta E = hc/\lambda$.

EXECUTE: $hf = hc/\lambda$ so $\lambda = \frac{c}{f} = \frac{2.998 \times 10^8 \text{ m/s}}{1.24 \times 10^{14} \text{ Hz}} = 2.42 \times 10^{-6} \text{ m} = 2.42 \mu\text{m}$

EVALUATE: This photon is infrared, which is typical for vibrational transitions.

42.14. For an average spacing a , the density is $\rho = m/a^3$, where m is the average of the ionic masses, and so

$$a^3 = \frac{m}{\rho} = \frac{(6.49 \times 10^{-26} \text{ kg} + 1.33 \times 10^{-25} \text{ kg})/2}{(2.75 \times 10^3 \text{ kg/m}^3)} = 3.60 \times 10^{-29} \text{ m}^3,$$

and $a = 3.30 \times 10^{-10} \text{ m} = 0.330 \text{ nm}$.

(b) The larger (higher atomic number) atoms have the larger spacing.

42.15. IDENTIFY and SET UP: Find the volume occupied by each atom. The density is the average mass of Na and Cl divided by this volume.

EXECUTE: Each atom occupies a cube with side length 0.282 nm . Therefore, the volume occupied by each atom is $V = (0.282 \times 10^{-9} \text{ m})^3 = 2.24 \times 10^{-29} \text{ m}^3$. In NaCl there are equal numbers of Na and Cl atoms, so the average mass of the atoms in the crystal is $m = \frac{1}{2}(m_{\text{Na}} + m_{\text{Cl}}) = \frac{1}{2}(3.82 \times 10^{-26} \text{ kg} + 5.89 \times 10^{-26} \text{ kg}) = 4.855 \times 10^{-26} \text{ kg}$

The density then is $\rho = \frac{m}{V} = \frac{4.855 \times 10^{-26} \text{ kg}}{2.24 \times 10^{-29} \text{ m}^3} = 2.17 \times 10^3 \text{ kg/m}^3$.

EVALUATE: The density of water is $1.00 \times 10^3 \text{ kg/m}^3$, so our result is reasonable.

42.16. (a) As a photon, $\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(6.20 \times 10^3 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})} = 0.200 \text{ nm}$.

(b) As a matter wave,

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})}{\sqrt{2(9.11 \times 10^{-31} \text{ kg})(37.6 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}} = 0.200 \text{ nm}$$

(c) As a matter wave,

$$\lambda = \frac{h}{\sqrt{2mE}} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})}{\sqrt{2(1.67 \times 10^{-27} \text{ kg})(0.0205 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}} = 0.200 \text{ nm}.$$

42.17. IDENTIFY: The energy gap is the energy of the maximum-wavelength photon.

SET UP: The energy difference is equal to the energy of the photon, so $\Delta E = hc/\lambda$.

EXECUTE: **(a)** Using the photon wavelength to find the energy difference gives

$$\Delta E = hc/\lambda = (4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})/(1.11 \times 10^{-6} \text{ m}) = 1.12 \text{ eV}$$

(b) A wavelength of $1.11 \mu\text{m} = 1110 \text{ nm}$ is in the infrared, shorter than that of visible light.

EVALUATE: Since visible photons have more than enough energy to excite electrons from the valence to the conduction band, visible light will be absorbed, which makes silicon opaque.

42.18. (a) $\frac{hc}{\Delta E} = 2.27 \times 10^{-7} \text{ m} = 227 \text{ nm}$, in the ultraviolet.

(b) Visible light lacks enough energy to excite the electrons into the conduction band, so visible light passes through the diamond unabsorbed.

(c) Impurities can lower the gap energy making it easier for the material to absorb shorter wavelength visible light. This allows longer wavelength visible light to pass through, giving the diamond color.

42.19. $\Delta E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{9.31 \times 10^{-13} \text{ m}} = 2.14 \times 10^{-13} \text{ J} = 1.34 \times 10^6 \text{ eV}$. So the number of electrons that can be

excited to the conduction band is $n = \frac{1.34 \times 10^6 \text{ eV}}{1.12 \text{ eV}} = 1.20 \times 10^6$ electrons

42.20. $1 = \int |\psi|^2 dV$

$$= A^2 \left(\int_0^L \sin^2 \left(\frac{n_x \pi x}{L} \right) dx \right) \left(\int_0^L \sin^2 \left(\frac{n_y \pi y}{L} \right) dy \right) \left(\int_0^L \sin^2 \left(\frac{n_z \pi z}{L} \right) dz \right) = A^2 \left(\frac{L}{2} \right)^3$$

so $A = (2/L)^{3/2}$ (assuming A to be real positive).

42.21. Density of states:

$$g(E) = \frac{(2m)^{3/2} V}{2\pi^2 \hbar^3} E^{1/2} = \frac{(2(9.11 \times 10^{-31} \text{ kg}))^{3/2} (1.0 \times 10^{-6} \text{ m}^3) (5.0 \text{ eV})^{1/2} (1.60 \times 10^{-19} \text{ J/eV})^{1/2}}{2\pi^2 (1.054 \times 10^{-34} \text{ J}\cdot\text{s})^3}$$

$$g(E) = (9.5 \times 10^{40} \text{ states/J}) (1.60 \times 10^{-19} \text{ J/eV}) = 1.5 \times 10^{22} \text{ states/eV.}$$

42.22. $v_{\text{rms}} = \sqrt{3kT/m} = 1.17 \times 10^5 \text{ m/s}$, as found in Example 42.9. The equipartition theorem does not hold for the electrons at the Fermi energy. Although these electrons are very energetic, they cannot lose energy, unlike electrons in a free electron gas.

42.23. (a) **IDENTIFY and SET UP:** The three-dimensional Schrödinger equation is $-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U\psi = E\psi$

(Eq.40.29). For free electrons, $U = 0$. Evaluate $\partial^2 \psi / \partial x^2$, $\partial^2 \psi / \partial y^2$, and $\partial^2 \psi / \partial z^2$ for ψ as given by Eq.(42.10). Put the results into Eq.(40.20) and see if the equation is satisfied.

EXECUTE: $\frac{\partial \psi}{\partial x} = \frac{n_x \pi}{L} A \cos\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$

$$\frac{\partial^2 \psi}{\partial x^2} = -\left(\frac{n_x \pi}{L}\right)^2 A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) = -\left(\frac{n_x \pi}{L}\right)^2 \psi$$

Similarly $\frac{\partial^2 \psi}{\partial y^2} = -\left(\frac{n_y \pi}{L}\right)^2 \psi$ and $\frac{\partial^2 \psi}{\partial z^2} = -\left(\frac{n_z \pi}{L}\right)^2 \psi$.

Therefore, $-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = \frac{\hbar^2}{2m} \left(\frac{\pi^2}{L^2} \right) (n_x^2 + n_y^2 + n_z^2) \psi = \frac{(n_x^2 + n_y^2 + n_z^2) \pi^2 \hbar^2}{2mL^2} \psi$

This equals $E\psi$, with $E = \frac{(n_x^2 + n_y^2 + n_z^2) \pi^2 \hbar^2}{2mL^2}$, which is Eq.(42.11).

EVALUATE: ψ given by Eq.(42.10) is a solution to Eq.(40.29), with E as given by Eq.(42.11).

(b) **IDENTIFY and SET UP:** Find the set of quantum numbers n_x , n_y , and n_z that give the lowest three values of E . The degeneracy is the number of sets n_x , n_y , n_z and m_s that give the same E .

EXECUTE: Ground level: lowest E so $n_x = n_y = n_z = 1$ and $E = \frac{3\pi^2 \hbar^2}{2mL^2}$. No other combination of n_x , n_y , and n_z gives this same E , so the only degeneracy is the degeneracy of two due to spin.

First excited level: next lower E so one n equals 2 and the others equal 1. $E = (2^2 + 1^2 + 1^2) \frac{\pi^2 \hbar^2}{2mL^2} = \frac{6\pi^2 \hbar^2}{2mL^2}$

There are three different sets of n_x , n_y , n_z values that give this E :

$$n_x = 2, n_y = 1, n_z = 1; n_x = 1, n_y = 2, n_z = 1; n_x = 1, n_y = 1, n_z = 2$$

This gives a degeneracy of 3 so the total degeneracy, with the factor of 2 from spin, is 6.

Second excited level: next lower E so two of n_x , n_y , n_z equal 2 and the other equals 1.

$$E = (2^2 + 2^2 + 1^2) \frac{\pi^2 \hbar^2}{2mL^2} = \frac{9\pi^2 \hbar^2}{2mL^2}$$

There are different sets of n_x , n_y , n_z values that give this E :

$$n_x = 2, n_y = 2, n_z = 1; n_x = 2, n_y = 1, n_z = 2; n_x = 1, n_y = 2, n_z = 2.$$

Thus, as for the first excited level, the total degeneracy, including spin, is 6.

EVALUATE: The wavefunction for the 3-dimensional box is a product of the wavefunctions for a 1-dimensional box in the x , y , and z coordinates and the energy is the sum of energies for three 1-dimensional boxes. All levels except for the ground level have a degeneracy greater than two. Compare to the 3-dimensional isotropic harmonic oscillator treated in Problem 40.53.

42.24. Eq.(42.13) may be solved for $n_{\text{fs}} = (2mE)^{1/2} (L/\hbar\pi)$, and substituting this into Eq. (42.12), using $L^3 = V$, gives Eq.(42.14).

42.25. (a) **IDENTIFY and SET UP:** The electron contribution to the molar heat capacity at constant volume of a metal is

$$C_V = \left(\frac{\pi^2 KT}{2E_F} \right) R.$$

EXECUTE: $C_V = \frac{\pi^2 (1.381 \times 10^{-23} \text{ J/K})(300 \text{ K})}{2(5.48 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV})} R = 0.0233R.$

(b) **EVALUATE:** The electron contribution found in part (a) is $0.0233R = 0.194 \text{ J/mol} \cdot \text{K}$. This is $0.194/25.3 = 7.67 \times 10^{-3} = 0.767\%$ of the total C_V .

(c) Only a small fraction of C_V is due to the electrons. Most of C_V is due to the vibrational motion of the ions.

42.26. (a) From Eq. (42.22), $E_{\text{av}} = \frac{3}{5}E_F = 1.94 \text{ eV}$.

$$(b) \sqrt{2E/m} = \sqrt{\frac{2(1.94 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{9.11 \times 10^{-31} \text{ kg}}} = 8.25 \times 10^5 \text{ m/s}.$$

$$(c) \frac{E_F}{k} = \frac{(3.23 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{(1.38 \times 10^{-23} \text{ J/K})} = 3.74 \times 10^4 \text{ K}.$$

42.27. **IDENTIFY:** The probability is given by the Fermi-Dirac distribution.

SET UP: The Fermi-Dirac distribution is $f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$.

EXECUTE: We calculate the value of $f(E)$, where $E = 8.520 \text{ eV}$, $E_F = 8.500 \text{ eV}$, $k = 1.38 \times 10^{-23} \text{ J/K} = 8.625 \times 10^{-5} \text{ eV/K}$, and $T = 20^\circ\text{C} = 293 \text{ K}$. The result is $f(E) = 0.312 = 31.2\%$.

EVALUATE: Since the energy is close to the Fermi energy, the probability is quite high that the state is occupied by an electron.

42.28. (a) See Example 42.10: The probabilities are 1.78×10^{-7} , 2.37×10^{-6} , and 1.51×10^{-5} .

(b) The Fermi distribution, Eq.(42.17), has the property that $f(E_F - E) = 1 - f(E)$ (see Problem (42.48)), and so the probability that a state at the top of the valence band is occupied is the same as the probability that a state of the bottom of the conduction band is filled (this result depends on having the Fermi energy in the middle of the gap).

42.29. **IDENTIFY:** Use Eq.(42.17), $f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$. Solve for $E - E_F$.

$$\text{SET UP: } e^{(E-E_F)/kT} = \frac{1}{f(E)} - 1$$

The problem states that $f(E) = 4.4 \times 10^{-4}$ for E at the bottom of the conduction band.

$$\text{EXECUTE: } e^{(E-E_F)/kT} = \frac{1}{4.4 \times 10^{-4}} - 1 = 2.272 \times 10^3.$$

$$E - E_F = kT \ln(2.272 \times 10^3) = (1.3807 \times 10^{-23} \text{ J/T})(300 \text{ K}) \ln(2.272 \times 10^3) = 3.201 \times 10^{-20} \text{ J} = 0.20 \text{ eV}$$

$E_F = E - 0.20 \text{ eV}$; the Fermi level is 0.20 eV below the bottom of the conduction band.

EVALUATE: The energy gap between the Fermi level and bottom of the conduction band is large compared to kT at $T = 300 \text{ K}$ and as a result $f(E)$ is small.

42.30. **IDENTIFY:** The current depends on the voltage across the diode and its temperature, so the resistance also depends on these quantities.

SET UP: The current is $I = I_s(e^{eV/kT} - 1)$ and the resistance is $R = V/I$.

$$\text{EXECUTE: (a) The resistance is } R = \frac{V}{I} = \frac{V}{I_s(e^{eV/kT} - 1)}. \text{ The exponent is } \frac{eV}{kT} = \frac{e(0.0850 \text{ V})}{(8.625 \times 10^{-5} \text{ eV/K})(293 \text{ K})} =$$

$$3.3635, \text{ giving } R = \frac{85.0 \text{ mV}}{(0.750 \text{ mA})(e^{3.3635} - 1)} = 4.06 \Omega.$$

$$(b) \text{ In this case, the exponent is } \frac{eV}{kT} = \frac{e(-0.050 \text{ V})}{(8.625 \times 10^{-5} \text{ eV/K})(293 \text{ K})} = -1.979$$

$$\text{which gives } R = \frac{-50.0 \text{ mV}}{(0.750 \text{ mA})(e^{-1.979} - 1)} = 77.4 \Omega$$

EVALUATE: Reversing the voltage can make a considerable change in the resistance of a diode.

42.31. **IDENTIFY and SET UP:** The voltage-current relation is given by Eq.(42.23): $I = I_s(e^{eV/kT} - 1)$. Use the current for $V = +15.0 \text{ mV}$ to solve for the constant I_s .

EXECUTE: (a) Find I_s : $V = +15.0 \times 10^{-3} \text{ V}$ gives $I = 9.25 \times 10^{-3} \text{ A}$

$$\frac{eV}{kT} = \frac{(1.602 \times 10^{-19} \text{ C})(15.0 \times 10^{-3} \text{ V})}{(1.381 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.5800$$

$$I_s = \frac{I}{e^{eV/kT} - 1} = \frac{9.25 \times 10^{-3} \text{ A}}{e^{0.5800} - 1} = 1.177 \times 10^{-2} = 11.77 \text{ mA}$$

Then can calculate I for $V = 10.0$ mV: $\frac{eV}{kT} = \frac{(1.602 \times 10^{-19} \text{ C})(10.0 \times 10^{-3} \text{ V})}{(1.381 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.3867$

$$I = I_s (e^{eV/kT} - 1) = (11.77 \text{ mA})(e^{0.3867} - 1) = 5.56 \text{ mA}$$

(b) $\frac{eV}{kT}$ has the same magnitude as in part (a) but not V is negative so $\frac{eV}{kT}$ is negative.

$$V = -15.0 \text{ mV}: \frac{eV}{kT} = -0.5800 \text{ and } I = I_s (e^{eV/kT} - 1) = (11.77 \text{ mA})(e^{-0.5800} - 1) = -5.18 \text{ mA}$$

$$V = -10.0 \text{ mV}: \frac{eV}{kT} = -0.3867 \text{ and } I = I_s (e^{eV/kT} - 1) = (11.77 \text{ mA})(e^{-0.3867} - 1) = -3.77 \text{ mA}$$

EVALUATE: There is a directional asymmetry in the current, with a forward-bias voltage producing more current than a reverse-bias voltage of the same magnitude, but the voltage is small enough for the asymmetry not be pronounced. Compare to Example 42.11, where more extreme voltages are considered.

42.32. (a) Solving Eq.(42.23) for the voltage as a function of current,

$$V = \frac{kT}{e} \ln \left(\frac{I}{I_s} + 1 \right) = \frac{kT}{e} \ln \left(\frac{40.0 \text{ mA}}{3.60 \text{ mA}} + 1 \right) = 0.0645 \text{ V.}$$

(b) From part (a), the quantity $e^{eV/kT} = 12.11$, so far a reverse-bias voltage of the same magnitude,

$$I = I_s (e^{-eV/kT} - 1) = I_s \left(\frac{1}{12.11} - 1 \right) = -3.30 \text{ mA.}$$

42.33. IDENTIFY: During the transition, the molecule emits a photon of light having energy equal to the energy difference between the two vibrational states of the molecule.

SET UP: The vibrational energy is $E_n = \left(n + \frac{1}{2} \right) \hbar \omega = \left(n + \frac{1}{2} \right) \hbar \sqrt{\frac{k'}{m_r}}$.

EXECUTE: (a) The energy difference between two adjacent energy states is $\Delta E = \hbar \sqrt{\frac{k'}{m_r}}$, and this is the energy of

the photon, so $\Delta E = hc/\lambda$. Equating these two expressions for ΔE and solving for k' , we have $k' = m_r \left(\frac{\Delta E}{\hbar} \right)^2 =$

$\frac{m_H m_O}{m_H + m_O} \left(\frac{\Delta E}{\hbar} \right)^2$, and using $\frac{\Delta E}{\hbar} = \frac{hc/\lambda}{\hbar} = \frac{2\pi c}{\lambda}$ with the appropriate numbers gives us

$$k' = \frac{(1.67 \times 10^{-27} \text{ kg})(2.656 \times 10^{-26} \text{ kg})}{1.67 \times 10^{-27} \text{ kg} + 2.656 \times 10^{-26} \text{ kg}} \left[\frac{2\pi(3.00 \times 10^8 \text{ m/s})}{2.39 \times 10^{-6} \text{ m}} \right]^2 = 977 \text{ N/m}$$

(b) $f = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k'}{m_r}} = \frac{1}{2\pi} \sqrt{\frac{m_H m_O}{m_H + m_O} \frac{k'}{m_r}}$. Substituting the appropriate numbers gives us

$$f = \frac{1}{2\pi} \sqrt{\frac{(1.67 \times 10^{-27} \text{ kg})(2.656 \times 10^{-26} \text{ kg})}{1.67 \times 10^{-27} \text{ kg} + 2.656 \times 10^{-26} \text{ kg}} \frac{977 \text{ N/m}}{m_r}} = 1.25 \times 10^{14} \text{ Hz}$$

EVALUATE: The frequency is close to, but not quite in, the visible range.

42.34. $I = \frac{2\hbar^2}{\Delta E} = \frac{h\lambda}{2\pi^2 c} = 7.14 \times 10^{-48} \text{ kg} \cdot \text{m}^2$.

42.35. IDENTIFY and SET UP: Eq.(21.14) gives the electric dipole moment as $p = qd$, where the dipole consists of charges $\pm q$ separated by distance d .

EXECUTE: (a) Point charges $+e$ and $-e$ separated by distance d , so

$$p = ed = (1.602 \times 10^{-19} \text{ C})(0.24 \times 10^{-9} \text{ m}) = 3.8 \times 10^{-29} \text{ C} \cdot \text{m}$$

(b) $p = qd$ so $q = \frac{p}{d} = \frac{3.0 \times 10^{-29} \text{ C} \cdot \text{m}}{0.24 \times 10^{-9} \text{ m}} = 1.3 \times 10^{-19} \text{ C}$

(c) $\frac{q}{e} = \frac{1.3 \times 10^{-19} \text{ C}}{1.602 \times 10^{-19} \text{ C}} = 0.81$

$$(d) q = \frac{p}{d} = \frac{1.5 \times 10^{-30} \text{ C} \cdot \text{m}}{0.16 \times 10^{-9} \text{ m}} = 9.37 \times 10^{-21} \text{ C}$$

$$\frac{q}{e} = \frac{9.37 \times 10^{-21} \text{ C}}{1.602 \times 10^{-19} \text{ C}} = 0.058$$

EVALUATE: The fractional ionic character for the bond in HI is much less than the fractional ionic character for the bond in NaCl. The bond in HI is mostly covalent and not very ionic.

42.36. The electrical potential energy is $U = -5.13 \text{ eV}$, and $r = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{U} = 2.8 \times 10^{-10} \text{ m}$.

42.37. (a) IDENTIFY: $E(\text{Na}) + E(\text{Cl}) = E(\text{Na}^+) + E(\text{Cl}^-) + U(r)$. Solving for $U(r)$ gives

$$U(r) = -[E(\text{Na}^+) - E(\text{Na})] + [E(\text{Cl}) - E(\text{Cl}^-)].$$

SET UP: $[E(\text{Na}^+) - E(\text{Na})]$ is the ionization energy of Na, the energy required to remove one electron, and is equal to 5.1 eV. $[E(\text{Cl}) - E(\text{Cl}^-)]$ is the electron affinity of Cl, the magnitude of the decrease in energy when an electron is attached to a neutral Cl atom, and is equal to 3.6 eV.

EXECUTE: $U = -5.1 \text{ eV} + 3.6 \text{ eV} = -1.5 \text{ eV} = -2.4 \times 10^{-19} \text{ J}$, and $-\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} = -2.4 \times 10^{-19} \text{ J}$

$$r = \left(\frac{1}{4\pi\epsilon_0} \right) \frac{e^2}{2.4 \times 10^{-19} \text{ J}} = (8.988 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2) \frac{(1.602 \times 10^{-19} \text{ C})^2}{2.4 \times 10^{-19} \text{ J}}$$

$$r = 9.6 \times 10^{-10} \text{ m} = 0.96 \text{ nm}$$

(b) ionization energy of K = 4.3 eV; electron affinity of Br = 3.5 eV

Thus $U = -4.3 \text{ eV} + 3.5 \text{ eV} = -0.8 \text{ eV} = -1.28 \times 10^{-19} \text{ J}$, and $-\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} = -1.28 \times 10^{-19} \text{ J}$

$$r = \left(\frac{1}{4\pi\epsilon_0} \right) \frac{e^2}{1.28 \times 10^{-19} \text{ J}} = (8.988 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2) \frac{(1.602 \times 10^{-19} \text{ C})^2}{1.28 \times 10^{-19} \text{ J}}$$

$$r = 1.8 \times 10^{-9} \text{ m} = 1.8 \text{ nm}$$

EVALUATE: K has a smaller ionization energy than Na and the electron affinities of Cl and Br are very similar, so it takes less energy to make $\text{K}^+ + \text{Br}^-$ from $\text{K} + \text{Br}$ than to make $\text{Na}^+ + \text{Cl}^-$ from $\text{Na} + \text{Cl}$. Thus, the stabilization distance is larger for KBr than for NaCl.

42.38. The energies corresponding to the observed wavelengths are $3.29 \times 10^{-21} \text{ J}$, $2.87 \times 10^{-21} \text{ J}$, $2.47 \times 10^{-21} \text{ J}$, $2.06 \times 10^{-21} \text{ J}$ and $1.65 \times 10^{-21} \text{ J}$. The average spacing of these energies is $0.410 \times 10^{-21} \text{ J}$ and these are seen to

correspond to transition from levels 8, 7, 6, 5 and 4 to the respective next lower levels. Then, $\frac{\hbar^2}{I} = 0.410 \times 10^{-21} \text{ J}$,

from which $I = 2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2$.

42.39. (a) IDENTIFY: The rotational energies of a molecule depend on its moment of inertia, which in turn depends on the separation between the atoms in the molecule.

SET UP: Problem 42.38 gives $I = 2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2$. $I = m_r r^2$. Calculate m_r and solve for r .

EXECUTE: $m_r = \frac{m_{\text{H}} m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} = \frac{(1.67 \times 10^{-27} \text{ kg})(5.81 \times 10^{-26} \text{ kg})}{1.67 \times 10^{-27} \text{ kg} + 5.81 \times 10^{-26} \text{ kg}} = 1.623 \times 10^{-27} \text{ kg}$

$$r = \sqrt{\frac{I}{m_r}} = \sqrt{\frac{2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2}{1.623 \times 10^{-27} \text{ kg}}} = 1.29 \times 10^{-10} \text{ m} = 0.129 \text{ nm}$$

EVALUATE: This is a typical atomic separation for a diatomic molecule; see Example 42.2 for the corresponding distance for CO.

(b) IDENTIFY: Each transition is from the level l to the level $l-1$. The rotational energies are given by Eq.(42.3). The transition energy is related to the photon wavelength by $\Delta E = hc/\lambda$.

SET UP: $E_l = l(l+1)\hbar^2/2I$, so $\Delta E = E_l - E_{l-1} = [l(l+1) - l(l-1)] \left(\frac{\hbar^2}{2I} \right) = l \left(\frac{\hbar^2}{I} \right)$.

EXECUTE: $l \left(\frac{\hbar^2}{I} \right) = \frac{hc}{\lambda}$

$$l = \frac{2\pi c I}{\hbar \lambda} = \frac{2\pi(2.998 \times 10^8 \text{ m/s})(2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2)}{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})\lambda} = \frac{4.843 \times 10^{-4} \text{ m}}{\lambda}$$

$$\text{For } \lambda = 60.4 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{60.4 \times 10^{-6} \text{ m}} = 8.$$

$$\text{For } \lambda = 69.0 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{69.0 \times 10^{-6} \text{ m}} = 7.$$

$$\text{For } \lambda = 80.4 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{80.4 \times 10^{-6} \text{ m}} = 6.$$

$$\text{For } \lambda = 96.4 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{96.4 \times 10^{-6} \text{ m}} = 5.$$

$$\text{For } \lambda = 120.4 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{120.4 \times 10^{-6} \text{ m}} = 4.$$

EVALUATE: In each case l is an integer, as it must be.

(c) IDENTIFY and SET UP: Longest λ implies smallest ΔE , and this is for the transition from $l=1$ to $l=0$.

$$\text{EXECUTE: } \Delta E = l \left(\frac{\hbar^2}{I} \right) = (1) \frac{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2} = 4.099 \times 10^{-22} \text{ J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{4.099 \times 10^{-22} \text{ J}} = 4.85 \times 10^{-4} \text{ m} = 485 \mu\text{m}.$$

EVALUATE: This is longer than any wavelengths in part (b).

(d) IDENTIFY: What changes is m_r , the reduced mass of the molecule.

SET UP: The transition energy is $\Delta E = l \left(\frac{\hbar^2}{I} \right)$ and $\Delta E = \frac{hc}{\lambda}$, so $\lambda = \frac{2\pi cl}{l\hbar}$ (part (b)). $I = m_r r^2$, so λ is directly

$$\text{proportional to } m_r. \quad \frac{\lambda(\text{HCl})}{m_r(\text{HCl})} = \frac{\lambda(\text{DCl})}{m_r(\text{DCl})} \quad \text{so } \lambda(\text{DCl}) = \lambda(\text{HCl}) \frac{m_r(\text{DCl})}{m_r(\text{HCl})}$$

EXECUTE: The mass of a deuterium atom is approximately twice the mass of a hydrogen atom, so $m_D = 3.34 \times 10^{-27} \text{ kg}$.

$$m_r(\text{DCl}) = \frac{m_D m_{\text{Cl}}}{m_D + m_{\text{Cl}}} = \frac{(3.34 \times 10^{-27} \text{ kg})(5.81 \times 10^{-27} \text{ kg})}{3.34 \times 10^{-27} \text{ kg} + 5.81 \times 10^{-26} \text{ kg}} = 3.158 \times 10^{-27} \text{ kg}$$

$$\lambda(\text{DCl}) = \lambda(\text{HCl}) \left(\frac{3.158 \times 10^{-27} \text{ kg}}{1.623 \times 10^{-27} \text{ kg}} \right) = (1.946)\lambda(\text{HCl})$$

$$l = 8 \rightarrow l = 7; \lambda = (60.4 \mu\text{m})(1.946) = 118 \mu\text{m}$$

$$l = 7 \rightarrow l = 6; \lambda = (69.0 \mu\text{m})(1.946) = 134 \mu\text{m}$$

$$l = 6 \rightarrow l = 5; \lambda = (80.4 \mu\text{m})(1.946) = 156 \mu\text{m}$$

$$l = 5 \rightarrow l = 4; \lambda = (96.4 \mu\text{m})(1.946) = 188 \mu\text{m}$$

$$l = 4 \rightarrow l = 3; \lambda = (120.4 \mu\text{m})(1.946) = 234 \mu\text{m}$$

EVALUATE: The moment of inertia increases when H is replaced by D, so the transition energies decrease and the wavelengths increase. The larger the rotational inertia the smaller the rotational energy for a given l (Eq.42.3).

42.40. From the result of Problem 42.11, the moment inertia of the molecule is $I = \frac{\hbar^2 l}{\Delta E} = \frac{hl\lambda}{4\pi^2 c} = 6.43 \times 10^{-46} \text{ kg} \cdot \text{m}^2$ and

$$\text{from Eq.(42.6) the separation is } r_0 = \sqrt{\frac{I}{m_r}} = 0.193 \text{ nm}.$$

42.41. (a) $E_{\text{ex}} = \frac{L^2}{2I} = \frac{\hbar^2 l(l+1)}{2I}$. $E_g = 0$ ($l=0$), and there is an additional multiplicative factor of $2l+1$ because for each l

state there are really $(2l+1) m_l$ -states with the same energy. So $\frac{n_l}{n_0} = (2l+1)e^{-\hbar^2 l(l+1)/(2lRT)}$.

(b) $T = 300 \text{ K}, I = 1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2$.

$$(i) E_{l=1} = \frac{\hbar^2(1)(1+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)} = 7.67 \times 10^{-23} \text{ J}. \quad \frac{E_{l=1}}{kT} = \frac{7.67 \times 10^{-23} \text{ J}}{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.0185.$$

$$(2l+1) = 3, \text{ so } \frac{n_{l=1}}{n_0} = (3)e^{-0.0185} = 2.95.$$

$$(ii) \frac{E_{l=2}}{kT} = \frac{\hbar^2(2)(2+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.0556.$$

$$(2l+1) = 5, \text{ so } \frac{n_{l=1}}{n_0} = (5)(e^{-0.0556}) = 4.73.$$

$$(iii) \frac{E_{l=10}}{kT} = \frac{\hbar^2(10)(10+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 1.02.$$

$$(2l+1) = 21, \text{ so } \frac{n_{l=10}}{n_0} = (21)(e^{-1.02}) = 7.57.$$

$$(iv) \frac{E_{l=20}}{kT} = \frac{\hbar^2(20)(20+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 3.89.$$

$$(2l+1) = 41, \text{ so } \frac{n_{l=20}}{n_0} = (41)e^{-3.89} = 0.838.$$

$$(v) \frac{E_{l=50}}{kT} = \frac{\hbar^2(50)(50+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 23.6.$$

$$(2l+1) = 101, \text{ so } \frac{n_{l=50}}{n_0} = (101)e^{-23.6} = 5.69 \times 10^{-9}.$$

(c) There is a competing effect between the $(2l+1)$ term and the decaying exponential. The $2l+1$ term dominates for small l , while the exponential term dominates for large l .

42.42. (a) $I_{\text{CO}} = 1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2.$

$$E_{l=1} = \frac{\hbar^2 l(l+1)}{2I} = \frac{(1.054 \times 10^{-34} \text{ J} \cdot \text{s})^2 (1)(1+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)} = 7.67 \times 10^{-23} \text{ J}. \quad E_{l=0} = 0.$$

$$\Delta E = 7.67 \times 10^{-23} \text{ J} = 4.79 \times 10^{-4} \text{ eV}.$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(7.67 \times 10^{-23} \text{ J})} = 2.59 \times 10^{-3} \text{ m} = 2.59 \text{ mm}.$$

(b) Let's compare the value of kT when $T = 20 \text{ K}$ to that of ΔE for the $l=1 \rightarrow l=0$ rotational transition:

$$kT = (1.38 \times 10^{-23} \text{ J/K})(20 \text{ K}) = 2.76 \times 10^{-22} \text{ J}.$$

$$\Delta E = 7.67 \times 10^{-23} \text{ J (from part (a)). So } \frac{kT}{\Delta E} = 3.60.$$

Therefore, although T is quite small, there is still plenty of energy to excite CO molecules into the first rotational level. This allows astronomers to detect the 2.59 mm wavelength radiation from such molecular clouds.

42.43. IDENTIFY and SET UP: $E_l = l(l+1)\hbar^2/2I$, so E_l and the transition energy ΔE depend on l . Different isotopic molecules have different I .

EXECUTE: (a) Calculate I for Na^{35}Cl : $m_r = \frac{m_{\text{Na}}m_{\text{Cl}}}{m_{\text{Na}} + m_{\text{Cl}}} = \frac{(3.8176 \times 10^{-26} \text{ kg})(5.8068 \times 10^{-26} \text{ kg})}{3.8176 \times 10^{-26} \text{ kg} + 5.8068 \times 10^{-26} \text{ kg}} = 2.303 \times 10^{-26} \text{ kg}$

$$I = m_r r^2 = (2.303 \times 10^{-26} \text{ kg})(0.2361 \times 10^{-9} \text{ m})^2 = 1.284 \times 10^{-45} \text{ kg} \cdot \text{m}^2$$

$l=2 \rightarrow l=1$ transition

$$\Delta E = E_2 - E_1 = (6-2) \left(\frac{\hbar^2}{2I} \right) = \frac{2\hbar^2}{I} = \frac{2(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{1.284 \times 10^{-45} \text{ kg} \cdot \text{m}^2} = 1.734 \times 10^{-23} \text{ J}$$

$$\Delta E = \frac{hc}{\lambda} \text{ so } \lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{1.734 \times 10^{-23} \text{ J}} = 1.146 \times 10^{-2} \text{ m} = 1.146 \text{ cm}$$

$l=1 \rightarrow l=0$ transition

$$\Delta E = E_1 - E_0 = (2-0) \left(\frac{\hbar^2}{2I} \right) = \frac{\hbar^2}{I} = \frac{1}{2}(1.734 \times 10^{-23} \text{ J}) = 8.67 \times 10^{-24} \text{ J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{8.67 \times 10^{-24} \text{ J}} = 2.291 \text{ cm}$$

(b) Calculate I for Na^{37}Cl : $m_r = \frac{m_{\text{Na}}m_{\text{Cl}}}{m_{\text{Na}} + m_{\text{Cl}}} = \frac{(3.8176 \times 10^{-26} \text{ kg})(6.1384 \times 10^{-26} \text{ kg})}{3.8176 \times 10^{-26} \text{ kg} + 6.1384 \times 10^{-26} \text{ kg}} = 2.354 \times 10^{-26} \text{ kg}$

$$I = m_r r^2 = (2.354 \times 10^{-26} \text{ kg})(0.2361 \times 10^{-9} \text{ m})^2 = 1.312 \times 10^{-45} \text{ kg} \cdot \text{m}^2$$

$l = 2 \rightarrow l = 1$ transition

$$\Delta E = \frac{2\hbar^2}{I} = \frac{2(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{1.312 \times 10^{-45} \text{ kg} \cdot \text{m}^2} = 1.697 \times 10^{-23} \text{ J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{1.697 \times 10^{-23} \text{ J}} = 1.171 \times 10^{-2} \text{ m} = 1.171 \text{ cm}$$

$l = 1 \rightarrow l = 0$ transition

$$\Delta E = \frac{\hbar^2}{I} = \frac{1}{2}(1.697 \times 10^{-23} \text{ J}) = 8.485 \times 10^{-24} \text{ J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{8.485 \times 10^{-24} \text{ J}} = 2.341 \text{ cm}$$

The differences in the wavelengths for the two isotopes are:

$$l = 2 \rightarrow l = 1 \text{ transition: } 1.171 \text{ cm} - 1.146 \text{ cm} = 0.025 \text{ cm}$$

$$l = 1 \rightarrow l = 0 \text{ transition: } 2.341 \text{ cm} - 2.291 \text{ cm} = 0.050 \text{ cm}$$

EVALUATE: Replacing ^{35}Cl by ^{37}Cl increases I , decreases ΔE and increases λ . The effect on λ is small but measurable.

- 42.44.** The vibration frequency is, from Eq.(42.8), $f = \frac{\Delta E}{h} = 1.12 \times 10^{14} \text{ Hz}$. The force constant is

$$k' = (2\pi f)^2 m_r = 777 \text{ N/m.}$$

- 42.45.** $E_n = \left(n + \frac{1}{2}\right) \hbar \sqrt{\frac{k'}{m_r}} \Rightarrow E_0 = \frac{1}{2} \hbar \sqrt{\frac{2k'}{m_H}}$
- $$\Rightarrow E_0 = \frac{1}{2} (1.054 \times 10^{-34} \text{ J} \cdot \text{s}) \sqrt{\frac{2(576 \text{ N/m})}{1.67 \times 10^{-27} \text{ kg}}} = 4.38 \times 10^{-20} \text{ J} = 0.274 \text{ eV.}$$

This is much less than the H_2 bond energy.

- 42.46.** (a) The frequency is proportional to the reciprocal of the square root of the reduced mass, and in terms of the atomic masses, the frequency of the isotope with the deuterium atom is

$$f = f_0 \left(\frac{m_F m_H / (m_H + m_F)}{m_F m_D / (m_D + m_F)} \right)^{1/2} = f_0 \left(\frac{1 + (m_F / m_D)}{1 + (m_F / m_H)} \right)^{1/2}.$$

Using f_0 from Exercise 42.13 and the given masses, $f = 8.99 \times 10^{13} \text{ Hz}$.

- 42.47.** **IDENTIFY and SET UP:** Use Eq.(42.6) to calculate I . The energy levels are given by Eq.(42.9). The transition energy ΔE is related to the photon wavelength by $\Delta E = hc / \lambda$.

EXECUTE: (a) $m_r = \frac{m_H m_1}{m_H + m_1} = \frac{(1.67 \times 10^{-27} \text{ kg})(2.11 \times 10^{-25} \text{ kg})}{1.67 \times 10^{-27} \text{ kg} + 2.11 \times 10^{-25} \text{ kg}} = 1.657 \times 10^{-27} \text{ kg}$

$$I = m_r r^2 = (1.657 \times 10^{-27} \text{ kg})(0.160 \times 10^{-9} \text{ m})^2 = 4.24 \times 10^{-47} \text{ kg} \cdot \text{m}^2$$

- (b) The energy levels are $E_n = l(l+1) \left(\frac{\hbar^2}{2I} \right) + (n + \frac{1}{2}) \hbar \sqrt{\frac{k'}{m_r}}$ (Eq.(42.9))

$$\sqrt{\frac{k'}{m}} = \omega = 2\pi f \text{ so } E_n = l(l+1) \left(\frac{\hbar^2}{2I} \right) + (n + \frac{1}{2}) hf$$

(i) transition $n = 1 \rightarrow n = 0$, $l = 1 \rightarrow l = 0$

$$\Delta E = (2-0) \left(\frac{\hbar^2}{2I} \right) + (1 + \frac{1}{2} - \frac{1}{2}) hf = \frac{\hbar^2}{I} + hf$$

$$\Delta E = \frac{hc}{\lambda} \text{ so } \lambda = \frac{hc}{\Delta E} = \frac{hc}{(\hbar^2/I) + hf} = \frac{c}{(\hbar/2\pi I) + f}$$

$$\frac{\hbar}{2\pi I} = \frac{1.055 \times 10^{-34} \text{ J} \cdot \text{s}}{2\pi(4.24 \times 10^{-47} \text{ kg} \cdot \text{m}^2)} = 3.960 \times 10^{11} \text{ Hz}$$

$$\lambda = \frac{c}{(\hbar/2\pi I) + f} = \frac{2.998 \times 10^8 \text{ m/s}}{3.960 \times 10^{11} \text{ Hz} + 6.93 \times 10^{13} \text{ Hz}} = 4.30 \mu\text{m}$$

(ii) transition $n = 1 \rightarrow n = 0, l = 2 \rightarrow l = 1$

$$\Delta E = (6 - 2) \left(\frac{\hbar^2}{2I} \right) + hf = \frac{2\hbar^2}{I} + hf$$

$$\lambda = \frac{c}{2(\hbar/2\pi I) + f} = \frac{2.998 \times 10^8 \text{ m/s}}{2(3.960 \times 10^{11} \text{ Hz}) + 6.93 \times 10^{13} \text{ Hz}} = 4.28 \mu\text{m}$$

(iii) transition $n = 2 \rightarrow n = 1, l = 2 \rightarrow l = 3$

$$\Delta E = (6 - 12) \left(\frac{\hbar^2}{2I} \right) + hf = -\frac{3\hbar^2}{I} + hf$$

$$\lambda = \frac{c}{-3(\hbar/2\pi I) + f} = \frac{2.998 \times 10^8 \text{ m/s}}{-3(3.960 \times 10^{11} \text{ Hz}) + 6.93 \times 10^{13} \text{ Hz}} = 4.40 \mu\text{m}$$

EVALUATE: The vibrational energy change for the $n = 1 \rightarrow n = 0$ transition is the same as for the $n = 2 \rightarrow n = 1$ transition. The rotational energies are much smaller than the vibrational energies, so the wavelengths for all three transitions don't differ much.

42.48. The sum of the probabilities is $f(E_F + \Delta E) + f(E_F - \Delta E) = \frac{1}{e^{-\Delta E/kT} + 1} + \frac{1}{e^{\Delta E/kT} + 1} = \frac{1}{e^{-\Delta E/kT} + 1} + \frac{e^{-\Delta E/kT}}{1 + e^{-\Delta E/kT}} = 1$.

42.49. Since potassium is a metal we approximate $E_F = E_{F0}$. $\Rightarrow E_F = \frac{3^{2/3} \pi^{4/3} \hbar^2 n^{2/3}}{2m}$.

But the electron concentration $n = \frac{\rho}{m} \Rightarrow n = \frac{851 \text{ kg/m}^3}{6.49 \times 10^{-26} \text{ kg}} = 1.31 \times 10^{28} \text{ electron/m}^3$

$\Rightarrow E_F = \frac{3^{2/3} \pi^{4/3} (1.054 \times 10^{-34} \text{ J} \cdot \text{s})^2 (1.31 \times 10^{28} / \text{m}^3)^{2/3}}{2(9.11 \times 10^{-31} \text{ kg})} = 3.24 \times 10^{-19} \text{ J} = 2.03 \text{ eV}$.

42.50. IDENTIFY: The only difference between the two isotopes is their mass, which will affect their reduced mass and hence their moment of inertia.

SET UP: The rotational energy states are given by $E = l(l+1) \frac{\hbar^2}{2I}$ and the reduced mass is given by $m_r = m_1 m_2 / (m_1 + m_2)$.

EXECUTE: (a) If we call m the mass of the H-atom, the mass of the deuterium atom is $2m$ and the reduced masses of the molecules are

$$\text{H}_2 \text{ (hydrogen): } m_r(\text{H}) = mm/(m + m) = m/2$$

$$\text{D}_2 \text{ (deuterium): } m_r(\text{D}) = (2m)(2m)/(2m + 2m) = m$$

Using $I = m_r r_0^2$, the moments of inertia are $I_H = m r_0^2 / 2$ and $I_D = m r_0^2$. The ratio of the rotational energies is then

$$\frac{E_H}{E_D} = \frac{l(l+1) \left(\frac{\hbar^2}{2I_H} \right)}{l(l+1) \left(\frac{\hbar^2}{2I_D} \right)} = \frac{I_D}{I_H} = \frac{m r_0^2}{\frac{m r_0^2}{2}} = 2.$$

(b) The ratio of the vibrational energies is $\frac{E_H}{E_D} = \frac{\left(n + \frac{1}{2} \right) \hbar \sqrt{\frac{k'}{m_r(\text{H})}}}{\left(n + \frac{1}{2} \right) \hbar \sqrt{\frac{k'}{m_r(\text{D})}}} = \sqrt{\frac{m_r(\text{D})}{m_r(\text{H})}} = \sqrt{\frac{m}{m/2}} = \sqrt{2}$.

EVALUATE: The electrical force is the same for both molecules since both H and D have the same charge, so it is reasonable that the force constant would be the same for both of them.

41.51. IDENTIFY and SET UP: Use the description of the bcc lattice in Fig.42.12c in the textbook to calculate the number of atoms per unit cell and then the number of atoms per unit volume.

EXECUTE: (a) Each unit cell has one atom at its center and 8 atoms at its corners that are each shared by 8 other unit cells. So there are $1 + 8/8 = 2$ atoms per unit cell.

$$\frac{n}{V} = \frac{2}{(0.35 \times 10^{-9} \text{ m})^3} = 4.66 \times 10^{28} \text{ atoms/m}^3$$

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

In this equation N/V is the number of free electrons per m^3 . But the problem says to assume one free electron per atom, so this is the same as n/V calculated in part (a).

$m = 9.109 \times 10^{-31} \text{ kg}$ (the electron mass), so $E_{F0} = 7.563 \times 10^{-19} \text{ J} = 4.7 \text{ eV}$

EVALUATE: Our result for metallic lithium is similar to that calculated for copper in Example 42.8.

42.52. (a) $\frac{d}{dr}U_{\text{tot}} = \frac{ae^2}{4\pi\epsilon_0 r^2} - 8A\frac{1}{r^9}$. Setting this equal to zero when $r = r_0$ gives $r_0^7 = \frac{8A4\pi\epsilon_0}{ae^2}$

and so $U_{\text{tot}} = \frac{ae^2}{4\pi\epsilon_0} \left(-\frac{1}{r} + \frac{r_0^7}{8r^8} \right)$. At $r = r_0$, $U_{\text{tot}} = -\frac{7ae^2}{32\pi\epsilon_0 r_0} = -1.26 \times 10^{-18} \text{ J} = -7.85 \text{ eV}$.

(b) To remove a Na^+Cl^- ion pair from the crystal requires 7.85 eV. When neutral Na and Cl atoms are formed from the Na^+ and Cl^- atoms there is a net release of energy $-5.14 \text{ eV} + 3.61 \text{ eV} = -1.53 \text{ eV}$, so the net energy required to remove a neutral Na, Cl pair from the crystal is $7.85 \text{ eV} - 1.53 \text{ eV} = 6.32 \text{ eV}$.

42.53. (a) **IDENTIFY and SET UP:** $p = -\frac{dE_{\text{tot}}}{dV}$. Relate E_{tot} to E_{F0} and evaluate the derivative.

EXECUTE: $E_{\text{tot}} = NE_{\text{av}} = \frac{3N}{5}E_{\text{F0}} = \frac{3}{5} \left(\frac{3^{2/3} \pi^{4/3} \hbar^2}{2m} \right) N^{5/3} V^{-2/3}$

$\frac{dE_{\text{tot}}}{dV} = \frac{3}{5} \left(\frac{3^{2/3} \pi^{4/3} \hbar^2}{2m} \right) N^{5/3} \left(-\frac{2}{3} V^{-5/3} \right)$ so $p = \left(\frac{3^{2/3} \pi^{4/3} \hbar^2}{5m} \right) \left(\frac{N}{V} \right)^{5/3}$, as was to be shown.

(b) $N/V = 8.45 \times 10^{28} \text{ m}^{-3}$

$p = \left(\frac{3^{2/3} \pi^{4/3} (1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{5(9.109 \times 10^{-31} \text{ kg})} \right) (8.45 \times 10^{28} \text{ m}^{-3})^{5/3} = 3.81 \times 10^{10} \text{ Pa} = 3.76 \times 10^5 \text{ atm}$.

(c) **EVALUATE:** Normal atmospheric pressure is about 10^5 Pa , so these pressures are extremely large. The electrons are held in the metal by the attractive force exerted on them by the copper ions.

42.54. (a) From Problem 42.53, $p = \frac{3^{2/3} \pi^{4/3} \hbar^2}{5m} \left(\frac{N}{V} \right)^{5/3}$. $B = -V \frac{dp}{dV} = -V \left[\frac{5}{3} \cdot \frac{3^{2/3} \pi^{4/3} \hbar^2}{5m} \cdot \left(\frac{N}{V} \right)^{2/3} \left(\frac{-N}{V^2} \right) \right] = \frac{5}{3} p$.

(b) $\frac{N}{V} = 8.45 \times 10^{28} \text{ m}^{-3}$. $B = \frac{5}{3} \cdot \frac{3^{2/3} \pi^{4/3} \hbar^2}{5m} (8.45 \times 10^{28} \text{ m}^{-3})^{5/3} = 6.33 \times 10^{10} \text{ Pa}$.

(c) $\frac{6.33 \times 10^{10} \text{ Pa}}{1.4 \times 10^{11} \text{ Pa}} = 0.45$. The copper ions themselves make up the remaining fraction.

42.55. (a) $E_{\text{F0}} = \frac{3^{2/3} \pi^{4/3} \hbar^2}{2m} \left(\frac{N}{V} \right)^{2/3}$. Let $E_{\text{F0}} = \frac{1}{100} mc^2$.

$\left(\frac{N}{V} \right) = \left[\frac{2m^2 c^2}{(100) 3^{2/3} \pi^{4/3} \hbar^2} \right]^{3/2} = \frac{2^{3/2} m^3 c^3}{100^{3/2} 3\pi^2 \hbar^3} = \frac{2^{3/2} m^3 c^3}{3000\pi^2 \hbar^3} = 1.67 \times 10^{33} \text{ m}^{-3}$.

(b) $\frac{8.45 \times 10^{28} \text{ m}^{-3}}{1.67 \times 10^{33} \text{ m}^{-3}} = 5.06 \times 10^{-5}$. Since the real concentration of electrons in copper is less than one part in 10^4 of the concentration where relativistic effects are important, it is safe to ignore relativistic effects for most applications.

(c) The number of electrons is $N_e = \frac{6(2 \times 10^{30} \text{ kg})}{1.99 \times 10^{-26} \text{ kg}} = 6.03 \times 10^{56}$. The concentration is

$\frac{N_e}{V} = \frac{6.03 \times 10^{56}}{\frac{4}{3} \pi (6.00 \times 10^6 \text{ m})^3} = 6.66 \times 10^{35} \text{ m}^{-3}$.

(d) Comparing this to the result from part (a) $\frac{6.66 \times 10^{35} \text{ m}^{-3}}{1.67 \times 10^{33} \text{ m}^{-3}} \cong 400$ so relativistic effects will be very important.

42.56. **IDENTIFY:** The current through the diode is related to the voltage across it.

SET UP: The current through the diode is given by $I = I_S (e^{eV/kT} - 1)$.

EXECUTE: (a) The current through the resistor is $(35.0 \text{ V})/(125 \Omega) = 0.280 \text{ A} = 280 \text{ mA}$, which is also the current through the diode. This current is given by $I = I_S (e^{eV/kT} - 1)$, giving $280 \text{ mA} = 0.625 \text{ mA} (e^{eV/kT} - 1)$ and $1 +$

$(280/0.625) = 449 = e^{eV/kT}$. Solving for V at $T = 293 \text{ K}$ gives $V = \frac{kT \ln 449}{e} = \frac{(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K}) \ln 449}{1.60 \times 10^{-19} \text{ C}} =$

0.154 V

(b) $R = V/I = (0.154 \text{ V})/(0.280 \text{ A}) = 0.551 \Omega$

EVALUATE: At a different voltage, the diode would have different resistance.

$$42.57. \quad (\text{a}) \quad U = \frac{1}{4\pi\epsilon_0} \sum_{i < j} \frac{q_i q_j}{r_{ij}} = \frac{q^2}{4\pi\epsilon_0} \left(\frac{-1}{d} + \frac{1}{r} - \frac{1}{r+d} - \frac{1}{r-d} + \frac{1}{r} - \frac{1}{d} \right) = \frac{q^2}{4\pi\epsilon_0} \left(\frac{2}{r} - \frac{2}{d} - \frac{1}{r+d} - \frac{1}{r-d} \right).$$

$$\text{But } \frac{1}{r+d} + \frac{1}{r-d} = \frac{1}{r} \left(\frac{1}{1+\frac{d}{r}} + \frac{1}{1-\frac{d}{r}} \right) \approx \frac{1}{r} \left(1 - \frac{d}{r} + \frac{d^2}{r^2} + \dots + 1 + \frac{d}{r} + \frac{d^2}{r^2} \right) \approx \frac{2}{r} + \frac{2d^2}{r^3}$$

$$\Rightarrow U = \frac{-2q^2}{4\pi\epsilon_0} \left(\frac{1}{d} + \frac{d^2}{r^3} \right) = \frac{-2p^2}{4\pi\epsilon_0 r^3} - \frac{2p^2}{4\pi\epsilon_0 d^3}.$$

$$(\text{b}) \quad U = \frac{1}{4\pi\epsilon_0} \sum_{i < j} \frac{q_i q_j}{r_{ij}} = \frac{q^2}{4\pi\epsilon_0} \left(\frac{-1}{d} - \frac{1}{r} + \frac{1}{r+d} + \frac{1}{r-d} - \frac{1}{r} - \frac{1}{d} \right) = \frac{q^2}{4\pi\epsilon_0} \left(\frac{-2}{d} - \frac{2}{r} + \frac{2}{r} + \frac{2d^2}{r^3} \right) =$$

$$\frac{-2q^2}{4\pi\epsilon_0} \left(\frac{1}{d} - \frac{d^2}{r^3} \right) \Rightarrow U = \frac{-2p^2}{4\pi\epsilon_0 d^3} + \frac{2p^2}{4\pi\epsilon_0 r^3}.$$

If we ignore the potential energy involved in forming each individual molecule, which just involves a different choice for the zero of potential energy, then the answers are:

$$(\text{a}) \quad U = \frac{-2p^2}{4\pi\epsilon_0 r^3}. \quad \text{The interaction is attractive.}$$

$$(\text{b}) \quad U = \frac{+2p^2}{4\pi\epsilon_0 r^3}. \quad \text{The interaction is repulsive.}$$

$$42.58. \quad (\text{a}) \quad \text{Following the hint, } k'dr = -d \left(\frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \right)_{r=r_0} = \frac{1}{2\pi\epsilon_0} \frac{e^2}{r_0^3} dr \quad \text{and} \quad \hbar\omega = \hbar\sqrt{2k'/m} = \hbar\sqrt{\frac{1}{\pi\epsilon_0} \frac{e^2}{mr_0^3}} =$$

$1.23 \times 10^{-19} \text{ J} = 0.77 \text{ eV}$, where $(m/2)$ has been used for the reduced mass.

(b) The reduced mass is doubled, and the energy is reduced by a factor of $\sqrt{2}$ to 0.54 eV .