# 42

# Molecules and Solids

* An asterisk indicates a question or problem new to this edition.

## ANSWERS TO THINK-PAIR-SHARE ACTIVITES

**\*TP 42.1**  **Conceptualize** In a gas, all of the atoms of the gas are free to translate around the interior of the container. In a solid, the atoms are locked into place, so they can only vibrate. A simplified version of the Dulong-Petit law argues that each atom has three dimensions in which it can vibrate, each dimension involving two types of energy, kinetic and potential, for a total of six degrees of freedom: $6(R/2) = 3R$. In a

metal, we have additional degrees of freedom associated with the freely moving electrons.

**Categorize** We categorize the problem as one involving the band theory of metals in association with the treatment of molar specific heats from kinetic theory.

**Analyze** We wish to evaluate the ratio

$$\frac{C_{\text{free electrons}}}{C_{\text{total}}} = \frac{C_{\text{free electrons}}}{3R} \qquad (1)$$

where we have used the result from the Dulong–Petit law for the denominator.

The molar specific heat due to the free electrons will be the product of the fraction of the electrons that are free and the molar specific heat for translational motion of particles in three dimensions, given by Equation 20.29:

$$C_{\text{free electrons}} = \frac{k_{\text{B}}T}{E_{\text{F}}}\left(\tfrac{3}{2}R\right) \qquad (2)$$

Substitute Equation (2) into Equation (1):

$$\frac{C_{\text{free electrons}}}{C_{\text{total}}} = \frac{\dfrac{k_{\text{B}}T}{E_{\text{F}}}\left(\tfrac{3}{2}R\right)}{3R} = \frac{k_{\text{B}}T}{2E_{\text{F}}}$$

Substitute numerical values, using the Fermi energy for gold from Table 42.1:

$$\frac{C_{\text{free electrons}}}{C_{\text{total}}} = \frac{\left(1.381 \times 10^{-23}\ \text{J/K}\right)\left(300\ \text{K}\right)}{2\left(5.53\ \text{eV}\right)}\left(\frac{1\,\text{eV}}{1.602 \times 10^{-19}\ \text{J}}\right)$$

$$= 2.34 \times 10^{-3} = \boxed{0.234\%}$$

**Finalize** We have performed a simplified calculation here. A more detailed calculation shows that the percentage is closer to 0.8%. In either case, the free electrons provide only a very small fraction of the total molar specific heat.

*Answer:* 0.234%

**\*TP 42.2** **Conceptualize** Both molecules can be analyzed using the material in Section 42.2.

**Categorize** We categorize the problem as one in which we analyze the molecular spectrum of a diatomic molecule.

**Analyze** (a) The energy of the photon emitted in a vibrational transition is given by Equation 42.11:

$$E_{photon} = \frac{h}{2\pi}\sqrt{\frac{k_{H_2}}{\mu_{H_2}}} \qquad (1)$$

From Equation 42.4, find an expression for the reduced mass of a symmetric diatomic molecule:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m^2}{2m} = \tfrac{1}{2}m \qquad (2)$$

From Equation (2), substitute for the reduced mass in Equation (1), and use Equation 39.5 to express the photon energy in terms of its frequency:

$$hf_{photon} = \frac{h}{2\pi}\sqrt{\frac{k_{H_2}}{\tfrac{1}{2}m_H}} \quad \rightarrow \quad f_{H_2} = \frac{1}{2\pi}\sqrt{\frac{k_{H_2}}{\tfrac{1}{2}m_H}} \qquad (3)$$

Substitute numerical values:

$$f_{H_2} = \frac{1}{2\pi}\sqrt{\frac{576\ \text{N/m}}{\tfrac{1}{2}\left(1.674\ ´\ 10^{-27}\ \text{kg}\right)}} = \boxed{1.32\ ´\ 10^{14}\ \text{Hz}}$$

(b) From Figure 33.13, we see that this photon is in the near-infrared

region of the spectrum.

(c) From Figure 33.13, we see that the photon of frequency $1.15 \times 10^{11}$

Hz is at the extreme of the far-infrared region of the spectrum,

overlapping with the microwave region.

(d) For astronomers to see these *emitted* photons, the molecules must

be thermally excited to the higher energy level first. After that, the

transition to the lower level can occur. Let us find the energy difference

between the levels using Equation 39.5:

$$E_{H_2} = hf_{H_2} = \left(6.626 \text{ ' } 10^{-34} \text{ J} \cdot \text{s}\right)\left(1.32 \text{ ' } 10^{14} \text{ Hz}\right)\left(\frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}}\right)$$

$$= 0.548 \text{ eV}$$

$$E_{CO} = hf_{CO} = \left(6.626 \times 10^{-34} \text{ J} \cdot \text{s}\right)\left(1.15 \times 10^{11} \text{ Hz}\right)\left(\frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}}\right)$$

$$= 4.76 \times 10^{-4} \text{ eV}$$

Now, let's calculate a typical amount of energy available thermally at $T$

= 20 K:

$$E = k_B T = \left(1.381 \times 10^{-23} \text{ J/ K}\right)\left(20 \text{ K}\right)\left(\frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}}\right) = 1.72 \times 10^{-3} \text{ eV}$$

This energy is enough to excite the first level of CO, but is only 0.3% of

that necessary to excite $H_2$. Therefore, while there are many $H_2$ molecules

in a molecular cloud, virtually none of them will emit photons!

**Finalize** The formation of new stars occurs in molecular clouds.

Therefore, these clouds are sometimes called *stellar nurseries*.]

*Answers:* (a) $1.32 \times 10^{14}$ Hz  (b) near-infrared  (c) far-

infrared/microwave  (d) Virtually no $H_2$ molecules are excited.

**\*TP 42.3** **Conceptualize** Imagine a photon entering the material and exciting an electron from the valence band to the conduction band. The photon must have energy at least equal to the band gap energy to do this.

**Categorize** We will be using the relationships between photon energy, frequency, and wavelength.

**Analyze** (a) Use Equations 39.5 and Equation 16.12 to find the wavelength of the photon in terms of its energy:

$$E = hf = \frac{hc}{\lambda} \quad \rightarrow \quad \lambda = \frac{hc}{E} \qquad (1)$$

The maximum wavelength of a photon making the transition from the valence band to the conduction band, will be for a photon with energy equal to the band gap energy. Use Equation (1) to find that wavelength for each of the entries in the table:

| Material | Chemical Symbol | Band Gap (eV) | Photon Wavelength ($\mu$m) |
|---|---|---|---|
| Lead sulfide | PbS | 0.37 | 3. 4 |
| Germanium | Ge | 0.67 | 1.9 |
| Silicon | Si | 1.11 | 1.12 |
| Gallium arsenide | GaAs | 1.43 | 0.867 |
| Copper oxide | $Cu_2O$ | 2.1 | 0.59 |
| Gallium phosphide | GaP | 2.26 | 0.549 |
| Gallium nitride | GaN | 3.4 | 0.36 |
| Silicon nitride | $Si_3N_4$ | 5.0 | 0.25 |
| Diamond | C | 5.5 | 0.23 |
| Silicon dioxide | $SiO_2$ | 9.0 | 0.14 |

(b) According to Table 33.1, the wavelengths of visible light are between 400 nm and 700 nm, or between 0.400 $\mu$m and 0.700 $\mu$m. Therefore, the final four materials in the table will be transparent to visible light, because the required photon wavelengths are smaller than those of visible light photons. Consequently, visible light photons do not have sufficient energy to excite an electron across the band gap energy for these materials. Such a photon will not be absorbed in the material by exciting an electron to the conduction band, so it will pass through the material, making the material transparent.

**Finalize** Notice the simple criterion for whether a material is transparent to visible light or not.]

*Answers:* (a) See the revised table below.

| Material | Chemical Symbol | Band Gap (eV) | Photon Wavelength ($\mu$m) |
|---|---|---|---|
| Lead sulfide | PbS | 0.37 | 3. 4 |
| Germanium | Ge | 0.67 | 1.9 |
| Silicon | Si | 1.11 | 1.12 |
| Gallium arsenide | GaAs | 1.43 | 0.867 |
| Copper oxide | $Cu_2O$ | 2.1 | 0.59 |
| Gallium phosphide | GaP | 2.26 | 0.549 |
| Gallium nitride | GaN | 3.4 | 0.36 |
| Silicon nitride | $Si_3N_4$ | 5.0 | 0.25 |
| Diamond | C | 5.5 | 0.23 |
| Silicon dioxide | $SiO_2$ | 9.0 | 0.14 |

(b) The final four materials in the table will be transparent.
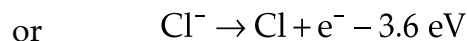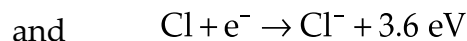
## Section 42.1    Molecular Bonds

**P42.1**    At the boiling or condensation temperature,

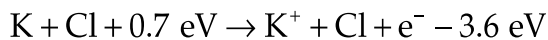$$E = \frac{3}{2}k_B T \approx 10^{-3} \text{ eV} = 10^{-3}\left(1.6 \times 10^{-19} \text{ J}\right)$$

Solving for the temperature $T$ gives,

$$T = \frac{E}{k_B} \approx \frac{2\left(1.6 \times 10^{-22} \text{ J}\right)}{3\left(1.38 \times 10^{-23} \text{ J/K}\right)} \boxed{\sim 10 \text{ K}}$$

**P42.2**    We are told that

$$K + Cl + 0.70 \text{ eV} \rightarrow K^+ + Cl^-$$

and    $$Cl + e^- \rightarrow Cl^- + 3.6 \text{ eV}$$

or    $$Cl^- \rightarrow Cl + e^- - 3.6 \text{ eV}$$

By substitution,

$$K + Cl + 0.7 \text{ eV} \rightarrow K^+ + Cl + e^- - 3.6 \text{ eV}$$

$$K + 4.3 \text{ eV} \rightarrow K^+ + e^-$$

or the ionization energy of potassium is $\boxed{4.3 \text{ eV}}$.

**P42.3**    (a)    The minimum energy of the molecule at $r = r_0$ is found from

$$\frac{dU}{dr} = -12Ar_0^{-13} + 6Br_0^{-7} = 0$$

yielding

$$r_0 = \left[\frac{2A}{B}\right]^{1/6}$$

$$= \left[\frac{2\left(0.124 \times 10^{-120} \text{ eV} \cdot \text{m}^{12}\right)}{1.488 \times 10^{-60} \text{ eV} \cdot \text{m}^6}\right]^{1/6} = 7.42 \times 10^{-11} \text{ m} = \boxed{74.2 \text{ pm}}$$

(b)  The energy required to break up the molecule would separate the atoms from $r = r_0$ to $r = \infty$:

$$E = U\big|_{r=\infty} - U\big|_{r=r_0} = 0 - \left[\frac{A}{4A^2/B^2} - \frac{B}{2A/B}\right] = -\left[\frac{1}{4} - \frac{1}{2}\right]\frac{B^2}{A} = \frac{B^2}{4A}$$

$$E = \frac{\left(1.488 \times 10^{-60} \text{ eV} \cdot \text{m}^6\right)^2}{4\left(0.124 \times 10^{-120} \text{ eV} \cdot \text{m}^{12}\right)} = \boxed{4.46 \text{ eV}}$$

This is also the equal to the binding energy, the amount of energy given up by the two atoms as they come together to form a molecule.

**P42.4**  (a)  The minimum energy of the molecule at $r = r_0$ is found from

$$\frac{dU}{dr} = -12Ar_0^{-13} + 6Br_0^{-7} = 0$$

yielding

$$r_0 = \left[\frac{2A}{B}\right]^{1/6}$$

(b)  The energy required to break up the molecule would separate the atoms from $r = r_0$ to $r = \infty$:

$$E = U\big|_{r=\infty} - U\big|_{r=r_0} = 0 - \left[\frac{A}{4A^2/B^2} - \frac{B}{2A/B}\right] = -\left[\frac{1}{4} - \frac{1}{2}\right]\frac{B^2}{A} = \boxed{\frac{B^2}{4A}}$$

## Section 42.2      Energy States and Spectra of Molecules

**P42.5**      (a)   Recall from Chapter 41 that the energy of the photon is given by

$$hf = \Delta E = \frac{\hbar^2}{2I}[2(2+1)] - \frac{\hbar^2}{2I}[1(1+1)] = \frac{\hbar^2}{2I}(4)$$

Then,

$$I = \frac{4(h/2\pi)^2}{2hf} = \frac{h}{2\pi^2 f} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{2\pi^2 (2.30 \times 10^{11} \text{ Hz})}$$

$$= \boxed{1.46 \times 10^{-46} \text{ kg} \cdot \text{m}^2}$$

(b)   The results are the same, suggesting that the bond length of the molecule does not change measurably between the two transitions.

**P42.6**      (a)   From Equation 42.10, the energy separation between the ground and first excited state is

$$\Delta E_{\text{vib}} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} = hf \qquad \text{so} \qquad k = 4\pi^2 f^2 \mu$$

and the reduced mass is

$$\mu = \frac{k}{4\pi^2 f^2} = \frac{1530 \text{ N/m}}{4\pi^2 (56.3 \times 10^{12} \text{ s}^{-1})^2} = \boxed{1.22 \times 10^{-26} \text{ kg}}$$

(b) From Equation 42.4, the reduced mass is

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(14.007 \text{ u})(15.999 \text{ u})}{14.007 \text{ u} + 15.999 \text{ u}}\left(\frac{1.66 \times 10^{-27} \text{ kg}}{1 \text{ u}}\right)$$

$$= \boxed{1.24 \times 10^{-26} \text{ kg}}$$

(c)   They agree because the small apparent difference can be attributed to uncertainty in the data.

**P42.7** (a) With $r$ representing the distance of each atom from the center of mass, the moment of inertia is

$$mr^2 + mr^2 = 2mr^2$$

$$= 2(1.008 \text{ u}) \left( \frac{1.66 \times 10^{-27} \text{ kg}}{\text{u}} \right) \left( \frac{0.750 \times 10^{-10} \text{ m}}{2} \right)^2$$

$$= 4.71 \times 10^{-48} \text{ kg} \cdot \text{m}^2$$

The allowed rotational energies (from Equation 42.6) are

$$E_{\text{rot}} = \frac{\hbar^2}{2I} J(J+1)$$

The $J = 0$ state has energy $E_{\text{rot}} = 0$, and the $J = 1$ state has energy

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

$$= \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s}/2\pi)^2}{(4.71 \times 10^{-48} \text{ kg} \cdot \text{m}^2)} \left( \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} \right)$$

$$= 1.48 \times 10^{-2} \text{ eV} = \boxed{0.014\ 8 \text{ eV}}$$

(b) The energy of the photon that raises the molecule from 0 to 0.014 8 eV is 0.014 8 eV. The photon's wavelength is

$$\lambda = \frac{h}{E} = \frac{1240 \text{ eV} \cdot \text{nm}}{0.0148 \text{ eV}} = 8.41 \times 10^4 \text{ nm}$$

$$= 84.1 \times 10^3 \text{ nm} = \boxed{84.1 \ \mu\text{m}}$$

**P42.8** From Equation 42.10, the energy separation between the ground and first excited state is

$$\Delta E_{\text{vib}} = \hbar \sqrt{\frac{k}{\mu}} = \hbar \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

Substituting numerical values,

$$\Delta E_{vib} = \left(1.055 \times 10^{-34} \text{ J} \cdot \text{s}\right)\sqrt{\frac{(480 \text{ N/m})(35+1)}{(35)(1)\left(1.66 \times 10^{-27} \text{ kg}\right)}}$$

$$= 5.75 \times 10^{-20} \text{ J} = 0.359 \text{ eV}$$

To excite a transition with this energy difference, the wavelength of incident photons must be

$$\lambda = \frac{hc}{\Delta E_{vib}} = \frac{1\,240 \text{ eV} \cdot \text{nm}}{0.359 \text{ eV}} = 3.45 \times 10^{3} \text{ nm}$$

The incident photons have a wavelength longer than this, which means they have less energy than 0.359 eV. Therefore, these photons cannot excite the molecule to the first excited state.

**P42.9**    The mass to consider is the molecule's reduced mass. Iodine has atomic mass 126.90 u and a hydrogen atom is 1.007 9 u, so the reduced mass of HI is

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(126.90 \text{ u})(1.007\ 9 \text{ u})}{126.90 \text{ u} + 1.007\ 9 \text{ u}} = 0.999\ 96 \text{ u}$$

Now for the energy of the ground state we have

$$E = \frac{1}{2}kA^2 = \left(0 + \frac{1}{2}\right)hf = \frac{1}{2}\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

So the amplitude is

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

(a)   For HI we have

$$A = \left( \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{2\pi} \right)^{1/2}$$

$$\times \left( \frac{1}{(320 \text{ N/m})(0.999 \ 96)(1.66 \times 10^{-27} \text{kg})} \right)^{1/4}$$

$$= \boxed{1.20 \times 10^{-11} \text{ m} = 12.0 \text{ pm}}$$

(b)   Flourine has an atomic mass of 18.998 4 u, so, for HF,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(18.998 \ 4 \text{ u})(1.007 \ 9 \text{ u})}{18.998 \ 4 \text{ u} + 1.007 \ 9 \text{ u}} = 0.957 \ 12 \text{ u}$$

and

$$A = \left( \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{2\pi} \right)^{1/2}$$

$$\times \left( \frac{1}{(970 \text{ N/m})(0.957 \ 12)(1.66 \times 10^{-27} \text{kg})} \right)^{1/4}$$

$$= \boxed{9.22 \times 10^{-12} \text{ m} = 9.22 \text{ pm}}$$

**P42.10**   Masses $m_1$ and $m_2$ have the respective distances $r_1$ and $r_2$ from the center of mass. Then,

$$m_1 r_1 = m_2 r_2 \quad \text{and} \quad r_1 + r_2 = r$$

So,        $r_1 = \dfrac{m_2 r_2}{m_1}$

and thus,   $\dfrac{m_2 r_2}{m_1} + r_2 = r \quad \rightarrow \quad r_2 = \dfrac{m_1 r}{m_1 + m_2}$

Also,      $r_2 = \dfrac{m_1 r_1}{m_2}$

thus,      $r_1 + \dfrac{m_1 r_1}{m_2} = r \quad \rightarrow \quad r_1 = \dfrac{m_2 r}{m_1 + m_2}$

The moment of inertia of the molecule is then

$$I = m_1 r_1^2 + m_2 r_2^2 = m_1 \frac{m_2^2 r^2}{\left(m_1 + m_2\right)^2} + m_2 \frac{m_1^2 r^2}{\left(m_1 + m_2\right)^2}$$

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

**P42.11** We carry extra digits through the solution because part (c) involves the subtraction of two close numbers. The longest wavelength corresponds to the smallest energy difference between the rotational energy levels. It is between $J = 0$ and $J = 1$, namely

$$\Delta E_{min} = \frac{\hbar^2}{I}$$

The wavelength is then

$$\lambda = \frac{hc}{\Delta E_{min}} = \frac{hc}{\hbar^2 / I} = \frac{4\pi^2 I c}{h}$$

If $\mu = \dfrac{m_H m_{Cl}}{m_H + m_{Cl}}$ is the reduced mass, then

$$I = \mu r^2 = \mu \left(0.127\ 46 \times 10^{-9}\ \text{m}\right)^2$$

and therefore,

$$\lambda = \frac{4\pi^2 \left[\mu \left(0.127\ 46 \times 10^{-9}\ \text{m}\right)^2\right]\left(2.997\ 925 \times 10^8\ \text{m/s}\right)}{6.626\ 075 \times 10^{-34}\ \text{J} \cdot \text{s}}$$

$$= \left(2.901\ 830 \times 10^{23}\ \text{m/kg}\right)\mu \tag{1}$$

(a) For $^{35}$Cl,

$$\mu_{35} = \frac{\left(1.007\ 825u\right)\left(34.968\ 853u\right)}{1.007\ 825u + 34.968\ 853u}\left(\frac{1.660540 \times 10^{-27}\ \text{kg}}{u}\right)$$

$$= 1.626\ 653 \times 10^{-27}\ \text{kg}$$

From equation [1],

$$\lambda_{35} = (2.901\,830 \times 10^{23} \text{ m/kg})(1.626\,653 \times 10^{-27} \text{ kg})$$
$$= \boxed{472 \ \mu\text{m}}$$

(b) For $^{37}$Cl,

$$\mu_{37} = \frac{(1.007\,825\text{u})(36.965\,903\text{u})}{1.007\,825\text{u} + 36.965\,903\text{u}} \left( \frac{1.660\,540 \times 10^{-27} \text{ kg}}{\text{u}} \right)$$
$$= 1.629\,118 \times 10^{-27} \text{ kg}$$

From equation [1],

$$\lambda_{37} = (2.901\,830 \times 10^{23} \text{ m/kg})(1.629\,118 \times 10^{-27} \text{ kg}) = \boxed{473 \ \mu\text{m}}$$

(c) The separation in wavelength is

$$\lambda_{37} - \lambda_{35} = 472.742\,4 \ \mu\text{m} - 472.027\,0 \ \mu\text{m} = \boxed{0.715 \ \mu\text{m}}$$

**\*P42.12** **Conceptualize** While the spectrum in Figure P42.11 is often used to determine *rotational* information, there is a piece of *vibrational* information contained within it. The peaks in the spectrum correspond to the selection rules $\Delta J = +1$ and $\Delta J = -1$. They also correspond to a vibrational change of $\Delta v = +1$. Between the peaks for $\Delta J = +1$ and $\Delta J = -1$ is a gap. The center of that gap would correspond to the forbidden $\Delta J = 0$ transition.

**Categorize** We model the HCl molecule as a *nonisolated system* for *energy*.

**Analyze** Write the appropriate reduction of Equation 8.2 for this system:

$$\Delta E_{\text{vib}} = T_{\text{ER}} \quad (1)$$

where $\Delta E_{vib}$ includes both kinetic and potential energy contributions. Substitute for both sides of the equation for the time interval during which a photon is absorbed and raises the molecule to the next allowed vibrational state, using Equation 42.11:

$$\hbar\sqrt{\frac{k}{\mu}} = hf \qquad (2)$$

Solve for the effective spring constant $k$:

$$k = 4\pi^2 \mu f^2 \qquad (3)$$

Substitute for the reduced mass of the HCl molecule:

$$k = 4\pi^2 \left( \frac{m_H m_{Cl}}{m_H + m_{Cl}} \right) f^2 \qquad (4)$$

Substitute numerical values, estimating the frequency $f$ as halfway between the peaks on either side of the gap in the middle of Figure 42.2:

$$k = 4\pi^2 \left[ \frac{(1\,u)(35\,u)}{1\,u + 35\,u} \right] \left( \frac{1.66 \times 10^{-27}\,kg}{1\,u} \right) (8.64 \times 10^{13}\,Hz)^2 = \boxed{476\,N/m}$$

**Finalize** This value for $k$ is smaller than that for the CO molecule in Example 42.2, but consistent with values for HCl reported elsewhere. Watch for the look on the face of your colleague as you effortlessly report this value!]

*Answer:* 476 N/m

**P42.13**   We carry extra digits through the solution because the given wavelengths are close together.

(a)   The energy levels are given by

$$E_{vJ} = \left(v + \frac{1}{2}\right)hf + \frac{\hbar^2}{2I}J(J+1)$$

Therefore,

$$E_{00} = \frac{1}{2}hf, \quad E_{11} = \frac{3}{2}hf + \frac{\hbar^2}{I}, \text{ and } E_{02} = \frac{1}{2}hf + \frac{3\hbar^2}{I}$$

Then,

$$\Delta E_1 = E_{11} - E_{00} = hf + \frac{\hbar^2}{I} = \frac{hc}{\lambda_1}$$

$$= \frac{\left(6.626\,075 \times 10^{-34} \text{ J·s}\right)\left(2.997\,925 \times 10^8 \text{ m/s}\right)}{2.211\,2 \times 10^{-6} \text{ m}}$$

$$\Delta E_1 = hf + \frac{\hbar^2}{I} = 8.983\,573 \times 10^{-20} \text{ J} \qquad \textbf{[1]}$$

and

$$\Delta E_2 = E_{11} - E_{02} = hf - \frac{2\hbar^2}{I} = \frac{hc}{\lambda_2}$$

$$= \frac{\left(6.626\,075 \times 10^{-34} \text{ J·s}\right)\left(2.997\,925 \times 10^8 \text{ m/s}\right)}{2.405\,4 \times 10^{-6} \text{ m}}$$

$$\Delta E_2 = hf - \frac{2\hbar^2}{I} = 8.258\,284 \times 10^{-20} \text{ J} \qquad \textbf{[2]}$$

Subtracting equation [2] from [1] gives,

$$\Delta E_1 - \Delta E_2 = \left(hf + \frac{\hbar^2}{I}\right) - \left(hf - \frac{2\hbar^2}{I}\right) = \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2}$$

solving,

$$\frac{3\hbar^2}{I} = hc\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right) \quad \rightarrow \quad \frac{3h}{4\pi^2 I} = c\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)$$

Then,

$$\frac{3h}{4\pi^2 I} = c\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)$$

$$= \left(2.997\,925 \times 10^8 \text{ m/s}\right)$$

$$\times \left(\frac{1}{2.211\,2 \times 10^{-6} \text{ m}} - \frac{1}{2.405\,4 \times 10^{-6} \text{ m}}\right)$$

$$= 1.0946 \times 10^{13} \text{ s}^{-1}$$

Solving for the moment of inertia then gives

$$I = \frac{3\left(6.626\,075 \times 10^{-34} \text{ J} \cdot \text{s}\right)}{4\pi^2\left(1.094\,6 \times 10^{13} \text{ s}^{-1}\right)} = \boxed{4.60 \times 10^{-48} \text{ kg} \cdot \text{m}^2}$$

(b)   From equation [1]:

$$f_1 = \frac{\Delta E_1}{h} - \frac{\hbar^2}{2\pi I}$$

$$= \frac{8.983\,573 \times 10^{-20} \text{ J}}{6.626\,075 \times 10^{-34} \text{ J} \cdot \text{s}} - \frac{\left(6.626\,075 \times 10^{-34} \text{ J} \cdot \text{s}\right)}{2\pi\left(4.600\,060 \times 10^{-48} \text{ kg} \cdot \text{m}^2\right)}$$

$$= \boxed{1.32 \times 10^{14} \text{ Hz}}$$

(c)   The moment of inertia of the molecule is given by $I = \mu r^2$, where $\mu$ is the reduced mass,

$$\mu = \frac{1}{2}m_H = \frac{1}{2}\left(1.007\,825\text{u}\right) = 8.367\,669 \times 10^{-28} \text{ kg}$$

The equilibrium separation distance is then,

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{4.600\,060 \times 10^{-48} \text{ kg} \cdot \text{m}^2}{8.367\,669 \times 10^{-28} \text{ kg}}} = \boxed{0.074\,1 \text{ nm}}$$

**P42.14**   (a)   In benzene, the dashed lines form equilateral triangles, so the carbon atoms are each 0.110 nm from the axis and each hydrogen atom is (0.110 + 0.100 nm) = 0.210 nm from the axis. Thus, the moment of inertia is given by

$$I = \sum mr^2 = 6\left(1.99 \times 10^{-26} \text{ kg}\right)\left(0.110 \times 10^{-9} \text{ m}\right)^2$$

$$+ 6\left(1.67 \times 10^{-27} \text{ kg}\right)\left(0.210 \times 10^{-9} \text{ m}\right)^2$$

$$= \boxed{1.89 \times 10^{-45} \text{ kg} \cdot \text{m}^2}$$

(b)   The allowed rotational energies are then

$$E_{\text{rot}} = \frac{\hbar^2}{2I} J(J+1) = \frac{\left(1.055 \times 10^{-34} \text{ J} \cdot \text{s}\right)^2}{2\left(1.89 \times 10^{-45} \text{ kg} \cdot \text{m}^2\right)} J(J+1)$$

$$= \left(2.95 \times 10^{-24} \text{ J}\right) J(J+1) = \left(18.4 \times 10^{-6} \text{ eV}\right) J(J+1)$$

$$\boxed{E_{\text{rot}} = 18.4 J(J+1) \text{, where } E_{\text{rot}} \text{ is in microelectron volts and } J = 0,1,2,3,\ldots .}$$

The first five of these allowed energies are:

$$E_{\text{rot}} = 0, \ 36.9 \ \mu\text{eV}, \ 111 \ \mu\text{eV}, \ 221 \ \mu\text{eV, and } 369 \ \mu\text{eV}$$

**P42.15**   The moment of inertia about the molecular axis is

$$I_y = \frac{2}{5} mr^2 + \frac{2}{5} mr^2 = \frac{4}{5} m \left(2.00 \times 10^{-15} \text{ m}\right)^2$$

The moment of inertia about a perpendicular axis is

$$I_x = m\left(\frac{R}{2}\right)^2 + m\left(\frac{R}{2}\right)^2 = \frac{m}{2}\left(2.00 \times 10^{-10} \text{ m}\right)^2$$

The allowed rotational energies are $E_{\text{rot}} = \left(\dfrac{\hbar^2}{2I}\right) J(J+1)$, so the energy

of the first excited state is $E_1 = \dfrac{\hbar^2}{I}$. The ratio is therefore

$$\frac{E_{1,y}}{E_{1,x}} = \frac{\left(\hbar^2/I_y\right)}{\left(\hbar^2/I_x\right)} = \frac{I_x}{I_y} = \frac{(1/2)m\left(2.00\times10^{-10}\ \text{m}\right)^2}{(4/5)m\left(2.00\times10^{-15}\ \text{m}\right)^2}$$

$$= \frac{5}{8}\left(10^5\right)^2 = \boxed{6.25\times10^9}$$

**P42.16** We find an average spacing between peaks by counting 22 gaps (counting the central gap as two) between $7.96\times10^{13}$ Hz and $9.24\times10^{13}$ Hz:

$$\Delta f = \frac{(9.24-7.96)\times10^{13}\ \text{Hz}}{22} = 0.058\ 2\times10^{13}\ \text{Hz}$$

$$= 5.82\times10^{11}\ \text{Hz} = \frac{1}{h}\left(\frac{h^2}{4\pi^2 I}\right)$$

The moment of inertia is then

$$I = \frac{h}{4\pi^2 \Delta f} = \frac{6.626\times10^{-34}\ \text{J}\cdot\text{s}}{4\pi^2\left(5.82\times10^{11}\ \text{s}^{-1}\right)} = \boxed{2.88\times10^{-47}\ \text{kg}\cdot\text{m}^2}$$

---

# Section 42.3 Bonding in Solids

**P42.17** (a) Consider a cubical salt crystal of edge length 0.1 mm.

The number of atoms is $\left(\dfrac{10^{-4}\ \text{m}}{0.261\times10^{-9}\ \text{m}}\right)^3 = 6\times10^{16}\ \boxed{\sim 10^{17}}$.
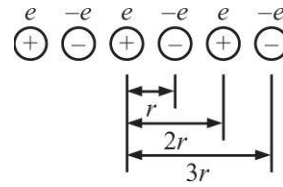
(b) This number of salt crystals would have volume

$$\left(10^{-4}\ \text{m}\right)^3 6\times10^{16} = 6\times10^4\ \boxed{\sim 10^5\ \text{m}^3}$$

If it is cubic, it has edge length 40 m.

**P42.18** We assume the ions are all singly ionized.

The total potential energy is obtained by summing over all interactions of our ion with others:



**ANS. FIG. P42.18**

$$U = \sum_{i \neq j} k_e \frac{q_i q_j}{r_{ij}}$$

$$= -k_e \left[ \frac{e^2}{r} + \frac{e^2}{r} - \frac{e^2}{2r} - \frac{e^2}{2r} + \frac{e^2}{3r} + \frac{e^2}{3r} - \frac{e^2}{4r} - \frac{e^2}{4r} + \cdots \right]$$

$$U = -2k_e \frac{e^2}{r} \left[ 1 - \tfrac{1}{2} + \tfrac{1}{3} - \tfrac{1}{4} + \cdots \right]$$

But from Appendix B.5,

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

Our series follows this pattern with $x = 1$, so the potential energy of one ion due to its interactions with all the others is

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

## Section 42.4 Free-Electron Theory of Metals

**P42.19** (a) Setting the kinetic energy equal to the Fermi energy,

$$\frac{1}{2} mv^2 = 7.05 \text{ eV}$$

we solve for the speed of the conduction electron as

$$v = \sqrt{\frac{2(7.05 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{9.11 \times 10^{-31} \text{ kg}}}$$

$$= 1.57 \times 10^6 \text{ m/s} = \boxed{1.57 \text{ Mm/s}}$$

(b) Compared to the drift velocity of 0.1 mm/s = $10^{-4}$ mm/s, the $\boxed{\text{speed}}$ $\boxed{\text{is larger by ten orders of magnitude.}}$ The energy of an electron at room temperature is typically $k_B T = \dfrac{1}{40}$ eV.

**P42.20** (a) $\boxed{\text{The Fermi energy is proportional to the spatial concentration of free electrons to the two-thirds power.}}$

(b) From Equation 42.21,

$$E_F = \frac{h^2}{2m}\left(\frac{3n_e}{8\pi}\right)^{2/3}$$

$$= \frac{\left(6.626 \times 10^{-34} \text{ J·s}\right)^2}{2\left(9.11 \times 10^{-31} \text{ kg}\right)\left(1.60 \times 10^{-19} \text{ J/eV}\right)}\left(\frac{3}{8\pi}\right)^{2/3} n_e^{2/3}$$

becomes

$$E_F = \left(3.65 \times 10^{-19}\right)n_e^{2/3}$$

where $E_F$ is in electron volts and $n_e$ in electrons per cubic meter.

(c) Copper has the greater concentration of free electrons by a factor of

$$\frac{n_e(\text{Cu})}{n_e(\text{K})} = \frac{8.46 \times 10^{-19} \text{ m}^{-3}}{1.40 \times 10^{-19} \text{ m}^{-3}} = \boxed{6.04}$$

(d) $\boxed{\text{Copper}}$ has the greater Fermi energy, 7.05 eV.

(e) The Fermi energy is larger by a factor of $7.05 \text{ eV}/2.12 \text{ eV} = \boxed{0.333}$.

(f)   This behavior agrees with the proportionality because $E_F \sim n_e^{2/3}$

and $6.04^{2/3} = 3.32$.

**P42.21**   (a)   From Equation 42.24,

$$E_{avg} = \frac{3}{5}E_F = 0.6(7.05 \text{ eV}) = \boxed{4.23 \text{ eV}}$$

(b)   The average energy of a molecule in an ideal gas is $\frac{3}{2}k_B T$ so we

have

$$T = \frac{2}{3}\frac{4.23 \text{ eV}}{1.38 \times 10^{-23} \text{ J/K}}\frac{1.6 \times 10^{-19} \text{ J}}{1 \text{ eV}} = \boxed{3.27 \times 10^4 \text{ K}}$$

**P42.22**   For sodium, $M = 23.0$ g/mol and $\rho = 0.971$ g/cm³. Sodium contributes
one electron per atom to the conduction band.

(a)   The density of conduction electrons is

$$n_e = \frac{N_A \rho}{M} = \frac{(6.02 \times 10^{23} \text{ electrons/mol})(0.971 \text{ g/cm}^3)}{23.0 \text{ g/mol}}$$

$$n_e = 2.54 \times 10^{22} \text{ electrons/cm}^3 = \boxed{2.54 \times 10^{28} \text{ m}^{-3}}$$

(b)   From Equation 42.25,

$$E_F = \left(\frac{h^2}{2m}\right)\left(\frac{3n_e}{8\pi}\right)^{2/3}$$

$$= \frac{(6.626 \times 10^{-34} \text{ J·s})^2}{2(9.11 \times 10^{-31} \text{ kg})}\left[\frac{3(2.54 \times 10^{28} \text{ m}^{-3})}{8\pi}\right]^{2/3}$$

$$= 5.05 \times 10^{-19} \text{ J} = \boxed{3.15 \text{ eV}}$$

**P42.23**   Consider first the wave function in $x$. At $x = 0$ and $x = L$, $\Psi = 0$.

Therefore,

$$\sin k_x L = 0 \quad \text{and} \quad k_x L = \pi,\, 2\pi,\, 3\pi,\, \dots$$

Similarly, $\sin k_y L = 0 \quad \text{and} \quad k_y L = \pi,\, 2\pi,\, 3\pi,\, \dots$

and $\qquad \sin k_z L = 0 \quad \text{and} \quad k_z L = \pi,\, 2\pi,\, 3\pi,\, \dots$

Then,

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

From Schrödinger's Equation, $\dfrac{\partial^2 \psi}{\partial x^2} + \dfrac{\partial^2 \psi}{\partial y^2} + \dfrac{\partial^2 \psi}{\partial z^2} = \dfrac{2m_e}{\hbar^2}(U - E)\psi$, we

have inside the box, where $U = 0$,

$$\left( -\frac{n_x^2 \pi^2}{L^2} - \frac{n_y^2 \pi^2}{L^2} - \frac{n_z^2 \pi^2}{L^2} \right) \psi = \frac{2m_e}{\hbar^2}(-E)\psi$$

Therefore,

$$\boxed{\; E = \frac{\hbar^2 \pi^2}{2m_e L^2}\left( n_x^2 + n_y^2 + n_z^2 \right) \qquad n_x,\, n_y,\, n_z = 1,\, 2,\, 3,\, \dots \;}$$

Outside the box we require $\psi = 0$. The minimum energy state inside the

box is $n_x = n_y = n_z = 1$, with $E = \dfrac{3\hbar^2 \pi^2}{2m_e L^2}$.

**P42.24**   From Equation 42.22, the number density of free electrons is

$$n_e = \frac{2}{3}\frac{8\sqrt{2}\pi m_e^{3/2}}{h^3} E_F^{3/2}$$

$$= \frac{2}{3}\frac{8\sqrt{2}\pi \left(9.11\times 10^{-31}\,\text{kg}\right)^{3/2}}{\left(6.626\times 10^{-34}\,\text{J}\cdot\text{s}\right)^3}\left(5.48\,\text{eV}\right)^{3/2}\left(\frac{1.602\times 10^{-19}\,\text{J}}{1\,\text{eV}}\right)^{3/2}$$

$$= 5.83\times 10^{28}\,\text{m}^{-3}$$

Then, the number density of atoms in the metal is

$$n_{\text{atoms}} = \frac{nN_A}{V} = \frac{mN_A}{MV} = \frac{\rho N_A}{M}$$

$$= \frac{\left(4.90 \times 10^3 \text{ kg/m}^3\right)\left(6.02 \times 10^{23} \text{ mol}^{-1}\right)}{0.100 \text{ kg/mol}}$$

$$= 2.95 \times 10^{28} \text{ m}^{-3}$$

Then the number of free electrons per atom is

$$\frac{n_e}{n_{\text{atoms}}} = \frac{5.83 \times 10^{28} \text{ m}^{-3}}{2.95 \times 10^{28} \text{ m}^{-3}} = 1.97$$

Therefore, there are approximately two free electrons per atom for this metal, not one.

**P42.25** We are to compute

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

where from Equation 42.22,

$$N(E) = \frac{CE^{1/2}}{e^{(E-E_F)/k_B T} + 1} = Cf(E)E^{1/2}$$

with $\qquad C = \dfrac{8\sqrt{2}\pi m_e^{3/2}}{h^3}$

But at $T = 0$ the Fermi-Dirac distribution function is $f(E) = 0$ for $E > E_F$, and $f(E) = 1$ for $E < E_F$. So we can take $N(E) = CE^{1/2}$ just for energies up to the Fermi energy. The average we want is then

$$E_{\text{avg}} = \frac{1}{n_e} \int_0^{E_F} CE^{3/2} dE = \frac{2C}{5n_e} E_F^{5/2}$$

But from Equation 42.22, $\dfrac{C}{n_e} = \dfrac{3}{2} E_F^{-3/2}$, so

$$E_{avg} = \left(\frac{2}{5}\right)\left(\frac{3}{2}\right)\left(E_F^{-3/2}\right)E_F^{5/2} = \boxed{\frac{3}{5}E_F}$$

**P42.26** The density of states at the energy $E$ is $g(E) = CE^{1/2}$.

(a) Hence, the required ratio is

$$R_{states} = \frac{g(8.50 \text{ eV})}{g(7.05 \text{ eV})} = \frac{C(8.50)^{1/2}}{C(7.05)^{1/2}} = \boxed{1.10}$$

(b) From Equation 42.20, we see that the number of occupied states between energy $E$ and energy $E + dE$ is

$$N(E)dE = \frac{CE^{1/2}}{e^{(E-E_F)/k_BT} + 1}dE$$

Hence, the required ratio is

$$R_{occupied\ states} = \frac{N(8.50 \text{ eV})}{N(7.05 \text{ eV})} = \sqrt{\frac{8.50}{7.05}}\left[\frac{e^{(7.05-7.05)/k_BT} + 1}{e^{(8.50-7.05)/k_BT} + 1}\right]$$

At $T = 300$ K, we compute

$$k_BT = \left(1.380\ 65\times10^{-23}\ \frac{\text{J}}{\text{K}}\right)(300.000 \text{ K})\left(\frac{1 \text{ eV}}{1.602\ 18\times10^{-19}\text{J}}\right)$$
$$= 0.025\ 852\ 0 \text{ eV}$$

so $\quad R_{occ.st} = \left(\frac{8.50}{7.05}\right)^{1/2}\left(\frac{2}{e^{1.45/0.025\ 852\ 0} + 1}\right) = \boxed{9.61\times10^{-25}}$

With an exponent of 56.1, the derivative of the exponential function is so large that none of the digits in 9.61 is really significant. Different-looking answers would result from different choices of how precisely to represent the input data.

(c) The answer to part (b) is vastly smaller than the answer to (a). Very few states well above the Fermi energy are occupied at room temperature.

## Section 42.5    Electrical Conduction in Metals, Insulators and Semiconductors

**P42.27**    (a)    $E_g = 1.14$ eV for Si. The photon energy, given by $E = hf$, must be at least this energy. Then,

$$f = \frac{E}{h} = \frac{(1.14 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV})}{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}$$

$$= 2.76 \times 10^{14} \text{ Hz} = 276 \times 10^{12} \text{ Hz} = \boxed{276 \text{ THz}}$$

(b)    From $c = \lambda f$,

$$\lambda = \frac{c}{f} = \frac{3.00 \times 10^8 \text{ m/s}}{2.75 \times 10^{14} \text{ Hz}} = 1.09 \times 10^{-6} \text{ m} = \boxed{1.09 \text{ } \mu\text{m}} \text{ (infrared)}$$

**P42.28**    (a)    From Table 42.2, the energy gap for CdS is 2.42 eV, so photons of energy greater than 2.42 eV will be absorbed, corresponding to wavelengths shorter than

$$\lambda = \frac{hc}{E} = \frac{1240 \text{ eV} \cdot \text{nm}}{2.42 \text{ eV}} = 512 \text{ nm}$$

All the Balmer lines lie between the shortest (series limit) produced by the transition $n = \infty \rightarrow 2$, with energy

$$\Delta E = 13.6 \text{ eV} \left( \frac{1}{2^2} \right) = 3.40 \text{ eV}$$

is      $$\lambda = \frac{hc}{E} = \frac{1240 \text{ eV} \cdot \text{nm}}{3.40 \text{ eV}} = 365 \text{ nm}$$

The longest produced by the transition $n = 3 \rightarrow 2$, with energy

$$\Delta E = 13.6 \text{ eV} \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = 1.89 \text{ eV}$$

is    $\lambda = \dfrac{hc}{E} = \dfrac{1240 \text{ eV} \cdot \text{nm}}{1.89 \text{ eV}} = 656 \text{ nm}$

All the hydrogen Balmer lines except for the red line at 656 nm will be absorbed.

(b)   The red line at 656 nm will be transmitted.

**P42.29**   The wavelength 0.512 $\mu$m = 512 nm. The corresponding photon energy is just sufficient to promote an electron across the gap.

$$E_g = \dfrac{hc}{\lambda} = \dfrac{1240 \text{ eV} \cdot \text{nm}}{512 \text{ nm}} = \boxed{2.42 \text{ eV}}$$

**\*P42.30**   **Conceptualize** The issue involved is whether the ultraviolet photons will pass through the diamond window without interacting with it or the photons will excite electrons from the valence band to the conduction band.

**Categorize** We model the diamond crystal structure as a *nonisolated system* for *energy*.

**Analyze** Write the appropriate reduction of Equation 8.2 for this system:

$$\Delta E = T_{ER} \quad (1)$$

where $E$ represents all energy contributions to the crystal that result in its particular band structure. The radiation on the right side of Equation (1) is carried by a single ultraviolet photon:

$$\Delta E = hf = \dfrac{hc}{\lambda} \quad (2)$$

Substitute numerical values:

$$\Delta E = \frac{\left(6.626 \times 10^{-34} \text{ J} \cdot \text{s}\right)\left(3.00 \times 10^{8} \text{ m/s}\right)}{220 \times 10^{-9} \text{ m}} \left(\frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}}\right) = 5.64 \text{ eV}$$

This energy is larger than the energy gap of 5.47 eV, so many of the ultraviolet photons will be absorbed in the diamond by raising electrons from the valence band to the conduction band. So, no, the diamond window will not allow you to warm the sample with the laser.

**Finalize** Diamond is not a good choice for a window for this laser. Or, equivalently, this laser is not a good choice for a diamond window.]

*Answer:* no

**P42.31** (a) In the Bohr model we replace $k_e$ by $k_e/\kappa$ and $m_e$ by $m^*$. Then the radius of the first Bohr orbit, $a_0 = \frac{\hbar^2}{m_e k_e e^2}$ in hydrogen, changes to

$$a' = \frac{\hbar^2}{m^*\left(k_e/\kappa\right)e^2} = \frac{\hbar^2 \kappa}{m^* k_e e^2} = \left(\frac{m_e}{m^*}\right)\kappa \frac{\hbar^2}{m_e k_e e^2} = \boxed{\left(\frac{m_e}{m^*}\right)\kappa\, a_0}$$

(b) Substituting numerical values,

$$a' = \left(\frac{m_e}{m^*}\right)\kappa\, a_0 = \left(\frac{m_e}{0.220 m_e}\right)(11.7)(0.052\ 9 \text{ nm}) = \boxed{2.81 \text{ nm}}$$

(c) The energy levels for hydrogen are $E_n = -\frac{k_e e^2}{2a_0}\frac{1}{n^2}$. Making the replacements $k_e \rightarrow k_e/\kappa$ and $a_0 \rightarrow a'$, we have

$$E_n' = -\frac{\left(k_e/\kappa\right)e^2}{2\left[\left(m_e/m^*\right)\kappa\, a_0\right]}\frac{1}{n^2} = -\frac{k_e e^2}{2\kappa^2\left[\left(m_e/m^*\right)a_0\right]}\frac{1}{n^2}$$

$$= -\frac{1}{\kappa^2}\left(\frac{m^*}{m_e}\right)\left(\frac{k_e e^2}{2a_0}\frac{1}{n^2}\right) = \boxed{-\left(\frac{m^*}{m_e}\right)\frac{E_n}{\kappa^2}}$$

(d) For $n = 1$,

$$E_1' = -0.220\left(\frac{13.6 \text{ eV}}{11.7^2}\right) = \boxed{-0.021\ 9 \text{ eV}}.$$

## Section 42.6     Semiconductor Devices

**P42.32**    Equation 42.25 is

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

Thus,     $e^{e(\Delta V)/k_B T} = 1 + \dfrac{I}{I_0}$

and     $\Delta V = \dfrac{k_B T}{e}\ln\left(1 + \dfrac{I}{I_0}\right)$

At $T = 300$ K,

$$\Delta V = \frac{\left(1.38 \times 10^{-23} \text{ J/K}\right)(300 \text{ K})}{1.60 \times 10^{-19} \text{ C}}\ln\left(1 + \frac{I}{I_0}\right)$$

$$= (25.9 \text{ mV})\ln\left(1 + \frac{I}{I_0}\right)$$

(a) If $I = 9.00 I_0$,

$$\Delta V = (25.9 \text{ mV})\ln(10.0) = \boxed{59.5 \text{ mV}}$$

(b) If $I = -0.900 I_0$,

$$\Delta V = (25.9 \text{ mV})\ln(0.100) = \boxed{-59.5 \text{ mV}}$$

The basic idea behind a semiconductor device is that a large current or charge can be controlled by a small control voltage.

**P42.33**   First, we evaluate $I_0$ in $I = I_0\left(e^{e\Delta V/k_BT} - 1\right)$, given that $I = 200$ mA when

$\Delta V = 100$ mV and $T = 300$ K.

$$\frac{e\Delta V}{k_BT} = \frac{\left(1.60 \times 10^{-19} \text{ C}\right)\left(0.100 \text{ V}\right)}{\left(1.38 \times 10^{-23} \text{ J/K}\right)\left(300 \text{ K}\right)} = 3.86$$

so    $I_0 = \dfrac{I}{e^{e(\Delta V)/k_BT} - 1} = \dfrac{200 \text{ mA}}{e^{3.86} - 1} = 4.28$ mA

If $V = -100$ mV, $\dfrac{e(\Delta V)}{k_BT} = -3.86$; and the current will be

$$I = I_0\left(e^{e\Delta V/k_BT} - 1\right) = \left(4.28 \text{ mA}\right)\left(e^{-3.86} - 1\right) = \boxed{-4.19 \text{ mA}}$$

**P42.34**   (a)   The current in the diode, and thus in all elements of the series circuit,

is $I = I_0\left(e^{e\Delta V/k_BT} - 1\right)$. Appling Kirchhoff's loop rule in the direction of the current, going through the negative to the positive side of the battery, then through the diode, and then the resistor, we get

$$\mathcal{E} - \Delta V - IR = 0$$
$$\mathcal{E} - \Delta V - I_0R\left(e^{e\Delta V/k_BT} - 1\right) = 0$$

or    $\mathcal{E} - \Delta V = I_0R\left(e^{e\Delta V/k_BT} - 1\right)$
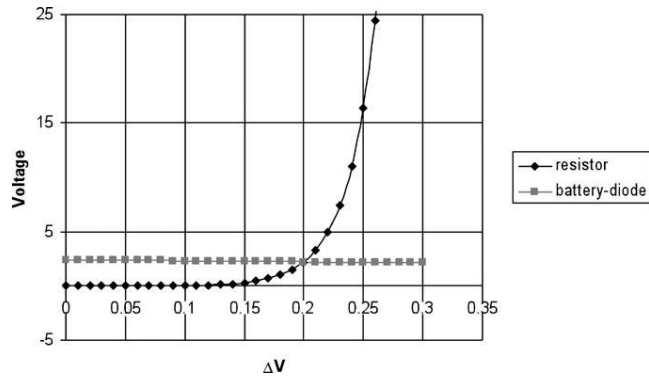
(b)   The graphs to be plotted are the voltage across the resistor,

$$\Delta V_{\text{resistor}} = IR = \left(1.00 \times 10^{-6} \text{ A}\right)\left(745 \text{ } \Omega\right)\left(e^{\Delta V/0.0250 \text{ V}} - 1\right)$$
$$= \left(7.45 \times 10^{-4} \text{ A}\right)\left(e^{\Delta V/0.025 \text{ V}} - 1\right)$$

and the voltage across the battery and diode combined,

$$\Delta V_{\text{BD}} = \mathcal{E} - \Delta V = 2.42 \text{ V} - \Delta V$$

The graphs are plotted in ANS. FIG. P42.34 below.

**ANS. FIG. P42.34**

(c) The two graphs intersect at $\Delta V = 0.200$ V. The current is then

$$I = \left(1.00 \times 10^{-6} \text{ A}\right)\left(e^{0.200 \text{ V}/0.025\,0 \text{ V}} - 1\right) = 2.98 \times 10^{-3} \text{ A} = \boxed{2.98 \text{ mA}}$$

(d) The ohmic resistance of the diode is

$$R_{\text{ohmic}} = \frac{\Delta V}{I} = \frac{0.200 \text{ V}}{2.98 \times 10^{-3} \text{ A}} = \boxed{67.1 \text{ }\Omega}$$

(e) The dynamic resistance of the diode is

$$R_{\text{dynamic}} = d\left(\Delta V\right)/dI = \left[dI/d\left(\Delta V\right)\right]^{-1}$$

where $I = I_0\left(e^{e\Delta V/k_B T} - 1\right)$. Then,

$$\frac{dI}{d\left(\Delta V\right)} = \frac{d}{d\left(\Delta V\right)}\left[I_0\left(e^{e\Delta V/k_B T} - 1\right)\right] = \frac{eI_0}{k_B T}e^{e\Delta V/k_B T}$$

Therefore,

$$R_{\text{dynamic}} = \frac{d\left(\Delta V\right)}{dI} = \left[\frac{dI}{d\left(\Delta V\right)}\right]^{-1} = \left[\frac{eI_0}{k_B T}e^{e\Delta V/k_B T}\right]^{-1}$$

$$= \left[\frac{1.00 \times 10^{-6} \text{ A}}{0.0250 \text{ V}}e^{0.200 \text{ V}/0.025\,0 \text{ V}}\right]^{-1} = \boxed{8.39 \text{ }\Omega}$$

**P42.35** From Equation 42.25, the current in the diode is a function of $\Delta V$ is

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

where $k_B T = 0.025\ 0$ eV. Therefore,

$$\frac{I(+\Delta V)}{I(-\Delta V)} = \frac{I_0\left(e^{e\Delta V/k_B T} - 1\right)}{I_0\left(e^{e(-\Delta V)/k_B T} - 1\right)} = \frac{e^{e\Delta V/k_B T} - 1}{e^{e(-\Delta V)/k_B T} - 1}$$

$$\frac{I(+1.00\text{ V})}{I(-1.00\text{ V})} = \frac{e^{1.00/0.025\ 0} - 1}{e^{-1.00/0.025\ 0} - 1} = \frac{e^{40} - 1}{e^{-40} - 1} = \boxed{-2.35 \times 10^{17}}$$

---

## Additional Problems

**P42.36**   For the $N_2$ molecule, $k = 2\ 297$ N/m, $m = 2.32 \times 10^{-26}$ kg, and

$r = 1.20 \times 10^{-10}$ m. The reduced mass is, from Equation 42.4,

$$\mu = \frac{mm}{m+m} = \frac{m}{2}$$

The frequency of vibration for the molecule is, from Equation 43.8,

$$\omega = \sqrt{\frac{k}{\mu}} = 4.45 \times 10^{14}\ \text{rad/s}$$

and the moment of inertia is, from Equation 43.3,

$$I = \mu r^2 = \left(1.16 \times 10^{-26}\ \text{kg}\right)\left(1.20 \times 10^{-10}\ \text{m}\right)^2$$
$$= 1.67 \times 10^{-46}\ \text{kg} \cdot \text{m}^2$$

The allowed vibrational energies are, from Equation 43.9,

$$E_{\text{vib}} = \left(v + \frac{1}{2}\right)\hbar\omega,\ \text{where } v = 1, 2, 3\ldots$$

The first excited vibrational state is above the vibrational ground state

by the energy difference $\Delta E = \hbar\omega$. For the rotational state that is above

the rotational ground state by the same energy difference, we require

$$\frac{\hbar^2}{2I}J(J+1)=\hbar\omega$$

or

$$J(J+1)=\frac{2I\omega}{\hbar}=\frac{2\left(1.67\times10^{-46}\ \text{kg}\cdot\text{m}^2\right)\left(4.45\times10^{14}\ \text{rad/s}\right)}{1.055\times10^{-34}\ \text{J}\cdot\text{s}}$$
$$=1\,410.$$

Thus, by inspection, $\boxed{J=37}$.

**P42.37** From Equation 42.9, the allowed vibrational energies are

$$E_{\text{vib}}=\left(v+\frac{1}{2}\right)\hbar\omega,\ \text{where } v=1,\,2,\,3\ldots$$

For the vibrational energy level that is just below the dissociation energy, we require

$$E_{\text{vib}}=\left(v+\frac{1}{2}\right)\hbar\omega\le E_{\text{max}}=4.48\ \text{eV}$$

or,  $\quad v\le\dfrac{E_{\text{max}}}{\hbar\omega}-\dfrac{1}{2}=\dfrac{E_{\text{max}}}{\hbar\omega}-\dfrac{1}{2}$

$$v\le\frac{\left(4.48\ \text{eV}\right)\left(1.60\times10^{-19}\ \text{J/eV}\right)}{\left[6.626\times10^{-34}\ \text{J}\cdot\text{s}/2\pi\right]\left(8.28\times10^{14}\ \text{rad/s}\right)}-\frac{1}{2}=7.7$$

Therefore, because $v$ is an integer, $\boxed{v=7}$.

**\*P42.38** **Conceptualize** Compare the first term in Equation 42.1 to Equation 42.16 and be sure to understand the difference between a potential energy for two atoms and a potential energy for an entire crystal.

**Categorize** The problem involves the relationship between force and the potential energy function discussed in Section 7.8. In parts (b) and (c), we will be modeling the ion as a *particle in simple harmonic motion*.

**Analyze** The modification of Equation 42.1 suggested in the problem statement for an entire crystal is

$$U_{total} = -\alpha k_e \frac{e^2}{r} + \frac{B}{r^m} \qquad (1)$$

To find an expression for the force on a single ion displaced from equilibrium, let us take a hint from Equation 7.29 and differentiate Equation (1) with respect to $r$:

$$F = -\frac{dU_{total}}{dr} = -\frac{d}{dr}\left(-\alpha k_e \frac{e^2}{r} + \frac{B}{r^m}\right) = -\alpha k_e \frac{e^2}{r^2} + m\frac{B}{r^{m+1}} \qquad (2)$$

The potential energy $U_{total}(r)$ is minimized when the atoms are separated by a distance $r = r_0$, determined by setting the derivative of the potential energy function with respect to $r$ equal to zero:

$$-\alpha k_e \frac{e^2}{r_0^2} + m\frac{B}{r_0^{m+1}} = 0 \quad \rightarrow \quad B = \alpha k_e \frac{e^2}{m} r_0^{m-1} \qquad (3)$$

Substitute for $B$ from Equation (3) into Equation (2):

$$F = -\alpha k_e \frac{e^2}{r^2} + m\frac{\left(\alpha k_e \dfrac{e^2}{m} r_0^{m-1}\right)}{r^{m+1}} = -\alpha k_e \frac{e^2}{r^2}\left[1 - \left(\frac{r_0}{r}\right)^{m-1}\right] \qquad (4)$$

(b) In Equation (4), let $r = r_0 + s$:

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

Use the binomial expansion to rewrite the parentheses, keeping only the first two terms in each expansion because $s$ is small compared to $r_0$:

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

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

where we have ignored the term with $s^2/r_0^2$, again because $s$ is small compared to $r_0$. This equation is of the form $F = -Ks$, where

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

(c) From Equation 15.45, the frequency of vibration of a sodium ion in the crystal is

$$f = \frac{1}{2\pi}\sqrt{\frac{K}{m_{Na^+}}} = \frac{1}{2\pi}\sqrt{\frac{\alpha k_e e^2}{r_0^3}\frac{(m-1)}{m_{Na^+}}} \qquad (5)$$

Substitute numerical values, using the sodium–chlorine spacing in Figure 37.20:

$$f = \frac{1}{2\pi}\sqrt{\frac{(1.747\,6)(8.99\times10^9\ \text{N}\cdot\text{m}^2/\text{C}^2)(1.60\times10^{-19}\ \text{C})^2}{\left(\dfrac{0.562\,737\times10^{-9}\ \text{m}}{2}\right)^3}\frac{(8-1)}{(23.0\ \text{u})}\left(\frac{1\,\text{u}}{1.66\times10^{-27}\ \text{kg}}\right)}$$

$$= 9.16\times10^{12}\ \text{Hz} = \boxed{9.16\ \text{THz}}$$

**Finalize** This frequency is in the infrared region of the electromagnetic spectrum. Notice that the vibration frequency in Equation (5) does not depend on the reduced mass of the sodium chloride molecule. When the ions are in a crystal structure, the identity of single molecules is not present and each ion vibrates independently in the field created by the entire crystal.]

*Answer:* (a) *See the solution.* (b) *See the solution.* (c) 9.16 THz

**P42.39**    We assume the potential well is that of a harmonic-oscillator. From Equation 42.9, the allowed energies of vibration of the molecule are

$$E_{vib} = \left( v + \frac{1}{2} \right) hf$$

To dissociate the atoms, enough energy must be supplied to raise their energy to the top of the potential well. The energy required to dissociate the atoms in the ground state ($v = 0$) is 4.48 eV; thus, the well depth is $\frac{1}{2} hf + 4.48$ eV. In the first excited vibrational state ($v = 1$), the dissociation energy is 3.96 eV; thus, the well depth is $\frac{3}{2} hf + 3.96$ eV. Then, the depth of the well is

$$\frac{1}{2} hf + 4.48 \text{ eV} = \frac{3}{2} hf + 3.96 \text{ eV}$$

from which we see that $hf = 0.52$ eV. Therefore, the depth of the well is

$$\frac{1}{2} hf + 4.48 \text{ eV} = \frac{1}{2} (0.520 \text{ eV}) + 4.48 \text{ eV} = \boxed{4.74 \text{ eV}}$$

**\*P42.40    Conceptualize** Figure 42.1b shows the potential energy curve for a pair of ions. The equilibrium separation distance $r_0$ corresponds to a binding energy of $U_0$. Equation 42.1 gives the mathematical form of the equation for the energy of the pair as a function of distance. We would like to modify this equation to represent the entire crystal, rather than just a pair of ions.

**Categorize** This problem will involve calculating the electric potential energy of a large number of ions in an ionic crystal.

**Analyze** Equation 42.16 shows the modified form of the first term in Equation 42.1, in terms of the Madelung constant. In Section 42.1, we mentioned that the second term in Equation 42.1 corresponds to repulsion due to the exclusion principle. This type of repulsion occurs only when the ions are very close together, so that electron shells overlap. Therefore, it will only be important for nearest neighbors; other ions are separated by too large a distance for this to be a consideration. As a result, the second term in Equation 42.1 is unaltered for a collection of ions. Therefore, the appropriate modification of Equation 42.1 for an entire crystal is

$$U_{\text{total}} = -\alpha k_e \frac{e^2}{r} + \frac{B}{r^m} \qquad (1)$$

The potential energy $U_{\text{total}}(r)$ is minimized when the atoms are separated by a distance $r = r_0$, determined by setting the derivative of the potential energy function with respect to $r$ equal to zero:

$$\frac{dU_{\text{total}}}{dr} = \frac{d}{dr}\left(-\alpha k_e \frac{e^2}{r} + \frac{B}{r^m}\right) = \alpha k_e \frac{e^2}{r^2} - m\frac{B}{r^{m+1}} = 0 \qquad (2)$$

Now, solve for $B$:

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

Substitute for $B$ from Equation (3) into Equation (1):

$$U_0 = -\alpha k_e \frac{e^2}{r_0} + \frac{\alpha k_e \dfrac{e^2}{m} r_0^{m-1}}{r_0^m} = -\alpha k_e \frac{e^2}{r_0}\left(1 - \frac{1}{m}\right) \qquad (4)$$

Equation (4) is the equation printed on the student's slip of paper.

**Finalize** The *ionic cohesive energy* is the energy per ion pair to separate the crystal into a collection of positive and negative ions infinitely far apart. For example, the ionic cohesive energy for NaCl is –7.84 eV per ion pair. The *atomic cohesive energy* is the energy per ion pair to separate the crystal into a collection of neutral atoms infinitely far apart. It differs due to the energy necessary to transfer an electron from on atom to the other to form the ions. The atomic cohesive energy for NaCl is –6.32 eV per ion pair.]

**Answer:** *See the solution.*

**P42.41** (a) For equilibrium, $\dfrac{dU}{dx} = 0$:

$$\frac{d}{dx}\left(Ax^{-3} - Bx^{-1}\right) = -3Ax^{-4} + Bx^{-2} = 0$$

$x \rightarrow \infty$ describes one equilibrium position, but the stable equilibrium position $x_0$ is at

$$-3Ax_0^{-4} + Bx_0^{-2} = 0$$

solving,

$$x_0^2 = \frac{3A}{B} \quad \rightarrow \quad x_0 = \sqrt{\frac{3A}{B}} = \sqrt{\frac{3\left(0.150 \text{ eV} \cdot \text{nm}^3\right)}{3.68 \text{ eV} \cdot \text{nm}}} = \boxed{0.350 \text{ nm}}$$

(b) The depth of the well is given by

$$U_0 = U\big|_{x=x_0} = \frac{A}{x_0^3} - \frac{B}{x_0} = \frac{AB^{3/2}}{3^{3/2} A^{3/2}} - \frac{BB^{1/2}}{3^{1/2} A^{1/2}}$$

$$U_0 = U\big|_{x=x_0} = -\frac{2B^{3/2}}{3^{3/2} A^{1/2}} = -\frac{2\left(3.68 \text{ eV} \cdot \text{nm}\right)^{3/2}}{3^{3/2}\left(0.150 \text{ eV} \cdot \text{nm}^3\right)^{1/2}} = \boxed{-7.02 \text{ eV}}$$

(c)  The force on the particle is given by $F_x = -\dfrac{dU}{dx} = 3Ax^{-4} - Bx^{-2}$. To

find the maximum force, we determine finite $x_m$ such that

$$\dfrac{dF}{dx}\bigg|_{x=x_m} = 0.$$

$$\dfrac{dF_x}{dx}\bigg|_{x=x_m} = \left[-12Ax^{-5} + 2Bx^{-3}\right]_{x=x_0} = 0$$

$$2Bx_m^{-3} = 12Ax_m^{-5}$$

$$x_m^2 = \dfrac{6A}{B} \qquad \rightarrow \qquad x_m = \sqrt{\dfrac{6A}{B}}$$

Then,

$$F_{max} = 3A\left(\dfrac{B}{6A}\right)^2 - B\left(\dfrac{B}{6A}\right) = -\dfrac{B^2}{12A} = -\dfrac{(3.68\ \text{eV}\cdot\text{nm})^2}{12(0.150\ \text{eV}\cdot\text{nm}^3)}$$

so   $F_{max} = -7.52\ \text{eV/nm}\left(\dfrac{1.60\times10^{-19}\ \text{J}}{1\ \text{eV}}\right)\left(\dfrac{1\ \text{nm}}{10^{-9}\ \text{m}}\right) = -1.20\times10^{-9}\ \text{N}$

$$= -1.20\ \text{nN}$$

or, as a vector, $\boxed{-1.20\hat{\mathbf{i}}\ \text{nN}}$.

**P42.42**  (a)  For equilibrium, $\dfrac{dU}{dx} = 0$:

$$\dfrac{d}{dx}(Ax^{-3} - Bx^{-1}) = -3Ax^{-4} + Bx^{-2} = 0$$

$x \rightarrow \infty$ describes one equilibrium position, but the stable

equilibrium position $x_0$ is at

$$-3Ax_0^{-4} + Bx_0^{-2} = 0$$
$$Bx_0^{-2} = 3Ax_0^{-4}$$

$$x_0^2 = \dfrac{3A}{B} \qquad \rightarrow \qquad \boxed{x_0 = \sqrt{\dfrac{3A}{B}}}$$

(b)   The depth of the well is given by

$$U_0 = U\big|_{x=x_0} = \frac{A}{x_0^3} - \frac{B}{x_0} = \frac{AB^{3/2}}{3^{3/2}A^{3/2}} - \frac{BB^{1/2}}{3^{1/2}A^{1/2}} = \boxed{-2\sqrt{\frac{B^3}{27A}}}$$

(c)   The force on the particle is given by $F_x = -\dfrac{dU}{dx} = 3Ax^{-4} - Bx^{-2}$.

To find the maximum force, we determine finite $x_m$ such that

$$\frac{dF_x}{dx}\bigg|_{x=x_m} = \left[-12Ax^{-5} + 2Bx^{-3}\right]_{x=x_0} = 0$$

$$2Bx_m^{-3} = 12Ax_m^{-5}$$

$$x_m^2 = \frac{6A}{B} \qquad \rightarrow \qquad x_m = \sqrt{\frac{6A}{B}}$$

then

$$F_{max} = 3A\left(\frac{B}{6A}\right)^2 - B\left(\frac{B}{6A}\right) = \boxed{-\frac{B^2}{12A}}$$

**\*P42.43**   **Conceptualize** Review the material associated with Figure 42.9 to understand the molecular spectrum of HCl.

**Categorize** We categorize the problem as one in which we analyze the molecular spectrum of a diatomic molecule.

**Analyze** (a) The different peaks in the spectrum in Figure 42.9 correspond to different values of $J$. Consider the peaks to the right of the center, for which Equation 42.13 gives the difference in energy between the peaks for the two isotopes of Cl:

$$\Delta E_{photon} = \left[hf + \frac{\hbar^2}{I_{Cl_{35}}}(J+1)\right] - \left[hf + \frac{\hbar^2}{I_{Cl_{37}}}(J+1)\right] = (J+1)\hbar^2\left(\frac{1}{I_{Cl_{35}}} - \frac{1}{I_{Cl_{37}}}\right) \qquad (1)$$

The moment of inertia of each molecule is given by Equation 42.3:

$$I = \left(\frac{m_H m_{Cl}}{m_H + m_{Cl}}\right) r^2 \qquad (2)$$

Therefore,

$$I_{Cl_{35}} = \left(\frac{m_H m_{Cl_{35}}}{m_H + m_{Cl_{35}}}\right) r^2 \qquad (3)$$

and

$$I_{Cl_{37}} = \left(\frac{m_H m_{Cl_{37}}}{m_H + m_{Cl_{37}}}\right) r^2 \qquad (4)$$

Substitute Equations (3) and (4) into Equation (1):

$$\Delta E_{photon} = (J+1)\frac{\hbar^2}{r^2}\left(\frac{m_H + m_{Cl_{35}}}{m_H m_{Cl_{35}}} - \frac{m_H + m_{Cl_{37}}}{m_H m_{Cl_{37}}}\right)$$

$$= (J+1)\frac{\hbar^2}{r^2}\left(\frac{m_H m_{Cl_{37}} + m_{Cl_{35}} m_{Cl_{37}}}{m_H m_{Cl_{35}} m_{Cl_{37}}} - \frac{m_H m_{Cl_{35}} + m_{Cl_{37}} m_{Cl_{35}}}{m_H m_{Cl_{37}} m_{Cl_{35}}}\right)$$

$$= (J+1)\frac{\hbar^2}{r^2}\left(\frac{m_H m_{Cl_{37}}}{m_H m_{Cl_{35}} m_{Cl_{37}}} - \frac{m_H m_{Cl_{35}}}{m_H m_{Cl_{37}} m_{Cl_{35}}}\right)$$

$$= (J+1)\frac{\hbar^2}{r^2 m_{Cl_{35}} m_{Cl_{37}}}\left(m_{Cl_{37}} - m_{Cl_{35}}\right) \qquad (5)$$

Finally, use Equation 39.5 to find the difference in frequency:

$$\Delta E_{photon} = h\Delta f = (J+1)\frac{\hbar^2}{r^2 m_{Cl_{35}} m_{Cl_{37}}}\left(m_{Cl_{37}} - m_{Cl_{35}}\right)$$

$$\rightarrow \boxed{\Delta f = (J+1)\frac{h\left(m_{Cl_{37}} - m_{Cl_{35}}\right)}{4\pi^2 r^2 m_{Cl_{35}} m_{Cl_{37}}}} \qquad (6)$$

(b) We can make an estimate for the frequency difference by

approximating the masses of the chlorine atoms in atomic mass units:

$$\Delta f = (0+1)\frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(37\text{ u}-35\text{ u})}{4\pi^2(0.127\,5\text{ nm})^2(35\text{ u})(37\text{ u})}\left(\frac{1\text{ nm}}{10^{-9}\text{ m}}\right)^2\left(\frac{1\text{ u}}{1.661\times10^{-27}\text{ kg}}\right)$$

$$= \boxed{9.60 \times 10^8 \text{ Hz}}$$

**Finalize** Notice that the problem stated that the molecule is rigid. If we relax that restriction, the molecule can stretch as it rotates, complicating the calculation of the moment of inertia.]

*Answer:* (a) $\Delta f = (J+1)\dfrac{h\left(m_{\text{Cl}_{37}}-m_{\text{Cl}_{35}}\right)}{4\pi^2 r^2 m_{\text{Cl}_{35}} m_{\text{Cl}_{37}}}$ (b) $9.60 \times 10^8$ Hz

P42.44 (a) The results of the spreadsheet are shown in two parts, in TABLE P42.44(a) and TABLE P42.44(b) for $f(E) = \dfrac{1}{e^{[(E/E_F-1)T_F]/T}+1}$. ANS. FIG. P42.44 shows the graphs of the tabulated values.

(b) The function is compared to the case $T = 0$. See the table and graphs below.

**Table 42.44 (a)**

| | T = 0 | | T = 0.1$T_F$ | |
|---|---|---|---|---|
| $\dfrac{E}{E_F}$ | $e^{[(E/E_F)-1](T_F/T)}$ | $f(E)$ | $e^{[(E/E_F)-1](T_F/T)}$ | $f(E)$ |
| 0 | $e^{-\infty}$ | 1.00 | $e^{-10.0}$ | 1.000 |
| 0.500 | $e^{-\infty}$ | 1.00 | $e^{-5.00}$ | 0.993 |
| 0.600 | $e^{-\infty}$ | 1.00 | $e^{-4.00}$ | 0.982 |

| $\frac{E}{E_F}$ | | | | |
|---|---|---|---|---|
| 0.700 | $e^{-\infty}$ | 1.00 | $e^{-3.00}$ | 0.953 |
| 0.800 | $e^{-\infty}$ | 1.00 | $e^{-2.00}$ | 0.881 |
| 0.900 | $e^{-\infty}$ | 1.00 | $e^{-1.00}$ | 0.731 |
| 1.00 | $e^{0}$ | 0.500 | $e^{0}$ | 0.500 |
| 1.10 | $e^{+\infty}$ | 0.00 | $e^{1.00}$ | 0.269 |
| 1.20 | $e^{+\infty}$ | 0.00 | $e^{2.00}$ | 0.119 |
| 1.30 | $e^{+\infty}$ | 0.00 | $e^{3.00}$ | 0.047 4 |
| 1.40 | $e^{+\infty}$ | 0.00 | $e^{4.00}$ | 0.018 0 |
| 1.50 | $e^{+\infty}$ | 0.00 | $e^{5.00}$ | 0.006 69 |

**Table 42.44 (b)**

| $\dfrac{E}{E_F}$ | $T = 0.2T_F$ | | $T = 0.5T_F$ | |
|---|---|---|---|---|
| | $e^{\left[(E/E_F)-1\right]\left(T_F/T\right)}$ | $f(E)$ | $e^{\left[(E/E_F)-1\right]\left(T_F/T\right)}$ | $f(E)$ |
| 0 | $e^{-5.00}$ | 0.993 | $e^{-2.00}$ | 0.881 |
| 0.500 | $e^{-2.50}$ | 0.924 | $e^{-1.00}$ | 0.731 |
| 0.600 | $e^{-2.00}$ | 0.881 | $e^{-0.800}$ | 0.690 |
| 0.700 | $e^{-1.50}$ | 0.818 | $e^{-0.600}$ | 0.646 |
| 0.800 | $e^{-1.00}$ | 0.731 | $e^{-0.400}$ | 0.599 |

| | | | | |
|---|---|---|---|---|
| 0.900 | $e^{-0.500}$ | 0.622 | $e^{-0.200}$ | 0.550 |
| 1.00 | $e^0$ | 0.500 | $e^0$ | 0.500 |
| 1.10 | $e^{0.500}$ | 0.378 | $e^{0.200}$ | 0.450 |
| 1.20 | $e^{1.00}$ | 0.269 | $e^{0.400}$ | 0.401 |
| 1.30 | $e^{1.50}$ | 0.182 | $e^{0.600}$ | 0.354 |
| 1.40 | $e^{2.00}$ | 0.119 | $e^{0.800}$ | 0.310 |
| 1.50 | $e^{2.50}$ | 0.075 9 | $e^{1.00}$ | 0.269 |



Fermi–Dirac Distribution Function
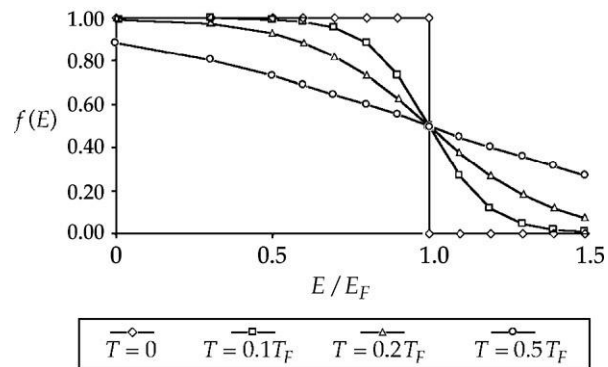
**ANS. FIG. P42.44**

## Challenge Problems

**P42.45**    (a)    Refer to Example 42.2 for details. Since the interatomic potential is the same for both molecules, the spring constant is the same.

Then,

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

where

$$\mu_{12} = \frac{(12\ \text{u})(16\ \text{u})}{12\ \text{u} + 16\ \text{u}} = 6.86\ \text{u} \quad \text{and} \quad \mu_{14} = \frac{(14\ \text{u})(16\ \text{u})}{14\ \text{u} + 16\ \text{u}} = 7.47\ \text{u}$$

Therefore,

$$f_{14} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{14}}} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{12}}\left(\frac{\mu_{12}}{\mu_{14}}\right)} = f_{12}\sqrt{\frac{\mu_{12}}{\mu_{14}}}$$

$$= \left(6.42 \times 10^{13}\ \text{Hz}\right)\sqrt{\frac{6.86\ \text{u}}{7.47\ \text{u}}}$$

$$= \boxed{6.15 \times 10^{13}\ \text{Hz}}$$

(b)  The equilibrium distance is the same for both molecules.

$$I_{14} = \mu_{14}r^2 = \left(\frac{\mu_{14}}{\mu_{12}}\right)\mu_{12}r^2 = \left(\frac{\mu_{14}}{\mu_{12}}\right)I_{12}$$

$$I_{14} = \left(\frac{7.47\ \text{u}}{6.86\ \text{u}}\right)\left(1.46 \times 10^{-46}\ \text{kg} \cdot \text{m}^2\right) = \boxed{1.59 \times 10^{-46}\ \text{kg} \cdot \text{m}^2}$$

(c)  The molecule can move to the ($v = 1$, $J = 9$) state or to the ($v = 1$, $J = 11$) state. The energy it can absorb is either

$$\Delta E = \frac{hc}{\lambda} = \left[\left(1 + \frac{1}{2}\right)hf_{14} + 11(11+1)\frac{\hbar^2}{2I_{14}}\right]$$

$$-\left[\left(0 + \frac{1}{2}\right)hf_{14} + 10(10+1)\frac{\hbar^2}{2I_{14}}\right]$$

$$\frac{hc}{\lambda} = hf_{14} + 22\frac{\hbar^2}{2I_{14}} = hf_{14} + 11\frac{h\hbar}{2\pi I_{14}}$$

$$\frac{c}{\lambda} = f_{14} + 11\frac{\hbar}{2\pi I_{14}}$$

or

$$\Delta E = \frac{hc}{\lambda} = \left[\left(1+\frac{1}{2}\right)hf_{14} + 9(9+1)\frac{\hbar^2}{2I_{14}}\right]$$

$$-\left[\left(0-\frac{1}{2}\right)hf_{14} + 10(10+1)\frac{\hbar^2}{2I_{14}}\right]$$

$$\frac{hc}{\lambda} = hf_{14} - 20\frac{\hbar^2}{2I_{14}} = hf_{14} - 10\frac{h\hbar}{2\pi I_{14}}$$

$$\frac{c}{\lambda} = f_{14} - 10\frac{\hbar}{2\pi I_{14}}$$

The wavelengths it can absorb are then

$$\lambda = \frac{c}{f_{14} + 11\hbar/(2\pi I_{14})} \quad \text{or} \quad \lambda = \frac{c}{f_{14} - 10\hbar/(2\pi I_{14})}$$

These are,

$$\lambda = \frac{2.998\times10^8 \text{ m/s}}{6.15\times10^{13} \text{ Hz} + \frac{\left[11\left(1.055\times10^{-34} \text{ J}\cdot\text{s}\right)\right]}{\left[2\pi\left(1.59\times10^{-46} \text{ kg}\cdot\text{m}^2\right)\right]}} = \boxed{4.78 \ \mu\text{m}}$$

or

$$\lambda = \frac{2.998\times10^8 \text{ m/s}}{6.15\times10^{13} \text{ Hz} - \frac{\left[10\left(1.055\times10^{-34} \text{ J}\cdot\text{s}\right)\right]}{\left[2\pi\left(1.59\times10^{-46} \text{ kg}\cdot\text{m}^2\right)\right]}} = \boxed{4.96 \ \mu\text{m}}$$

**\*P42.46** **Conceptualize** The primary conceptualization in this problem is that associated with Figure P42.46. Imagine a three-dimensional space of quantum numbers, with the only allowed values being integers, as represented by the dots in Figure P42.46. Once you are able to conceptualize this, the rest of the problem is relatively simple math.

**Categorize** We have no analysis model, but we have an important geometric model: representing the allowed quantum numbers in a

geometric three-dimensional space.

**Analyze** (a) Begin with Equation 42.18:

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

Use the definitions given in part (a) of the problem:

$$n_x^2 + n_y^2 + n_z^2 = \frac{2m_e L^2}{\hbar^2 \pi^2} E = \frac{E}{E_0} = n^2$$

(b) Imagine the thin shell of thickness $dn$ in Figure P42.46. The volume of this shell is

$$G(E)\,dE = \tfrac{1}{8} A_n\, dn$$

where we have multiplied by 1/8 because we want to restrict the count to that octant of quantum number space for which all three quantum numbers are positive. The area $A_n$ is the area of a sphere of radius $n$ in quantum number space. Therefore,

$$G(E)\,dE = \tfrac{1}{8}\left(4\pi n^2\right) dn = \tfrac{1}{2}\pi n^2\, dn$$

(c) Substitute for $n$:

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

Now substitute for $E_0$:

$$G(E)\,dE = \tfrac{1}{4}\pi\,\frac{E^{1/2}}{E_0^{3/2}}\,dE = \tfrac{1}{4}\pi\,\frac{E^{1/2}}{\left(\dfrac{\hbar^2\pi^2}{2m_e L^2}\right)^{3/2}}\,dE$$

$$= \tfrac{1}{4}\pi\left(\frac{2\sqrt{2}m_e^{3/2}L^3}{\hbar^3\pi^3}\right)E^{1/2}\,dE = \frac{\sqrt{2}}{2}\frac{m_e^{3/2}L^3}{\hbar^3\pi^2}E^{1/2}\,dE$$

(d) Divide by $V = L^3$ and multiply by 2 for the spin states:

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

Finally, note that the final result is in terms of $h$, not $\hbar$, so let's convert:

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

**Finalize** This result is Equation 42.19.

**P42.47**    (a)   At equilibrium separation $r = r_e$,

$$\left.\frac{dU}{dr}\right|_{r=r_e} = -2aB\left[e^{-a(r_e-r_0)}-1\right]e^{-a(r_e-r_0)} = 0$$

We have neutral equilibrium as $r_e \to \infty$ and stable equilibrium at

$$e^{-a(r_e-r_0)} = 1 \qquad \rightarrow \qquad r_e = \boxed{r_0}$$

(b)   At $r = r_0$, $U = 0$. As $r \to \infty$, $U \to B$. The depth of the well is $\boxed{B}$.

(c)   We expand the potential in a Taylor series about the equilibrium point $r = r_0$:

$$U(r) \approx U(r_0) + \left.\frac{dU}{dr}\right|_{r=r_0}(r - r_0) + \frac{1}{2}\left.\frac{d^2U}{dr^2}\right|_{r=r_0}(r - r_0)^2$$

or,

$$U(r) \approx 0 + 0 + \frac{1}{2}(-2Ba)\left[-2ae^{-2a(r-r_0)} + ae^{-a(r-r_0)}\right]_{r=r_0}(r-r_0)^2$$

$$\approx Ba^2(r-r_0)^2$$

This is of the form

$$\frac{1}{2}kx^2 = \frac{1}{2}k(r-r_0)^2$$

for a simple harmonic oscillator with $k = 2Ba^2$.

Then, the molecule vibrates with frequency

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{a}{2\pi}\sqrt{\frac{2B}{\mu}} = \boxed{\frac{a}{\pi}\sqrt{\frac{B}{2\mu}}}$$

(d) The ground state energy is

$$\frac{1}{2}\hbar\omega = \frac{1}{2}hf = \frac{ha}{\pi}\sqrt{\frac{B}{8\mu}}$$

The energy at infinity is $B$. Therefore, to separate the nuclei to infinity requires energy

$$\boxed{B - \frac{ha}{\pi}\sqrt{\frac{B}{8\mu}}}$$

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# ANSWERS TO QUICK-QUIZZES

**1.** (a) van der Waals (b) ionic (c) hydrogen (d) covalent

**2.** (c)

**3.** (a)

**4.** A: semiconductor; B: conductor; C: insulator

$$==$$

# ANSWERS TO EVEN-NUMBERED PROBLEMS

**P42.2**    4.3 eV

**P42.4**    (a) $r_0 = \left[ \dfrac{2A}{B} \right]^{1/6}$

(b) $E = U\big|_{r=\infty} - U\big|_{r=r_0} = 0 - \left[ \dfrac{A}{4A^2/B^2} - \dfrac{B}{2A/B} \right] = -\left[ \dfrac{1}{4} - \dfrac{1}{2} \right]\dfrac{B^2}{A} = \boxed{\dfrac{B^2}{4A}}$

**P42.6**    (a) $1.22 \times 10^{-26}$ kg; (b) $1.24 \times 10^{-26}$ kg; (c) They agree because the small apparent difference can be attributed to uncertainty in the data.

**P42.8**    The incident photons have a wavelength longer than this, which means they have less energy than 0.359 eV. Therefore, these photons cannot excite the molecule to the first excited state.

**P42.10**    $\mu r^2$

**P42.12**    476 N/m

**P42.14**    (a) $1.89 \times 10^{-45}$ kg·m²; (b) $E_{\mathrm{rot}} = 18.4\, J\,(J + 1)$, where $E_{\mathrm{rot}}$ is in microelectron volts and $J = 0, 1, 2, 3,\dots.$

**P42.16**    $2.88 \times 10^{-47}$ kg·m²

**P42.18**    $U = -k_e \alpha \dfrac{e^2}{r}$ where $\alpha = 2\ln 2$

**P42.20**    (a) The Fermi energy is proportional to the spatial concentration of free electrons to the two-thirds power; (b) See P43.28(b) for full

explanation; (c) 6.04; (d) Copper; (e) 0.333; (f) This behavior agrees

with the proportionality because $E_F \sim n_e^{2/3}$ and $6.04^{2/3} = 3.32$.

**P42.22**   (a) $2.54 \times 10^{28}$ m$^{-3}$ (b) 3.15 eV

**P42.24**   There are approximately two free electrons per atom for this metal, not

one (see P42.24 for full explanation).

**P42.26**   (a) 1.10; (b) $9.42 \times 10^{-25}$

**P42.28**   (a) All the hydrogen Balmer lines except for the red lien at 656 nm will

be absorbed; (b) The red line at 656 nm will be transmitted.

**P43.30**   no

**P42.32**   (a) 59.5 mV (b) -59.5 mV

**P42.34**   (a) See P42.34(a) for full explanation; (b) See ANS. FIG. P42.34;

(c) 2.98 mA; (d) 67.1 $\Omega$; (e) 8.39 $\Omega$

**P42.36**   $J = 37$

**P42.38**   (a) See the solution. (b) See the solution. (c) 9.16 THz

**P42.40**   See the solution.

**P42.42**   (a) $x_0 = \sqrt{\dfrac{3A}{B}}$; (b) $-2\sqrt{\dfrac{B^3}{27A}}$; (c) $-\dfrac{B^2}{12A}$

**P42.44**   (a–b) See P42.44 for full explanation.

**P42.46**   See P42.46 for full explanation.