9-20) The characteristic rotational energy for the $N_2$ molecule is $2.48\times10^{-6}$ eV. From this, find the separation distance of the nitrogen atoms in $N_2$.

The characteristic rotational energy of a molecule is given by $E_{rot} = \frac{1}{2} I \omega^2$, so from this energy we can find the moment of inertia:

$$I = \frac{\hbar^2}{2E_{rot}} = \frac{(6.58 \times 10^{-16} \text{ eV} \cdot s)^2}{2 \times 2.48 \times 10^{-10} \text{ eV}} = 8.73 \times 10^{-25} \text{ kg} \cdot \text{m}^2$$

If we treat the $N_2$ molecule as a simple barbell with separation distance $d=2r$, then $I = \frac{1}{2} m_n r^2$, where the mass of a nitrogen atom is $m_n = 14 \text{ amu}$.

Solving for $d$: $d = \left(\frac{\hbar}{m_n}\right)^{1/2} = \left(\frac{2 \times 1.40 \times 10^{-46} \text{ J} \cdot \text{m}^2}{14 \times 1.66 \times 10^{-27} \text{ kg}}\right)^{1/2} = 1.1 \times 10^{-10}$ m

\[d = 0.11 \text{ nm}\]

9-33) Determine the ratio of the number of molecules in the $v=1$ state to the number in the $v=0$ state for a sample of $O_2$ molecules at 273K. Repeat the calculation for 77K. (Ignore rotational motion.) [Answer: 2.4e-4]

$\nu = 0,1$ corresponds to vibrational states. From table 9-7 we find that the characteristic vibrational frequency for $O_2$ is $\nu = 4.74 \times 10^{13}$ Hz. The energy of these vibrational levels is given by $E_v = (\nu + 1) \hbar \nu$, so $E_0$ and $E_1$ are

$E_0 = \frac{1}{2} (4.14 \times 10^{-7} \text{ eV} \cdot s)(4.74 \times 10^{13} \text{ Hz}) = 0.098 \text{ eV}$

$E_1 = \frac{3}{2} \hbar \nu = 3(E_0) = 0.294 \text{ eV}$

The relative population of these states is given by the Boltzmann factor:

$$\frac{n(E_1)}{n(E_0)} = \frac{A e^{-E_1/kT}}{A e^{-E_0/kT}} = e^{\frac{(E_1-E_0)}{kT}} = e^{\frac{0.196 \text{ eV}}{0.0235 \text{ eV}}} = 2.4 \times 10^{-4} \text{ at } kT = \frac{(8.62 \times 10^{-5} \text{ eV}) \nu}{(273 \text{ K})}$$

At $T=77 \text{ K}$, $kT = 0.0666 \text{ eV}$

$\frac{n(E_1)}{n(E_0)} = e^{\frac{-0.196 \text{ eV}}{0.0666 \text{ eV}}} = 1.5 \times 10^{-13}$

**Very small**
9-41] The equilibrium separation of the K⁺ and Cl⁻ ions in KCl is about 0.267 nm. Calculate the potential energy of attraction of the ions assuming them to be point charges at this separation. The ionization energy of potassium is 4.34 eV and the electron affinity of Cl is 3.61 eV. Find the dissociation energy for KCl, neglecting any energy of repulsion. The measured dissociation energy for KCl is 4.40 eV. What is the energy due to repulsion of the ions at the equilibrium separation? [Answer: 0.26 eV]

The potential energy of the KCl molecule is composed of 3 components (eqn 9-1)

\[ U(r) = -\frac{k e^2}{r} + E_{\text{ex}} + E_{\text{ion}} \]

The potential energy of attraction at \( r_0 \) is

\[ -\frac{k e^2}{r_0} = \frac{1.44 \text{ eV nm}}{0.267 \text{ nm}} \]

\[ E_e = -5.39 \text{ eV} \]

Neglecting repulsion, the dissociation energy is minus the potential energy at \( r_0 \):

\[ U(r_0) = -\frac{k e^2}{r_0} + E_{\text{ion}} \]

where \( E_{\text{ion}} = 4.34 \text{ eV} - 3.61 \text{ eV} \) is energy required to form the ions.

\[ E_{\text{dis}} = -U(r_0) = 5.39 \text{ eV} - 0.73 \text{ eV} = 4.66 \text{ eV} \]

The difference between this value and the measured dissociation energy is the energy of repulsion due to the Pauli exclusion principle.

\[ E_{\text{ex}} = 4.66 \text{ eV} - 4.40 \text{ eV} = 0.26 \text{ eV} \]
9-51) The potential energy between two atoms in a molecule can often be described rather well by the Lenard-Jones potential:

\[
U(r) = U_0 \left[ \left( \frac{a}{r} \right)^{12} - 2 \left( \frac{a}{r} \right)^{6} \right]
\]

where \( U_0 \) and \( a \) are constants. Find the interatomic separation \( r_0 \) in terms of \( a \) for which the potential energy is a minimum. Find the corresponding value of \( U_{\text{min}} \). Use Figure 9-8 to obtain numerical values for \( r_0 \) and \( U_0 \) for the \( \text{H}_2 \) molecule. Express your answer in nm and eV. Make a plot of the potential energy \( U(r) \) versus the interatomic spacing \( r \) for the \( \text{H}_2 \) molecule. Plot each term separately, together with the total.

Find the minimum of \( U(r) \) by setting \( \frac{dU}{dr} = 0 \).

\[
\frac{dU}{dr} = \frac{U_o}{a} \left[ -12 \left( \frac{a}{r} \right)^{13} + 12 \left( \frac{a}{r} \right)^{7} \right] = 0 \Rightarrow \text{satisfied if} \quad r = a
\]

\[
U(r=a) = U_0 \left[ 1-2 \right] = -U_0 = U_{\text{min}}
\]

From the textbook: \( r_0 = 0.074 \text{ nm} \), \( U_{\text{min}} = -31.7 \text{ eV} \)

\[
U(r) = -31.7 \text{ eV} \left[ \left( \frac{0.074 \text{ nm}}{r} \right)^{12} - 2 \left( \frac{0.074 \text{ nm}}{r} \right)^{6} \right]
\]
10-19) What is the Fermi speed, i.e., the speed of a conduction electron whose energy is equal to the Fermi Energy, for Na, Au, and Sn? (See Table 10-3.)

\[ \text{The Fermi speed is defined by } \frac{1}{2} m u_F^2 = E_F, \text{ or} \]
\[ u_F = \left( \frac{2E_F}{m} \right)^{1/2} = \left( \frac{2E_F}{M_0 c^2} \right)^{1/2} = 3 \times 10^8 \left( \frac{2E_F}{510000 \text{ eV}} \right)^{1/2} \]

<table>
<thead>
<tr>
<th>metal</th>
<th>( E_F )</th>
<th>( u_F )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>3.26 eV</td>
<td>1.07 \times 10^6 m/s</td>
</tr>
<tr>
<td>Au</td>
<td>5.55 eV</td>
<td>1.40 \times 10^6 m/s</td>
</tr>
<tr>
<td>Sn</td>
<td>10.3 eV</td>
<td>1.90 \times 10^6 m/s</td>
</tr>
</tbody>
</table>

10-21) At what temperature is the heat capacity due to the electron gas in copper equal to 10% of that due to lattice vibrations? [Answer: 4980 K]

The molar heat capacity due to lattice vibrations is \( 3R \), and that due to the conduction electrons is given by equation 10-45 in the text:
\[ C_V = \frac{n^2}{2} \frac{T}{T_F} R \]

Solving for the temperature when \( C_V \) of the electrons = 0.3 \( R \):
\[ 0.3 R = \frac{n^2}{2} \frac{T}{T_F} R \Rightarrow T = 0.0608 T_F \]

The Fermi energy of copper is 7.06 eV (Table 10-3), giving a Fermi temperature of \( T_F = \frac{E_F}{k} = 8.19 \times 10^4 K \)

Our final temperature is \( T = (0.0608)(8.19 \times 10^4 K) \)
\[ T = 4,979 K \text{ hot!} \]
10-47) The density of electron states in a metal can be written \( g(E) = AE^{1/2} \), where \( A \) is a constant and \( E \) is measured from the bottom of the conduction band. Show that the total number of states is \((2/3)AE_F^{3/2}\). About what fraction of the conduction electrons are within \( kT \) of the Fermi energy? Evaluate this fraction for copper at 300 K? [Answer: 0.55%]

\[
N = A \int_0^{E_F} E^{1/2} \, dE = A \frac{2}{3} E_F^{3/2}
\]

Since \( E_F \gg kT \) for most metals, \((kT = 0.026 \text{ eV at } 300 \text{ K})\).

we can approximate the integral \((E_F = 7.04 \text{ eV for Cu})\)

\[
N^* \approx \int_{E_F-kT}^{E_F} g(E) dE \approx g(E_F) \cdot kT
\]

so fraction with energy within \( kT \) of \( E_F \) is

\[
\frac{N^*}{N} = \frac{AE_F^{1/2} kT}{A \frac{2}{3} E_F^{3/2}} = \frac{3kT}{2E_F} = \frac{3 \times 0.026 \text{ eV}}{2 \times 7.04 \text{ eV}} = 5.5 \times 10^{-3}
\]
The quantity $K$ is the force constant for a “spring” consisting of a line of alternating positive and negative ions. If these ions are displaced slightly from their equilibrium separation $r_0$, they will vibrate with a frequency $\omega = (K/m)^{1/2}$. Use equation 10-5 along with values of $a$, $n$, and $r_0$ given in the text for NaCl to calculate this frequency. Calculate the wavelength of electromagnetic radiation corresponding to this frequency, and compare your result with the characteristic strong infrared absorption bands in the region of about $\lambda = 61 \text{ nm}$. [Hint: Use the Taylor series to find an approximation to equation 10-5 in the vicinity of $r_0$ that follows the form for a simple harmonic oscillator, $U = \frac{1}{2}Kx^2$.]

The total potential energy of an ion in a crystal is given by

$$U(r) = -x \frac{k e^2}{r_0} \left[ \frac{r_{\hat{r}}}{r} - \frac{1}{n} \left( \frac{r_0}{r} \right)^n \right]$$

where $r_0$ is the equilibrium distance at which $\frac{dU}{dr} = 0$.

If the potential can be written in a form $U = \frac{1}{2}Kx^2$, where $x = r - r_0$ is the distance from equilibrium, then we know the ion will behave as a simple harmonic oscillator with frequency $\omega = \sqrt{K/m}$.

To find the value of $K$, use Taylor series

$$U(r) \approx U(r_0) + \frac{dU}{dr}\bigg|_{r_0} (r-r_0) + \frac{1}{2} \frac{d^2U}{dr^2}\bigg|_{r_0} (r-r_0)^2 + \ldots$$

$$\uparrow \quad r = 0 \text{ at } r = r_0$$

using only the third term.

$$U(r) \approx \frac{1}{2} \frac{d^2U}{dr^2}\bigg|_{r_0} (r-r_0)^2 = \frac{1}{2} K x^2$$

$$\frac{dU}{dr} = \frac{a k e^2}{r_0} \left[ - \frac{r_0}{r^2} + \frac{r_{\hat{r}}}{r^{n+1}} \right]$$

$$\frac{d^2U}{dr^2} = \frac{a k e^2}{r_0} \left[ + \frac{2r_0}{r^3} - \frac{n(n+1)}{r^{n+2}} \right]$$

Evaluate at $r = r_0:

$$U'' = \frac{a k e^2}{r_0^3} (n-1) \quad \text{use } a = 1.75$$

$$r_0 = 0.282 \text{ nm}$$

$$K = \frac{1.75 \times 1.44 \text{ eV} \cdot \text{nm}}{(0.282 \text{ nm})^3} = 8.35$$

$$n = 9.35$$
\[ k = 9.38 \text{eV/nm}^2 \]

\[ M = \frac{M_{Na} M_{Cl}}{M_{Na} + M_{Cl}} \text{ is reduced mass} \]

\[ = \frac{22.99 \text{u} \cdot 35.45 \text{u}}{22.99 \text{u} + 35.45 \text{u}} = 13.95 \text{u} \]

\[ = 13.95 \times 931 \text{ MeV/c}^2 \]

\[ \frac{k}{m} = \frac{9.38}{13.95 \times 931 \times 10^6} \frac{c^2 \text{eV}}{\text{eV \cdot nm}^2} \]

\[ = \frac{.0722}{10^6} \left( \frac{3 \times 10^8 \text{m/s}}{10^9 \text{m}} \right)^2 = 6.5 \times 10^{-7} \Rightarrow \omega = \sqrt{\frac{k}{m}} = 8 \times 10^{13} \text{s}^{-1} \]

A photon corresponding to this frequency would have a wavelength

\[ \lambda = \frac{c}{\omega} = \frac{2.99 \times 10^8 \text{m/s}}{8 \times 10^{13} \text{s}} = 2.3 \times 10^{-5} \text{m} \]

\[ \lambda = 23 \text{m} \]