8

Quantum Mechanics in Three Dimensions

8-1 $$E=\frac{\hbar^2\pi^2}{2m}\left[\left(\frac{n_1}{L_x}\right)^2+\left(\frac{n_2}{L_y}\right)^2+\left(\frac{n_3}{L_z}\right)^2\right]$$

$L_x=L$, $L_y=L_z=2L$. Let $\frac{\hbar^2\pi^2}{8mL^2}=E_0$. Then $E=E_0\left(4n_1^2+n_2^2+n_3^2\right)$. Choose the quantum numbers as follows:

n_1	n_2	n_3	$\frac{E}{E_0}$		
1	1	1	6		ground state
1	2	1	9	*	first two excited states
1	1	2	9	*	
2	1	1	18		
1	2	2	12	*	next excited state
2	1	2	21		
2	2	1	21		
2	2	2	24		
1	1	3	14	*	next two excited states
1	3	1	14	*	

Therefore the first 6 states are ψ_{111}, ψ_{121}, ψ_{112}, ψ_{122}, ψ_{113}, and ψ_{131} with relative energies $\frac{E}{E_0}=6, 9, 9, 12, 14, 14$. First and third excited states are doubly degenerate.

8-3 $n^2=11$

(a) $$E=\left(\frac{\hbar^2\pi^2}{2mL^2}\right)n^2=\frac{11}{2}\left(\frac{\hbar^2\pi^2}{mL^2}\right)$$

(b)

n_1	n_2	n_3	
1	1	3	
1	3	1	3-fold degenerate
3	1	1	

(c) $$\psi_{113} = A\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\sin\left(\frac{3\pi z}{L}\right)$$
$$\psi_{131} = A\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{3\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right)$$
$$\psi_{311} = A\sin\left(\frac{3\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right)$$

8-5 (a) $$n_1 = n_2 = n_3 = 1 \text{ and } E_{111} = \frac{3h^2}{8mL^2} = \frac{3\left(6.63\times10^{-34}\right)^2}{8\left(1.67\times10^{-27}\right)\left(4\times10^{-28}\right)} = 2.47\times10^{-13}\text{ J} \approx 1.54\text{ MeV}$$

(b) States 211, 121, 112 have the same energy and $E = \dfrac{\left(2^2+1^2+1^2\right)h^2}{8mL^2} = 2E_{111} \approx 3.08\text{ MeV}$

and states 221, 122, 212 have the energy $E = \dfrac{\left(2^2+2^2+1^2\right)h^2}{8mL^2} = 3E_{111} \approx 4.63\text{ MeV}$.

(c) Both states are threefold degenerate.

8-7 The stationary states for a particle in a cubic box are, from Equation 8.10

$$\begin{aligned}\Psi(x,\ y,\ z,\ t) &= A\sin(k_1x)\sin(k_2y)\sin(k_3z)e^{-iEt/\hbar} \quad 0 \le x,\ y,\ x \le L\\ &= 0 \text{ elsewhere}\end{aligned}$$

where $k_1 = \dfrac{n_1\pi}{L}$, etc. Since Ψ is nonzero only for $0 < x < L$, and so on, the normalization condition reduces to an integral over the volume of a cube with one corner at the origin:

$$1 = \int dx\int dy\int dz\left|\Psi(\mathrm{r},\ t)\right|^2 = A^2\left\{\int_0^L \sin^2(k_1x)dx\int_0^L \sin^2(k_2y)dy\int_0^L \sin^2(k_3z)dz\right\}$$

Using $2\sin^2\theta = 1-\cos 2\theta$ gives $\int_0^L \sin^2(k_1x)dx = \dfrac{L}{2} - \dfrac{1}{4k_1}\sin(2k_1x)\Big|_0^L$. But $k_1L = n_1\pi$, so the last term on the right is zero. The same result is obtained for the integrations over y and z. Thus, normalization requires $1 = A^2\left(\dfrac{L}{2}\right)^3$ or $A = \left(\dfrac{2}{L}\right)^{3/2}$ for any of the stationary states. Allowing the edge lengths to be different at L_1, L_2, and L_3 requires only that L^3 be replaced by the box volume $L_1L_2L_3$ in the final result: $A = \left\{\left(\dfrac{2}{L_1}\right)\left(\dfrac{2}{L_2}\right)\left(\dfrac{2}{L_3}\right)\right\}^{1/2} = \left(\dfrac{8}{L_1L_2L_3}\right)^{1/2} = \left(\dfrac{8}{V}\right)^{1/2}$ where $V = L_1L_2L_3$ is the volume of the box. This follows because it is still true that the wave must vanish at the walls of the box, so that $k_1L_1 = n_1\pi$, and so on.

8-9 $$L = [l(l+1)]^{1/2}\hbar$$
$$4.714\times10^{-34}\text{ Js} = [l(l+1)]^{1/2}\left(\frac{6.63\times10^{-34}\text{ Js}}{2\pi}\right)$$
$$l(l+1) = \frac{\left(4.714\times10^{-34}\right)^2(2\pi)^2}{\left(6.63\times10^{-34}\right)^2} = 1.996\times10^1 \approx 20 = 4(4+1)$$

so $l = 4$.

8-11 (a) $L=[l(l+1)]^{1/2}\hbar;\ 4.83\times10^{31}\ \text{Js}=[l(l+1)]^{1/2}\hbar$, so

$$l^2+l=\frac{\left(4.83\times10^{31}\ \text{Js}\right)^2}{\left(1.055\times10^{-34}\ \text{Js}\right)^2}\approx\left(4.58\times10^{65}\right)^2\approx l^2$$

$$l\approx4.58\times10^{65}$$

(b) With $L\approx l\hbar$ we get $\Delta L\approx\hbar$ and $\dfrac{\Delta L}{L}\approx\dfrac{1}{l}=2.18\times10^{-66}$

8-13 $Z=2$ for He^+

(a) For $n=3$, l can have the values of 0, 1, 2

$$\begin{aligned}l&=0 &\rightarrow\ & m_l=0\\ l&=1 &\rightarrow\ & m_l=-1,\ 0,\ +1\\ l&=2 &\rightarrow\ & m_l=-2,\ -1,\ 0,\ +1,\ +2\end{aligned}$$

(b) All states have energy $E_3=\dfrac{-Z^2}{3^2}(13.6\ \text{eV})$

$$E_3=-6.04\ \text{eV}.$$

8-15 (a) $E_n=-\left(\dfrac{ke^2}{2a_0}\right)\left(\dfrac{Z^2}{n^2}\right)$ from Equation 8.38. But $a_0=\dfrac{\hbar^2}{m_eke^2}$ so with $m_e\rightarrow\mu$ we get $E_n=-\left(\dfrac{\mu k^2e^4}{2\hbar^2}\right)\left(\dfrac{Z^2}{n^2}\right)$.

(b) For $n=3\rightarrow2$, $E_3-E_2=\dfrac{hc}{\lambda}=\dfrac{\mu k^2e^4Z^2}{2\hbar^2}\left(\dfrac{1}{2^2}-\dfrac{1}{3^2}\right)$ with $\lambda=656.3$ nm for H ($Z=1$, $\mu\approx m_e$). For He^+, $Z=2$, and $\mu\approx m_e$, so, $\lambda=\dfrac{656.3}{2^2}=164.1$ nm (ultraviolet).

(c) For positronium, $Z=1$ and $\mu=\dfrac{m_e}{2}$, so, $\lambda=(656.3)(2)=1\,312.6$ nm (infrared).

8-17 (a) For a *d* state, $l=2$

$$L=[l(l+1)]^{1/2}\hbar=(6)^{1/2}\left(1.055\times10^{-34}\ \text{Js}\right)=2.58\times10^{-34}\ \text{Js}$$

(b) For an *f* state, $l=3$

$$L=[l(l+1)]^{1/2}\hbar=(12)^{1/2}\left(1.055\times10^{-34}\ \text{Js}\right)=3.65\times10^{-34}\ \text{Js}$$

8-19 When the principal quantum number is n, the following values of l are possible: $l=0,\ 1,\ 2,\ \ldots,\ n-2,\ n-1$. For a given value of l, there are $2l+1$ possible values of m_l. The maximum number of electrons that can be accommodated in the n^{th} level is therefore:

$$(2(0)+1)+(2(1)+1)+\ldots+(2l+1)+\ldots+(2(n-1)+1)=2\sum_{l=0}^{n-1} l+\sum_{l=0}^{n-1} l=2\sum_{l=0}^{n-1} l+n.$$

But $\sum_{l=0}^{k} l=\dfrac{k(k+1)}{2}$ so the maximum number of electrons to be accommodated is $\dfrac{2(n-1)n}{2}+n=n^2$.

8-21 (a) $\psi_{2s}(r)=\dfrac{1}{4(2\pi)^{1/2}}\left(\dfrac{1}{a_0}\right)^{3/2}\left(2-\dfrac{r}{a_0}\right)e^{-r/2a_0}$. At $r=a_0=0.529\times10^{-10}$ m we find

$$\psi_{2s}(a_0)=\frac{1}{4(2\pi)^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}(2-1)e^{-1/2}=(0.380)\left(\frac{1}{a_0}\right)^{3/2}$$
$$=(0.380)\left[\frac{1}{0.529\times10^{-10}\ \text{m}}\right]^{3/2}=9.88\times10^{14}\ \text{m}^{-3/2}$$

(b) $|\psi_{2s}(a_0)|^2=\left(9.88\times10^{14}\ \text{m}^{-3/2}\right)^2=9.75\times10^{29}\ \text{m}^{-3}$

(c) Using the result to part (b), we get $P_{2s}(a_0)=4\pi a_0^2|\psi_{2s}(a_0)|^2=3.43\times10^{10}\ \text{m}^{-1}$.

8-23 (a) $$\frac{1}{\alpha}=\frac{\hbar c}{ke^2}=\frac{(6.63\times10^{-34}\ \text{Js})(3\times10^{8}\ \text{m/s})}{2\pi(9\times10^{9}\ \text{N m}^2/\text{C}^2)(1.6\times10^{-19}\ \text{C})^2}=137.036$$

(b) $$\frac{\lambda_c}{r_0}=\frac{h/m_ec}{ke^2/m_ec^2}=\frac{hc}{ke^2}=\frac{2\pi}{\alpha}=2\pi\times137$$

(c) $$\frac{a_0}{\lambda_c}=\frac{\hbar^2/m_eke^2}{h/m_ec}=\frac{1}{2\pi}\frac{\hbar c}{ke^2}=\frac{1}{2\pi\alpha}=\frac{137}{2\pi}$$

(d) $$\frac{1}{Ra_0}=\left(\frac{m_eke^2}{\hbar^2}\right)\left(\frac{4\pi c\hbar^3}{m_ek^2e^4}\right)=\frac{4\pi\hbar c}{ke^2}=\frac{4\pi}{\alpha}=4\pi(137)$$

8-25 The most probable distance is the value of r which maximizes the radial probability density $P(r)=|rR(r)|^2$. Since $P(r)$ is largest where $rR(r)$ reaches its maximum, we look for the most probable distance by setting $\dfrac{d\{rR(r)\}}{dr}$ equal to zero, using the functions $R(r)$ from Table 8.4. For clarity, we measure distances in bohrs, so that $\dfrac{r}{a_0}$ becomes simply r, etc. Then for the 2s state of hydrogen, the condition for a maximum is

$$0=\frac{d}{dr}\left\{(2r-r^2)e^{-r/2}\right\}=\left\{2-2r-\frac{1}{2}(2r-r^2)\right\}e^{-r/2}$$

or $0 = 4 - 6r + r^2$. There are two solutions, which may be found by completing the square to get $0 = (r-3)^2 - 5$ or $r = 3 \pm \sqrt{5}$ bohrs. Of these $r = 3 + \sqrt{5} = 5.236a_0$ gives the largest value of $P(r)$, and so is the most probable distance. For the 2*p* state of hydrogen, a similar analysis gives $0 = \frac{d}{dr}\{r^2 e^{-r/2}\} = \left\{2r - \frac{1}{2}r^2\right\}e^{-r/2}$ with the obvious roots $r = 0$ (a minimum) and $r = 4$ (a maximum). Thus, the most probable distance for the 2*p* state is $r = 4a_0$, in agreement with the simple Bohr model.

8-29 To find Δr we first compute $\langle r^2 \rangle$ using the radial probability density for the 1*s* state of hydrogen: $P_{1s}(r) = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$. Then $\langle r^2 \rangle = \int_0^\infty r^2 P_{1s}(r)dr = \frac{4}{a_0^3}\int_0^\infty r^4 e^{-2r/a_0} dr$. With $z = \frac{2r}{a_0}$, this is $\langle r^2 \rangle = \frac{4}{a_0^3}\left(\frac{a_0}{2}\right)^5 \int_0^\infty z^4 e^{-z} dz$. The integral on the right is (see Example 8.9) $\int_0^\infty z^4 e^{-z} dz = 4!$ so that $\langle r^2 \rangle = \frac{4}{a_0^3}\left(\frac{a_0}{2}\right)^5 (4!) = 3a_0^2$ and $\Delta r = \left(\langle r^2 \rangle - \langle r \rangle^2\right)^{1/2} = \left[3a_0^2 - (1.5a_0)^2\right]^{1/2} = 0.866a_0$. Since Δr is an appreciable fraction of the average distance, the whereabouts of the electron are largely unknown in this case.

8-31 Outside the surface, $U(x) = -\frac{A}{x}$ (to give $F = -\frac{dU}{dx} = -\frac{A}{x^2}$), and Schrödinger's equation is $-\left(\frac{\hbar^2}{2m_e}\right)\frac{d^2\psi}{dx^2} + \left(-\frac{A}{x}\right)\psi(x) = E\psi(x)$. From Equation 8.36 $g(r) = rR(r)$ satisfies a one-dimensional Schrödinger equation with effective potential $U_{eff}(r) = U(r) + \frac{l(l+1)\hbar^2}{2m_e r^2}$. With $l = 0$ (*s* states) and $U(r) = -\frac{kZe^2}{r}$ the equation for $g(r)$ has the same form as that for $\psi(x)$. Furthermore, $\psi(0) = 0$ if no electrons can cross the surface, while $g(0) = 0$ since $R(0)$ must be finite. It follows that the functions $g(r)$ and $\psi(x)$ are the same, and that the energies in the present case are the hydrogenic levels $E_n = -\left(\frac{Z^2 ke^2}{2a_0}\right)\left(\frac{1}{n^2}\right)$ with the replacement $kZe^2 \rightarrow A$. Remembering that $a_0 = \frac{\hbar^2}{m_e ke^2}$, we get $E_n = -\left(\frac{mA^2}{2\hbar^2}\right)\left(\frac{1}{n^2}\right)$ $n = 1, 2, \ldots$

9

Atomic Structure

9-1 $\Delta E = 2\mu_B B = hf$

$2(9.27\times10^{-24}\ \text{J/T})(0.35\ \text{T}) = (6.63\times10^{-34}\ \text{Js})f$ so $f = 9.79\times10^{9}\ \text{Hz}$

9-3 (a) $n=1$; for $n=1$, $l=0$, $m_l=0$, $m_s=\pm\frac{1}{2}$ $\rightarrow 2$ sets

n	l	m_l	m_s
1	0	0	−1/2
1	0	0	+1/2

$2n^2 = 2(1)^2 = 2$

(b) For $n=2$ we have

n	l	m_l	m_s
2	0	0	±1/2
2	1	−1	±1/2
2	1	0	±1/2
2	1	1	±1/2

Yields 8 sets; $2n^2 = 2(2)^2 = 8$. Note that the number is twice the number of m_l values. Also that for each l there are $2l+1$ m_l values. Finally, l can take on values ranging from 0 to $n-1$, so the general expression is $s = \sum_{0}^{n-1} 2(2l+1)$. The series is an arithmetic progression: $2+6+10+14\ldots$, the sum of which is

$$s = \frac{n}{2}[2a+(n-1)d] \qquad \text{where } a=2,\ d=4$$
$$s = \frac{n}{2}[4+(n-1)4] = 2n^2$$

(c) $n=3$: $2(1)+2(3)+2(5) = 2+6+10 = 18 = 2n^2 = 2(3)^2 = 18$

(d) $n=4$: $2(1)+2(3)+2(5)+2(7) = 32 = 2n^2 = 2(4)^2 = 32$

(e) $n=5$: $32+2(9) = 32+18 = 50 = 2n^2 = 2(5)^2 = 50$

9-5 The time of passage is $t = \frac{1\text{ m}}{100\text{ m/s}} = 0.01\text{ s}$. Since the field gradient is assumed uniform, so is the force, and hence the acceleration. Thus the deflection is $d = \frac{1}{2}at^2$, or $a = \frac{2d}{t^2}$ for the acceleration. The required force is then

$$F_z = \frac{M2d}{t^2} = \frac{2(108\text{ u})(1.66\times10^{-27}\text{ kg/u})(10^{-3}\text{ m})}{(10^{-2}\text{ s})^2} = 3.59\times10^{-24}\text{ N}.$$

The magnetic moment of the silver atom is due to a single unpaired electron spin, so

$$\mu_z = 2\left(\frac{e}{2m_e}\right)S_z = 2\left(\frac{e}{2m_e}\right)\left(\frac{\hbar}{2}\right) = \mu_B = 9.27\times10^{-24}\text{ J/T}.$$

Thus,

$$\frac{dB_z}{dz} = \frac{F_z}{\mu_z} = \frac{3.59\times10^{-24}\text{ N}}{9.27\times10^{-24}\text{ N}} = 0.387\text{ T/m}.$$

9-7 The angular momentum L of a spinning ball is related to the angular velocity of rotation ω as $\mathbf{L} = I\omega$. I, the moment of inertia, is given in terms of the mass m and radius R of the ball as $I = \frac{2}{5}mR^2$. For the electron this gives

$$I = \frac{2}{5}(511\times10^3\text{ eV}/c^2)(3\times10^{-6}\text{ nm})^2 = 1.840\times10^{-6}\text{ eV nm}^2/c^2.$$

Then, using $L = \frac{\sqrt{3}}{2}\hbar$, we find $\omega = \frac{L}{I} = \frac{\sqrt{3}}{2}\frac{(197.3\text{ eV nm}/c)}{1.840\times10^{-6}\text{ eV nm}^2/c^2} = 9.286\times10^7\ c/\text{nm}$. The equatorial speed is

$$v = R\omega = (3\times10^{-6}\text{ nm})(9.286\times10^7\ c/\text{nm}) = 278.6c$$

$$\frac{v}{c} = 278.6$$

9-9 With $s = \frac{3}{2}$, the spin magnitude is $|\mathbf{S}| = [s(s+1)]^{1/2}\hbar = \left(\frac{[15]^{1/2}}{2}\right)\hbar$. The z-component of spin is $S_z = m_s\hbar$ where m_s ranges from $-s$ to s in integer steps or, in this case, $m_s = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$. The spin vector S is inclined to the z-axis by an angle θ such that

$$\cos(\theta) = \frac{S_z}{|\mathbf{S}|} = \frac{m_s\hbar}{([15]^{1/2}/2)\hbar} = \frac{m_s}{[15]^{1/2}/2} = -\frac{3}{(15)^{1/2}}, -\frac{1}{(15)^{1/2}}, +\frac{1}{(15)^{1/2}}, +\frac{3}{(15)^{1/2}}$$

or $\theta = 140.8°, 105.0°, 75.0°, 39.2°$. The Ω^- *does* obey the Pauli Exclusion Principle, since the spin s of this particle is half-integral, as it is for all fermions.

9-11 For a d electron, $l=2$; $s=\frac{1}{2}$; $j=2+\frac{1}{2},\ 2-\frac{1}{2}$

For $j=\frac{5}{2}$; $m_j=-\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$

For $j=\frac{3}{2}$; $m_j=-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

9-13 (a) $4F_{5/2} \rightarrow n=4,\ l=3,\ j=\frac{5}{2}$

(b) $|\mathbf{J}|=[j(j+1)]^{1/2}\hbar=\left[\left(\frac{5}{2}\right)\left(\frac{7}{2}\right)\right]^{1/2}\hbar=\left[\frac{35}{4}\right]^{1/2}\hbar=\left[\frac{(35)^{1/2}}{2}\right]\hbar$

(c) $J_z=m_j\hbar$ where m_j can be $-j, -j+1, \ldots, j-1, j$ so here m_j can be $-\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$. J_z can be $-\frac{5}{2}\hbar, -\frac{3}{2}\hbar, -\frac{1}{2}\hbar, \frac{1}{2}\hbar, \frac{3}{2}\hbar$, or $\frac{5}{2}\hbar$.

9-15 The spin of the atomic electron has a magnetic energy in the field of the orbital moment given by Equations 9.6 and 9.12 with a g-factor of 2, or $U=-\boldsymbol{\mu}_s\cdot\mathbf{B}=2\left(\frac{e}{2m_e}\right)S_zB=2\mu_B m_s B$. The magnetic field **B** originates with the orbiting electron. To estimate **B**, we adopt the equivalent viewpoint of the atomic nucleus (proton) circling the electron, and borrow a result from classical electromagnetism for the **B** field at the center of a circular current loop with radius r: $B=\frac{2k_m\mu}{r^3}$. Here k_m is the magnetic constant and $\mu=i\pi r^2$ is the magnetic moment of the loop, assuming it carries a current i. In the atomic case, we identify r with the orbit radius and the current i with the proton charge $+e$ divided by the orbital period $T=\frac{2\pi r}{v}$. Then $\mu=\frac{evr}{2}=\left(\frac{e}{2m_e}\right)L$ where $L=m_e vr$ is the orbital angular momentum of the *electron*. For a p electron $l=1$ and $L=[l(l+1)]^{1/2}\hbar=\sqrt{2}\hbar$, so $\mu=\left(\frac{e\hbar}{2m_e}\right)\sqrt{2}=\mu_B\sqrt{2}=1.31\times10^{-23}\ \text{J/T}$. For r we take a typical atomic dimension, say $4a_0\left(=2.12\times10^{-10}\ \text{m}\right)$ for a $2p$ electron, and find

$$B=\frac{2\left(10^{-7}\ \text{N/A}^2\right)\left(1.31\times10^{-23}\ \text{J/T}\right)}{\left(2.12\times10^{-10}\ \text{m}\right)^3}=0.276\ \text{T}.$$

Since m_s is $\pm\frac{1}{2}$ the magnetic energy of the electron spin in this field is

$$U=\pm\mu_B B=\pm\left(9.27\times10^{-24}\ \text{J/T}\right)(0.276\ \text{T})=\pm2.56\times10^{-24}\ \text{J}=\pm1.59\times10^{-5}\ \text{eV}.$$

The up spin orientation (+) has the higher energy; the predicted energy difference between the up (+) and down (–) spin orientations is twice this figure, or about 3.18×10^{-5} eV—a result which compares favorably with the measured value, 5×10^{-5} eV.

9-17 From Equation 8.9 we have $E=\left(\frac{\hbar^2\pi^2}{2mL^2}\right)\left(n_1^2+n_2^2+n_3^2\right)$

$$E=\frac{\left(1.054\times10^{-34}\right)^2\left(\pi^2\right)\left(n_1^2+n_2^2+n_3^2\right)}{2\left(9.11\times10^{-31}\right)\left(2\times10^{-10}\right)^2}=\left(1.5\times10^{-18}\text{ J}\right)\left(n_1^2+n_2^2+n_3^2\right)=(9.4\text{ eV})\left(n_1^2+n_2^2+n_3^2\right)$$

(a) 2 electrons per state. The lowest states have

$$\left(n_1^2+n_2^2+n_3^2\right)=(1,\ 1,\ 1)\Rightarrow E_{111}=(9.4\text{ eV})\left(1^2+1^2+1^2\right)\text{ eV}=28.2\text{ eV}.$$

For $\left(n_1^2+n_2^2+n_3^2\right)=(1,\ 1,\ 2)$ or $(1,\ 2,\ 1)$ or $(2,1,1)$,

$$E_{112}=E_{121}=E_{211}=(9.4\text{ eV})\left(1^2+1^2+2^2\right)=56.4\text{ eV}$$
$$E_{\text{min}}=2\times\left(E_{111}+E_{112}+E_{121}+E_{211}\right)=2(28.2+3\times56.4)=398.4\text{ eV}$$

(b) All 8 particles go into the $\left(n_1^2+n_2^2+n_3^2\right)=(1,\ 1,\ 1)$ state, so

$$E_{\text{min}}=8\times E_{111}=225.6\text{ eV}.$$

9-21 (a) $1s^2\,2s^2\,2p^4$

(b) For the two 1*s* electrons, $n=1,\quad l=0,\ m_l=0,\ m_s=\pm\frac{1}{2}$.

For the two 2*s* electrons, $n=2,\ l=0,\ m_l=0,\ m_s=\pm\frac{1}{2}$.

For the four 2*p* electrons, $n=2,\ l=1,\ m_l=1,\ 0,\ -1,\ m_s=\pm\frac{1}{2}$.

9-23 All spins are paired for $[\text{Kr}]4d^{10}$ and two are unpaired for $[\text{Kr}]4d^9 5s^1$. Thus Hund's rule would favor the latter, but for the fact that completely filled subshells are especially stable. Thus $[\text{Kr}]4d^{10}$ with its completely filled 4*d* subshell has the lesser energy. The element is palladium (Pd).

9-25 A typical ionization energy is 8 eV. For internal energy to ionize most of the atoms would require $\frac{3}{2}k_BT=8\text{ eV}:\ T=\frac{2\times8\left(1.60\times10^{-19}\text{ J}\right)}{3\left(1.38\times10^{-23}\text{ J/K}\right)}\sim$ between 10^4 K and 10^5 K.

9-27 (a) The L_α photon can be thought of as arising from the $n=3$ to $n=2$ transition in a one-electron atom with an effective nuclear charge. The M electron making the transition is shielded by the remaining L shell electrons (5) and the innermost K shell electrons (2), leaving an effective nuclear charge of $Z-7$. Thus, the energy of the L_α photon should be $E[\text{L}_\alpha]=\frac{ke^2}{2a_0}\ \frac{(Z-7)^2}{3^2}+\frac{ke^2}{2a_0}\ \frac{(Z-7)^2}{2^2}+\frac{ke^2}{2a_0}\ \frac{5(Z-7)^2}{36}$. Writing $E=hf$ and noting that $\frac{ke^2}{2a_0}=13.6\text{ eV}$ this relation may be solved for the photon frequency *f*.

Taking the square root of the resulting equation gives $\sqrt{f}=\sqrt{\frac{5}{36}\left(\frac{13.6\text{ eV}}{h}\right)}(Z-7)$.

(b) According to part (a), the plot of $\sqrt{f}$ against Z should have intercept = 7 and slope $\sqrt{\frac{5}{36}\left(\frac{13.6\text{ eV}}{h}\right)} = \sqrt{\frac{5(13.6\text{ eV})}{36(4.14\times10^{-15}\text{ eV s})}} = 0.214\times10^{8}\text{ Hz}^{1/2}$. From Figure 9.18 we find data points on the L_α line [in the form $(\sqrt{f},\ Z)$] at (14, 74) and (8, 45). From this we obtain the slope $\frac{14-8}{74-45} = 0.21\times10^{8}\text{ Hz}^{1/2}$. Thus, the empirical line fitting the L_α data is $\sqrt{f} = 0.21(Z-I)$ where I is the intercept. Using (14, 74) for $(\sqrt{f},\ Z)$ in this equation gives the intercept $I = 7.3$, but with (8, 45) for $(\sqrt{f},\ Z)$ we get $I = 6.9$. Alternatively, using *both* data pairs and dividing, we eliminate the calculated value of the slope to get $\frac{14}{8} = \frac{74-I}{45-I}$. This last approach affords the best experimental value for I based on the available data and gives $I = \frac{(14)(45)-(8)(74)}{14-8} = 6.3$.

(c) The average screened nuclear charge seen by the M shell electron is just $Z - I = Z - 6.3$, indicating that shielding by the inner shell electrons is not quite as effective as our naïve screening arguments would suggest.

10

Statistical Physics

10-1 Using $\overline{n}_j = n_{j1}p_1 + n_{j2}p_2 + \ldots$ we obtain:

$$\begin{aligned}
\overline{n}_1 = n_{11}p_1 + n_{12}p_2 + n_{120}p_{20} &= (0)\left(\frac{6}{1\,287}\right) + (1)\left(\frac{30}{1\,287}\right) + (0)\left(\frac{30}{1\,287}\right) + (2)\left(\frac{60}{1\,287}\right) + (0)\left(\frac{30}{1\,287}\right) \\
&+ (1)\left(\frac{120}{1\,287}\right) + (3)\left(\frac{60}{1\,287}\right) + (0)\left(\frac{15}{1\,287}\right) + (1)\left(\frac{120}{1\,287}\right) + (0)\left(\frac{60}{1\,287}\right) + (2)\left(\frac{180}{1\,287}\right) + (4)\left(\frac{30}{1\,287}\right) \\
&+ (0)\left(\frac{60}{1\,287}\right) + (2)\left(\frac{90}{1\,287}\right) + (1)\left(\frac{180}{1\,287}\right) + (3)\left(\frac{120}{1\,287}\right) + (5)\left(\frac{6}{1\,287}\right) + (0)\left(\frac{15}{1\,287}\right) + (2)\left(\frac{60}{1\,287}\right) \\
&+ (4)\left(\frac{15}{1\,287}\right) \\
&= \frac{30 + 120 + 120 + 180 + 120 + 360 + 120 + 180 + 180 + 360 + 30 + 120 + 60}{1\,287} \\
&= 1.538\,46
\end{aligned}$$

$$p(1E) = \frac{\overline{n}_1}{6} = \frac{1.538}{6} = 0.256.$$

One can find $p(2E)$ through $p(8E)$ in similar fashion.

10-3 A molecule moving with speed v takes $\frac{d}{v}$ seconds to cross the cylinder, where d is the cylinder's diameter. In this time the detector rotates θ radians where $\theta = \omega t = \frac{\omega d}{v}$. This means the molecule strikes the curved glass plate at a distance from A of $s = \frac{d}{2}\theta = \frac{\omega d^2}{2v}$ as $m_{\mathrm{Bi}_2} = 6.94 \times 10^{-22}$ g and

$$\langle v \rangle = \left[\frac{8k_{\mathrm{B}}T}{\pi m}\right]^{1/2} = \left[\frac{(8)(1.38 \times 10^{-23}\ \mathrm{J/K})(850\ \mathrm{K})}{(\pi)(6.94 \times 10^{-25}\ \mathrm{kg})}\right] = 207\ \mathrm{m/s}$$

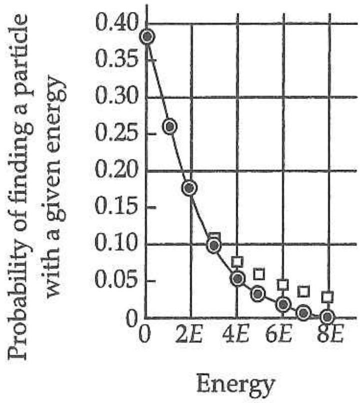
$$v_{\mathrm{rms}} = \left(\frac{3k_{\mathrm{B}}T}{m}\right)^{1/2} = 225\ \mathrm{m/s} \qquad v_{\mathrm{mp}} = \left(\frac{2k_{\mathrm{B}}T}{m}\right)^{1/2} = 184\ \mathrm{m/s}$$

$$s_{\mathrm{rms}} = \left(\frac{6\,250 \times 2\pi}{60\ \mathrm{s}}\right)\frac{(0.10\ \mathrm{m})^2}{(2)(225)\ \mathrm{m/s}} = 1.45\ \mathrm{cm}$$

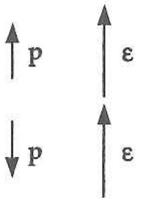
$$s_{\langle v \rangle} = 1.58\ \mathrm{cm} \qquad s_{\mathrm{mp}} = 1.78\ \mathrm{cm}$$

10-5 Fit a curve Ae^{-BE} to Figure 10.2. An ambitious solution would use a least squares fit to determine A and B. The quick fit suggested below uses a match only at 0 and $1E$. $P(E)=Ae^{-BE}$ thus $P(0)=A$ and $P(E_1)=Ae^{-BE_1}$. From Figure 10.2 one finds $P(0)=0.385$, and this gives $A=0.385$. To determine B use the value $P(1E)=0.256=Ae^{-BE_1}=0.385e^{-BE_1}$ thus $e^{-BE_1}=0.665$ and $B=-\dfrac{\ln(0.665)}{E_1}=\dfrac{0.408}{E_1}$ and so $P(E)=(0.385)e^{-(0.408E/E_1)}$. This equation was used to determine the probability as follows $P(0)=0.385$, $P(1E_1)=0.256$, $P(2E_1)=0.170$, $P(3E_1)=0.113$, $P(4E_1)=0.075$, $P(5E_1)=0.050$, $P(6E_1)=0.033$, $P(7E_1)=0.022$, $P(8E_1)=0.015$.

The exact values are $P(0)=0.385$, $P(1E_1)=0.256$, $P(2E_1)=0.167$, $P(3E_1)=0.078$, $P(4E_1)=0.054$, $P(5E_1)=0.027$, $P(6E_1)=0.012$, $P(7E_1)=0.003\,9$, $P(8E_1)=0.000\,717$. These values are plotted below. One sees that this approximation is good for low energy. There is exact agreement for $P(0)$ and $P(1E)$ and small deviations for the next two values with percent deviations for the higher energy values.



10-7 (a)



$$E_U=-\mathbf{p}\cdot\varepsilon=-\varepsilon\cos 0°=-p\varepsilon$$
$$E_D=-\mathbf{p}\cdot\varepsilon=-\varepsilon\cos 180°=+p\varepsilon$$

so $\Delta E=E_D-E_U=2p\varepsilon$.

(b) Let $n(2p\varepsilon)$ be the number of molecules in the excited state.

$$\frac{n(2p\varepsilon)}{n(0)}=\frac{g(2p\varepsilon)Ae^{-2p\varepsilon/k_BT}}{g(0)Ae^{0}}=2e^{-2p\varepsilon/k_BT}$$

(c) $\frac{1.90}{1} = \frac{n(2p\varepsilon)}{n(0)} = 2e^{-2p\varepsilon/k_BT}$. For $p = 1.0\times10^{-30}$ Cm and $\varepsilon = \left(1.0\times10^{6}\ \text{V/m}\right)$,

$$\frac{2p\varepsilon}{k_BT} = \frac{(2)\left(1.0\times10^{-30}\ \text{Cm}\right)\left(1.0\times10^{6}\ \text{V/m}\right)}{\left(1.38\times10^{-23}\ \text{J/K}\right)T} = \frac{0.144\,9}{T}$$

so $1.90 = 2e^{-0.1449/T}$ or $0.95 = e^{-0.1449/T}$. Solving for T, $\ln(0.95) = \frac{-0.149\,9}{T}$ or $T = 2.83\ \text{K}$.

(d) $\overline{E} = [n(2p\varepsilon)][2p\varepsilon] + \frac{[n(0)][0]}{n(2p\varepsilon)+n(0)} = \frac{[n(2p\varepsilon)/n(0)](2p\varepsilon)}{[n(2p\varepsilon)+n(0)]+1} = \frac{\left[2e^{-2p\varepsilon/k_BT}\right][2p\varepsilon]}{2e^{-2p\varepsilon/k_BT}+1}$

$= \frac{2p\varepsilon}{1+(1/2)e^{2p\varepsilon/k_BT}}$.

As $T\to0$, $\overline{E}\to0$ and as $T\to\infty$, $E\to\frac{2p\varepsilon}{3/2} = \frac{4p\varepsilon}{3}$.

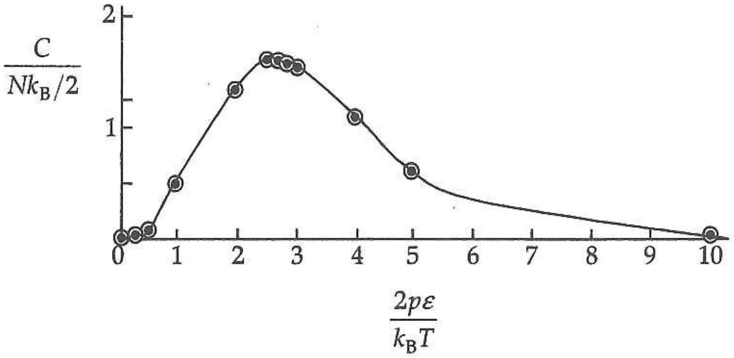
(e) $dE_{\text{total}} = \overline{N}E = \frac{2p\varepsilon N}{1+(1/2)e^{2p\varepsilon/k_BT}}$

$C = \frac{dE_{\text{total}}}{dT} = \frac{(Nk_B/2)(2p\varepsilon/k_BT)^2 e^{2p\varepsilon/k_BT}}{\left[1+(1/2)e^{2p\varepsilon/k_BT}\right]^2}$

(f) By expanding e^x where $x = \frac{2p\varepsilon}{k_BT}$ one can show that $C\to0$ for $T\to\infty$ as $C = \left(\frac{8N}{9}\right)\left(\frac{p^2\varepsilon^2}{k_B^2}\right)\left(\frac{1}{T^2}\right)$ and $C\to0$ for $T\to0$ as $C = \frac{(2Nk_B)[2p\varepsilon/(k_BT)]^2}{e^{2p\varepsilon/k_BT}}$. To find the maximum in $C = \left(\frac{Nk_B}{2}\right)\left(x^2\right)\left\{\frac{e^x}{\left[1+(1/2)e^x\right]^2}\right\}$ set $\frac{dC}{dT} = 0$ or $\left(\frac{dC}{dx}\right)\left(\frac{dx}{dT}\right) = 0$. Taking derivatives we get:

$$\left[\frac{-x^3e^x}{\left(1+(1/2)e^x\right)^2}\right]\left[\frac{2+x-xe^x}{1+(1/2)e^x}\right] = 0.$$

Setting the first factor equal to 0 yields the minima in C at $T = 0$ and $T = \infty$, while the second factor yields a maximum at the solution of the transcendental equation, $\frac{x+2}{x-2} = \frac{e^x}{2}$. This transcendental equation has a solution at $x\approx2.65$, which corresponds to a temperature of $\frac{2p\varepsilon}{k_BT} = 2.65$ or $T = \frac{2p\varepsilon}{2.65k_B} = \frac{0.144\,9}{2.65} = 0.054\,7\ \text{K}$. The expression for heat capacity can be rewritten as $C = A\left[e^x\frac{x}{\left(1+(1/2)e^x\right)^2}\right]$ where $A = \frac{Nk_B}{2}$ and $x = \frac{2p\varepsilon}{k_BT}$. Below is the sketch of C as a function of $\frac{2p\varepsilon}{k_BT}$.



The heat capacity is the change of internal energy with temperature. For both large temperature ($T \to \infty$) and low temperature ($T \to 0$) the internal energy is constant and so the heat capacity is zero. At T approximately equal to 0.0547 K there is a rapid change of energy with temperature; so the heat capacity becomes large and reaches its maximum value.

10-9 $\bar{v} = \sqrt{\frac{8k_BT}{\pi m}}$. Using a molar weight of 55.85 g for iron gives the mass of an iron atom:

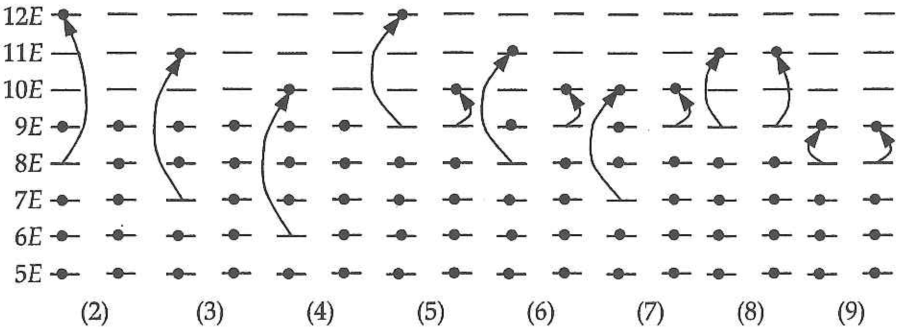
$m = \frac{55.85\text{ g}}{6.02\times10^{23}} = 9.28\times10^{-26}$ kg. Thus, $\bar{v} = \sqrt{\frac{(8)(1.38\times10^{-23}\text{ J/K})(6\,000\text{ K})}{(\pi)(9.28\times10^{-26}\text{ kg})}} = 1.51\times10^3$ m/s.

Since the speed of the emitting atoms is much less than c, we use the classical doppler shift, $f = f_0(1 \pm v/c)$. Then

$$\frac{\Delta f}{f_0} = \frac{f^+_{\max} - f^-_{\max}}{f_0} = \frac{f_0(1+v/c) - f_0(1-v/c)}{f_0} = \frac{2v}{c} = \frac{(2)(1.51\times10^3\text{ m/s})}{3.00\times10^8\text{ m/s}} = 1.01\times10^{-5}$$

or 1 part per 100 000.

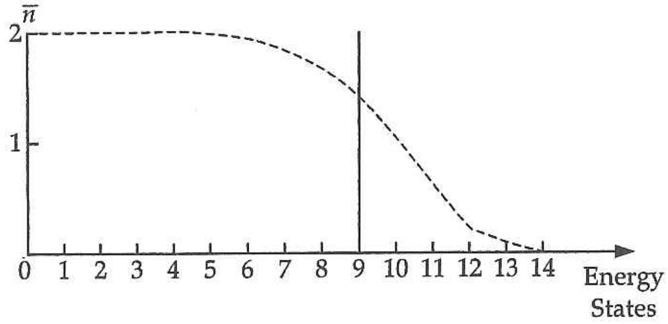
10-11



Thus,

$$\begin{aligned}
\bar{n}_{0E} &= \frac{1}{9}\times 2+\frac{1}{9}\times 2+\frac{1}{9}\times 2+\frac{1}{9}\times 2+\frac{1}{9}\times 2+\frac{1}{9}\times 2+\frac{1}{9}\times 2+\frac{1}{9}\times 2+\frac{1}{9}\times 2=2.00\\
\bar{n}_{0E} &\text{ through } \bar{n}_{5E}=2.00\\
\bar{n}_{6E} &= 8\left(\frac{1}{9}\times 2\right)+\left(\frac{1}{9}\times 1\right)=1.89\\
\bar{n}_{7E} &= 7\left(\frac{1}{9}\times 2\right)+\left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)=1.78\\
\bar{n}_{8E} &= 6\left(\frac{1}{9}\times 2\right)+\left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)=1.55\\
\bar{n}_{9E} &= 4\left(\frac{1}{9}\times 2\right)+\left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)=1.22\\
\bar{n}_{10E} &= \left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 2\right)+\left(\frac{1}{9}\times 2\right)=0.777\\
\bar{n}_{11E} &= \left(\frac{1}{9}\times 2\right)+\left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)=0.444\\
\bar{n}_{12E} &= \left(\frac{1}{9}\times 1\right)+\left(\frac{1}{9}\times 1\right)=0.222\\
\bar{n}_{13E} &= \left(\frac{1}{9}\times 1\right)=0.111\\
\bar{n}_{14E} &= 0.00
\end{aligned}$$

Minimum energy occurs for all levels filled up to $9E$, corresponding to a total energy of $90E$. So $E_F(0\text{ K})=9E$. Using Equation 10.2 the following plot is obtained.



10-13 (a) $C=(3R)\left(\frac{\hbar\omega}{k_B T_E}\right)^2 \frac{e^{\hbar\omega/k_B T_E}}{\left(e^{\hbar\omega/k_B T_E}-1\right)^2}$. For $T=T_E$, $k_B T_E=\hbar\omega$, so

$$C=(3R)\left(\frac{\hbar\omega}{\hbar\omega}\right)^2 \frac{e^{\hbar\omega/\hbar\omega}}{\left(e^{\hbar\omega/\hbar\omega}-1\right)^2}=(3R)\frac{e}{(e-1)^2}=(3R)(0.920\,7)=2.76R.$$

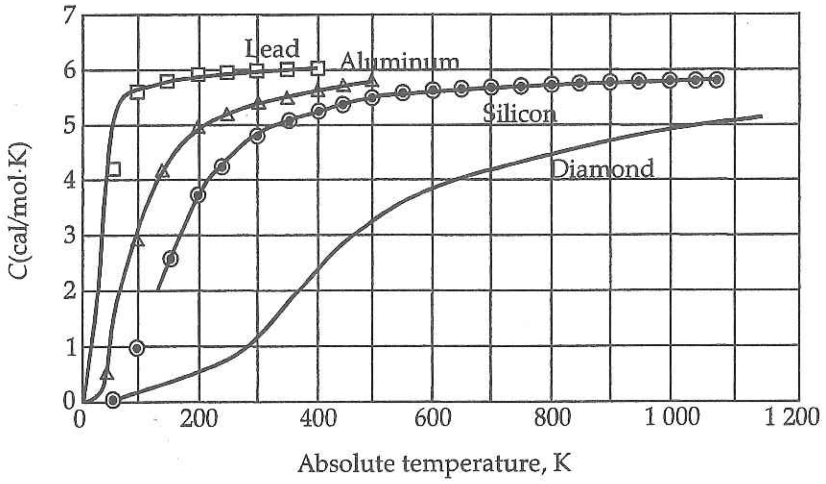
Using $R=1.986$ cal/mol K $\Rightarrow C=5.48$ cal/mol K.

(b) From Figure 10.9, T_E lead ≈ 100 K, T_E aluminum ≈ 300 K, T_E silicon ≈ 500 K.

(c) Using $C = (3R)\left(\frac{T_{\mathrm{E}}}{T}\right)^2 \frac{e^{T_{\mathrm{E}}/T}}{\left(e^{T_{\mathrm{E}}/T}-1\right)^2} = (5.97\ \text{cal/mol K})\left(\frac{T_{\mathrm{E}}/T}{e^{T_{\mathrm{E}}/T}-1}\right)^2 e^{T_{\mathrm{E}}/T}$ heat capacities for lead, aluminum, and silicon were obtained. These results can be summarized in the following tables.

Lead	$T_{\mathrm{E}} = 100$ K		
T(K)	C(cal/(mol K))	T(K)	C(cal/(mol K))
50	4.32	250	5.92
100	5.49	300	5.94
150	5.74	350	5.96
200	5.83	400	6.09
Aluminum	$T_{\mathrm{E}} = 300$ K		
T(K)	C(cal/(mol K))	T(K)	C(cal/(mol K))
50	0.535	250	5.30
100	2.96	300	5.509
150	4.32	350	5.62
200	4.97	400	5.70
Silicon	$T_{\mathrm{E}} = 500$ K		
T(K)	C(cal/(mol K))	T(K)	C(cal/(mol K))
50	0.027	600	5.64
100	1.02	650	5.67
150	2.55	700	5.74
200	3.64	750	5.75
250	4.97	800	5.78
300	4.76	850	5.81
350	5.05	900	5.84
400	5.25	950	5.85
450	5.41	1 000	5.83
500	5.50	1 050	5.85
550	5.59	1 100	5.95

These values are now plotted on Figure 10.9 as shown.



10-15 Al: $E_F = 11.63$ eV

(a) $$E_F = \frac{h^2}{2m_e}\left(\frac{3n}{8\pi}\right)^{2/3} \text{ or } n = \frac{8\pi}{3}\left(\frac{2m_e E_F}{h^2}\right)^{3/2} \text{ so}$$

$$n = \frac{8\pi}{3}\left[\frac{(2)(9.11\times10^{-31}\ \text{kg})(11.63\ \text{eV})(1.6\times10^{-19}\ \text{J/eV})}{(6.625\times10^{-34}\ \text{Js})^2}\right]^{3/2} = 1.80\times10^{29}\ \text{free electrons/m}^3.$$

(b) $$n' = \frac{\rho N_A}{M} = \frac{(2.7\ \text{g/cm}^3)(6.02\times10^{23}\ \text{atoms/mole})}{27\ \text{g/mole}}$$

$$n' = 6.02\times10^{22}\ \text{atoms/cm}^3 = 6.02\times10^{28}\ \text{atoms/m}^3$$

$$\text{Valence} = \frac{n}{n'} = \frac{18\times10^{28}}{6\times10^{28}} = 3$$

10-17 Equation 10.46 gives $E_F(0)$ in terms of $\frac{N}{V}$ as $E_F = \left(\frac{h^2}{2m}\right)\left(\frac{3N}{8\pi V}\right)^{2/3}$. Substituting the mass of a proton, and noting that $A = 64$ for Zn, $m = 1.67\times10^{-27}$ kg; $N = \frac{A}{2} = 32$ and $V = \frac{4}{3}\pi R^3 = \frac{4}{3}(\pi)(4.8\times10^{-15}\ \text{m})^3 = 4.6\times10^{-43}\ \text{m}^3$ yields

$$E_F = \frac{(6.62\times10^{-34})^2\ \text{J}^2\text{s}^2}{3.34\times10^{-27}\ \text{kg}} \times \left(\frac{(3)(32)}{(8\pi)(4.6\times10^{-43}\ \text{m}^3)}\right)^{2/3} = 5.3\times10^{-12}\ \text{J} = 33.4\ \text{MeV}$$

$$E_{\text{av}} = \frac{3}{5}E_F = 20\ \text{MeV}$$

These energies are of the correct order of magnitude for nuclear particles.

10-19 $f_{\text{FD}} = \left[e^{(E-E_F)/k_BT} + 1\right]^{-1}$; $E_F = 7.05$ eV; $k_BT = (1.38\times10^{-23}\ \text{J/K})(300\ \text{K}) = 4.14\times10^{-21}\ \text{J} = 0.025\,9$ eV

At $E = 0.99E_F$, $f_{\text{FD}} = \left[e^{-0.01E_F/k_BT} + 1\right]^{-1} = \frac{1}{e^{-0.070\,5/0.025\,9} + 1} = \frac{1}{1.065\,70} = 0.938$, thus 93.8% probability.

10-21 $\rho = 0.971\ \text{g/cm}^3$, $M = 23.0$ g/mole (sodium)

(a) $$n = \frac{N_A \rho}{M}$$

$$n = (6.02\times10^{23}\ \text{electrons/mole})(0.971\ \text{g/cm}^3)(23.0\ \text{g/mole})$$

$$n = 2.54\times10^{22}\ \text{electrons/cm}^3 = 2.54\times10^{28}\ \text{electrons/m}^3$$

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

$$E_F = \left[\frac{(6.625\times10^{-34}\ \text{Js})^2}{(2\times9.11\times10^{-31}\ \text{kg})}\right]\left[\frac{3\times2.54\times10^{28}\ \text{electrons/m}^3}{8\pi}\right]^{2/3}$$

$$E_F = 5.04\times10^{-19}\ \text{J} = 3.15\ \text{eV}$$

(c) $v_F = \left(\frac{2E_F}{m}\right)^{1/2} = \left[\frac{2 \times 5.04 \times 10^{-19}\ \text{J}}{9.11 \times 10^{-31}\ \text{kg}}\right]^{1/2}$

$v_F = 1.05 \times 10^6\ \text{m/s}$

10-23 $d = 1\ \text{mm} = 10^{-3}\ \text{m};\ V = (10^{-3}\ \text{m})^3 = 10^{-9}\ \text{m}^3$

The <u>density of states</u> $= g(E) = CE^{1/2} = \left\{\frac{8(2)^{1/2}\pi m_e^{3/2}}{h^3}\right\}E^{1/2}$

$$g(E) = 8(2)^{1/2}\pi(9.11 \times 10^{-31}\ \text{kg})^{3/2}\frac{[(4.0\ \text{eV})(1.6 \times 10^{-19}\ \text{J/eV})]^{1/2}}{(6.626 \times 10^{-34}\ \text{Js})^3}$$

$$g(E) = (8.50 \times 10^{46})\text{m}^{-3}\ \text{J}^{-1} = (1.36 \times 10^{28})\text{m}^{-3}\ \text{eV}^{-1}$$

$$f_{\text{FD}}(E) = \frac{1}{e^{(E-E_F)/k_BT} + 1}\ \text{or}$$

$$f_{\text{FD}}(4.0\ \text{eV}) = \frac{1}{e^{(4.0-5.5)/(8.6\times10^{-5}\ \text{eV/K})(300\ \text{K})} + 1} = \frac{1}{e^{-59} + 1} = 1$$

So the total number of electrons $= N = g(E)(\Delta E)Vf_{\text{FD}}(E)$ or
$N = (1.36 \times 10^{28}\ \text{m}^{-3}\ \text{eV}^{-1})(0.025\ \text{eV})(10^{-9}\ \text{m}^3)(1) = 3.40 \times 10^{17}$.

10-25 Use the equation $n(v) = \frac{4\pi N}{V}\frac{m}{(2\pi k_BT)^{3/2}}v^2e^{-mv^2/(2k_BT)}$ where m is the mass of the O_2 molecule in kg and $\frac{N}{V}$ is 10^4 molecules per cm^3. Rewrite the equation in the form $n(v) = A_1\left(\frac{A_2}{T}\right)^{3/2}v^2e^{-A_3v^2}$ where $A_1 = \frac{4\pi N}{V}$, $A_2 = \frac{m}{2\pi k_B}$, and $A_3 = \frac{m}{2k_B}$. Use the exponential format for large and small numbers to avoid computer errors.

(a) For $T = 300$ K the equation can be rewritten as $n(v) = B_1v^2e^{-B_2v^2}$ where $B_1 = A_1\left(\frac{A_2}{300}\right)^{3/2}$ and $B_2 = \frac{A_3}{300}$. Do a 21 step loop for v from 0 to 2 000 m/s storing $n300(i)$ as an array where $i = 1$ to 21 and corresponds to $v = 0$ to 2 000.

(b) Repeat the calculation in (a) except that the A's are now divided by 1 000 and call the array $n1000(j)$ where $j = 1$ to 21 and corresponds to $v = 0$ to 2 000.

(c) Use a plot routine to obtain a graph similar to Figure 10.4 for the arrays obtained in parts (a) and (b). To obtain the number of molecules with speeds between 800 m/s and 1 000 m/s do a summation. The number of molecules $= [n1\,000(9)](100) + [n1\,000(10)](100)$ where $n1\,000(9)$ and $n1\,000(10)$ is the number calculated in (b) for speed 800 m/s and 900 m/s, respectively.

(d) $v_{\text{rms}} = \left(\frac{3k_BT}{m}\right)^{1/2};\ v_{\text{av}} = \left(\frac{8k_BT}{\pi m}\right)^{1/2};\ v_{\text{mp}} = \left(\frac{2k_BT}{m}\right)^{1/2}$. These quantities should appear on your graph as shown in Figure 10.4.

10-27 (a) For a metal $g(E)=\left[\frac{8(2)^{1/2}\pi m_e^{3/2}}{h^3}\right]E^{1/2}=DE^{1/2}$ where $D=\frac{8(2)^{1/2}\pi m_e^{3/2}}{h^3}$ and $m_e=0.511\ \text{MeV}/c^2$ and $h=4.136\times10^{-15}\ \text{eV s}$. Using a loop calculate the array $g(E)$ for values of energy ranging from zero to 10 eV in steps of 0.5 eV. The array will be 21 dimensional, which can be plotted using a plot routine.

(b) $E_F(0)=\frac{h^2}{2m_e}\left(\frac{3N}{8\pi V}\right)^{2/3}=7.05\ \text{eV}$ from Table 10.1. For $T=0$ and $E_F<E$

$$f_{FD}=\frac{1}{e^{(E-E_F)/k_BT}+1}=\frac{1}{e^{\infty}+1}=0$$

$$n(E)=0.$$

For $T=0$ and $E_F=E$, $n(E)=\left(\frac{D}{2}\right)E_F^{1/2}$. For $T=0$ and $0<E<E_F$ one has $f_{FD}=\frac{1}{e^{-\infty}+1}=1$. Therefore $n(E)=g(E)$ where $g(E)$ is obtained from the array calculated in part (a). Use the same 0.5 eV steps in your loop.

(c) $n(E)=g(E)f_{FD}(E)$

Now calculate $f_{FD}=\frac{1}{e^{(E-E_F)/k_BT}+1}$ where $T=1\,000$ K in intervals of 0.5 eV for $E=0$ eV to 10 eV. E_F is determined for any temperature T numerically using the electron concentration

$$\frac{N}{V}=\int_0^{\infty}n(E)dE=D\int\frac{E^{1/2}dE}{e^{-(E-E_F)/k_BT}+1}\ k_BT$$

that is of the order of 10^{-20}. The dependence of E_F on temperature is weak for metals and will not differ much from its value at 0 K up to several thousand kelvin and $E-E_F$ should be less than 10, which means $\frac{E-E_F}{k_BT}$ is large. Thus

$\frac{N}{V}\simeq D\int_0^{\infty}E^{1/2}e^{(E-E_F)k_BT}dE$. This can now be evaluated numerically. Once E_F is determined then the Fermi Dirac distribution function, $f_{FD}=\frac{1}{e^{(E-E_F)/k_BT}+1}$, can be evaluated as an array using the same energy increments as before. The particle distribution function, $n(E)$, is the product of the arrays $g(E)$ and $f_{FD}(E)$. Now $n(E)$ can be plotted as a function of energy.