9

Atomic Structure

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

$2\left(9.27 \times 10^{-24} \text{ J/T}\right)(0.35 \text{ T}) = \left(6.63 \times 10^{-34} \text{ Js}\right) f$ so $f = 9.79 \times 10^{9}$ 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) $n=3:\quad 2(1)+2(3)+2(5) = 2+6+10 = 18 = 2n^2 = 2(3)^2 = 18$

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

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

9-4 (a) 3*d* subshell $\Rightarrow l=2 \Rightarrow m_l = -2,\ -1,\ 0,\ 1,\ 2$ and $m_s = \pm\frac{1}{2}$ for each m_l

n	l	m_l	m_s
3	2	–2	–1/2
3	2	–2	+1/2
3	2	–1	–1/2
3	2	–1	+1/2
3	2	0	–1/2
3	2	0	+1/2
3	2	1	–1/2
3	2	1	+1/2
3	2	2	–1/2
3	2	2	+1/2

(b) 3*p* subshell: for a *p* state, $l=1$. Thus m_l can take on values $-l$ to *l*, or –1, 0, 1. For each m_l, m_s can be $\pm\frac{1}{2}$.

n	l	m_l	m_s
3	1	–1	–1/2
3	1	–1	+1/2
3	1	0	–1/2
3	1	0	+1/2
3	1	1	–1/2
3	1	1	+1/2

9-6 The exiting beams differ in the spin orientation of the outermost atomic electron. The energy difference derives from the magnetic energy of this spin in the applied field **B**:

$$U = -\boldsymbol{\mu}_s \cdot \mathbf{B} = g\left(\frac{-e}{2m}\right)S_z B = -g\mu_B B m_s \,.$$

With $g = 2$ for electrons, the energy difference between the up spin $\left(m_s = \frac{1}{2}\right)$ and down spin $\left(m_s = -\frac{1}{2}\right)$ orientations is

$$\Delta U = g\mu_B B = (2)\left(9.273\times10^{-24}\ \text{J/T}\right)(0.5\ \text{T}) = 9.273\times10^{-24}\ \text{J} = 5.80\times10^{-5}\ \text{eV}\,.$$

9-8 (a) We find L from $L = I\omega$, where I is the moment of inertia for the cylinder about its longitudinal axis. To find I, consider first a cylindrical shell with radius r, thickness dr, and the same length as the cylinder. The shell has mass proportional to its volume:

$$\frac{dM}{M} = \frac{dV}{V} = \frac{2\pi\, r dr}{\pi R^2} \text{ or } dM = M\left(\frac{2r}{R^2}\right)dr .$$

Since all the shell mass is at the same perpendicular distance r from the rotation axis, the shell moment of inertia is $dI = r^2 dM = M\left(\frac{2r^3}{R^2}\right)dr$. Integrating r from zero to the cylinder radius R gives the moment of inertia for the solid cylinder:

$$I = \int dI = \frac{2M}{R^2}\int_0^R r^3 dr = \frac{1}{2}MR^2 .$$

Then $\mathbf{L} = I\boldsymbol{\omega} = \frac{1}{2}MR^2\boldsymbol{\omega}$. The direction of **L** is that of $\boldsymbol{\omega}$, or along the axis of rotation with a sense given by the right-hand rule.

(b) The charge Q on the curved surface of the rotating cylinder simulates a circular sheet of current. All of this charge passes a fixed line in the time it takes the cylinder to rotate once, $T = \frac{2\pi}{\omega}$, so the effective current is $i = \frac{Q}{T} = \frac{Q\omega}{2\pi}$ and the magnetic moment of the rotating cylinder becomes $\mu = iA = \left(\frac{Q\omega}{2\pi}\right)\pi R^2 = \frac{QR^2\omega}{2}$. The direction of $\boldsymbol{\mu}$ is that of $\boldsymbol{\omega}$, so that $\boldsymbol{\mu} = \left(\frac{QR^2}{2}\right)\boldsymbol{\omega}$. Comparing the results for $\boldsymbol{\mu}$ and **L**, we see they are related as $\boldsymbol{\mu} = \left(\frac{Q}{M}\right)\mathbf{L}$ implying a *g*-factor of 2 for this object.

9-10 $n = 2$; $l = 1$, 0; $s = \frac{1}{2}$

$j = 1+\frac{1}{2},\ 1-\frac{1}{2},\ 0+\frac{1}{2},\ \left|0-\frac{1}{2}\right|$

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

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

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

9-15 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 $U = -\boldsymbol{\mu}_s \cdot \mathbf{B} = 2\left(\frac{e}{2m_e}\right)S_z B = 2\mu_B m_s B$. 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 $\mu = \left(\frac{e\hbar}{2m_e}\right)\sqrt{2} = \mu_B\sqrt{2} = 1.31\times 10^{-23}\ \text{J/T}$. For r we take a typical atomic dimension, say $4a_0\left(= 2.12\times 10^{-10}\ \text{m}\right)$ for a $2p$ electron, and find

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

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

$$U = \pm\mu_B B = \pm\left(9.27\times 10^{-24}\ \text{J/T}\right)(0.276\ \text{T}) = \pm 2.56\times 10^{-24}\ \text{J} = \pm 1.59\times 10^{-5}\ \text{eV}.$$

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 $3.18\times 10^{-5}\ \text{eV}$ —a result which compares favorably with the measured value, $5\times 10^{-5}\ \text{eV}$.

9-16 In the symmetric combination

$$\psi_{ab}(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)$$

we interchange $\mathbf{r}_1$ and $\mathbf{r}_2$ to get

$$\psi_{ab}(\mathbf{r}_2, \mathbf{r}_1) = \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1) + \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2).$$

Comparing with the original shows clearly that $\psi_{ab}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{ab}(\mathbf{r}_2, \mathbf{r}_1)$, and therefore $\psi_{ab}(\mathbf{r}_1, \mathbf{r}_2)$ is a symmetric wavefunction as required for bosons. For two bosons in the same state, we set $a = b$. Because the resulting wavefunction is nonzero, two bosons may indeed occupy the same quantum state.

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),

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

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

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

9-18 Classically, $|\mathbf{L}|=|\mathbf{r}|p_\perp$, where $p_\perp$ is the component of the particle momentum perpendicular to **r**. Remembering that **p** is tangent to the orbit at every point, we see that a highly eccentric orbit is one for which **p** and **r** are nearly collinear over most of the orbit, making $p_\perp$ small almost everywhere. The exceptions occur at the perigee (nearest point), where **r** and **p** are perpendicular but $|\mathbf{r}|$ is small, and apogee (farthest point) where **r** and **p** are perpendicular again. Thus, we expect that $|\mathbf{L}|$ will be smaller for the more eccentric orbits. The extreme case is that for $L=0$, where the classical orbit degenerates to a straight line.

The quantum probabilities are found by integrating the radial probability density for each state, $P(r)$, from $r=0$ to $r=a_0$. For the 2*s* state we find from Table 8.4 (with $Z=1$ for hydrogen) $P_{2s}(r)=|rR_{2s}(r)|^2=(8a_0)^{-1}\left(\frac{r}{a_0}\right)^2\left(2-\frac{r}{a_0}\right)^2e^{-r/a_0}$ and

$P=(8a_0)^{-1}\int_0^{a_0}\left(\frac{r}{a_0}\right)^2\left(2-\frac{r}{a_0}\right)^2e^{-r/a_0}dr$. Changing variables from *r* to $z=\frac{r}{a_0}$ gives

$P=8^{-1}\int\left(4z^2-4z^3+z^4\right)e^{-z}dz$. Repeated integration by parts gives

$$P=8^{-1}\left\{-\left(4z^2-4z^3+z^4\right)-\left(8z-12z^2+4z^3\right)-\left(8-24z+12z^2\right)-(-24+24z)-(24)\right\}e^{-z}\Big|_0^1$$
$$=8^{-1}\left\{-(1+0-4+0+24)e^{-1}+8\right\}=0.034$$

For the 2*p* state of hydrogen $P_{2p}(r)=\left|rR_{2p}(r)\right|^2=(24a_0)^{-1}\left(\frac{r}{a_0}\right)^4e^{-r/a_0}$ and

$P=(24a_0)^{-1}\int_0^{a_0}\left(\frac{r}{a_0}\right)^4e^{-r/a_0}dr=24^{-1}\int_0^1z^4e^{-z}dz$. Again integrating by parts, we get

$$P = 24^{-1}\left\{-z^4 - 4z^3 - 12z^2 - 24z - 24\right\} e^{-z}\Big|_0^1 = 24^{-1}\left\{-65e^{-1} + 24\right\} = 0.003\,7$$

The probability for the 2*p* electron is nearly ten times smaller, suggesting that this electron spends more of its time in the outer regions of the atom where it is screened more effectively by the inner shell electrons.

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

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

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, $n = 2$, $l = 1$, $m_l = 1,\ 0,\ -1$, $m_s = \pm\frac{1}{2}$.

9-24

Ato	3*s*	3*p*			4*s*	Electron Configuration
Na	↑					[Ne]$3s^1$
Mg	↑↓					[Ne]$3s^2$
Al	↑↓	↑				[Ne]$3s^2 3p^1$
Si	↑↓	↑	↑			[Ne]$3s^2 3p^2$
P	↑↓	↑	↑	↑		[Ne]$3s^2 3p^3$
S	↑↓	↑↓	↑	↑		[Ne]$3s^2 3p^4$
Cl	↑↓	↑↓	↑↓	↑		[Ne]$3s^2 3p^5$
Ar	↑↓	↑↓	↑↓	↑↓		[Ne]$3s^2 3p^6$
K	↑↓	↑↓	↑↓	↑↓	↑	[Ar]$4s^1$

The 3*s* subshell is energetically lower and so fills before the 3*p*. According to Hund's rule, electrons prefer to align their spins so long as the exclusion principle can be satisfied.

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

9-26 (a) From Equation 9.26, the energy of a K_α photon is $E[\text{K}_\alpha] = \frac{ke^2}{2a_0}\frac{3(Z-1)^2}{4}$. 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* to get $f = \left(\frac{13.6\text{ eV}}{h}\right)\left(\frac{3(Z-1)^2}{4}\right)$. Taking the square root of this last equation gives the desired result: $\sqrt{f} = \sqrt{\left(\frac{3}{4}\right)\left(\frac{13.6\text{ eV}}{h}\right)}(Z-1)$.

(b) According to part (a), the plot of $\sqrt{f}$ against *Z* should have unit intercept and slope $\sqrt{\left(\frac{3}{4}\right)\left(\frac{13.6\text{ eV}}{h}\right)} = \sqrt{\frac{3(13.6\text{ eV})}{4\left(1.14\times 10^{-15}\text{ eV s}\right)}} = 0.496\times 10^8\text{ Hz}^{1/2}$. From Figure 9.18 we find data points on the K_α line [in the form $\left(\sqrt{f},\ Z\right)$] at (22, 45) and (8, 17). From this we obtain the slope $\frac{22-8}{45-17} = 0.50\times 10^8\text{ Hz}^{1/2}$. Thus, the empirical line fitting the K_α data is $\sqrt{f} = 0.5(Z-I)$, where *I* is the intercept. Using (22, 45) or (8, 17) for $\left(\sqrt{f},\ Z\right)$ in this equation gives the experimental value for the intercept, $I = 1$.

(c) Since $I = 1$, the *L* shell electron does see a nuclear charge of $Z-1$.

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 $\sqrt{\frac{5}{36}\left(\frac{13.6\text{ eV}}{h}\right)} = \sqrt{\frac{5(13.6\text{ eV})}{36\left(4.14\times10^{-15}\text{ eV s}\right)}} = 0.214\times10^{8}\text{ Hz}^{1/2}$. From Figure 9.18 we find data points on the L_α line [in the form $\left(\sqrt{f},\,Z\right)$] 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 $\left(\sqrt{f},\,Z\right)$ in this equation gives the intercept $I = 7.3$, but with (8, 45) for $\left(\sqrt{f},\,Z\right)$ 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.