8-24 $P_{1s}(r) = \dfrac{4}{a_0^3} r^2 e^{-2r/a_0}$ for hydrogen ground state, $U(r) = -\dfrac{ke^2}{r}$ is potential energy ($Z = 1$)

$$\langle U \rangle = \int_0^\infty U(r) P_{1s}(r) dr = -\frac{4ke^2}{a_0^3} \int_0^\infty r e^{-2r/a_0} dr$$

$$= -\frac{4ke^2}{a_0^3} \left(\frac{a_0}{2}\right)^2 \int_0^\infty z e^{-z} dz \quad \text{where} \ z = \frac{2r}{a_0}$$

$$= \frac{-ke^2}{a_0} = -2(13.6 \ \text{eV}) = -27.2 \ \text{eV}.$$

To find $\langle K \rangle$, we note that $\langle K \rangle + \langle U \rangle = \langle E \rangle = -\dfrac{ke^2}{2a_0} = -13.6 \ \text{eV}$ so, $\langle K \rangle = \dfrac{ke^2}{a_0} = +13.6 \ \text{eV}$.

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 $r = 3 + \sqrt{5} = 5.236 a_0$ gives the largest value of
$P(r)$, and so is the most probable distance. For the $2p$ state of hydrogen, a similar analysis
gives $0 = \dfrac{d}{dr} \left\{ r^2 e^{-r/2} \right\} = \left\{ 2r - \frac{1}{2}r^2 \right\} e^{-r/2}$ with the obvious roots $r = 0$ (a minimum) and $r = 4$ (a
maximum). Thus, the most probable distance for the $2p$ state is $r = 4a_0$, in agreement with the
simple Bohr model.

8-26   The probabilities are found by integrating the radial probability density for each state, $P(r)$,
from $r = 0$ to $r = 4a_0$. For the $2s$ state we find from Table 8.4 (with $Z = 1$ for hydrogen)

$$P_{2s}(r) = |rR_{2s}(r)|^2 = (8a_0)^{-1} \left(\frac{r}{a_0}\right)^2 \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} \ \text{and} \ P = (8a_0)^{-1} \int_0^{4a_0} \left(\frac{r}{a_0}\right)^2 \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} dr .$$

Changing variables from r to $z = \dfrac{r}{a_0}$ gives $P = 8^{-1} \int_0^4 (4z^2 - 4z^3 + z^4) e^{-z} dz$. Repeated
integration by parts gives

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

$$= 8^{-1} \left\{ -(64 + 96 + 104 + 72 + 24) e^{-4} + 8 \right\} = 0.176$$

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

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

$$P = 24^{-1}\left\{-z^4 - 4z^3 - 12z^2 - 24z - 24\right\}e^{-z}\Big|_0^4 = 24^{-1}\left\{-824e^{-4} + 24\right\} = 0.371\,.$$ The probability for the

2s electron is much smaller, suggesting that this electron spends more of its time in the outer regions of the atom. This is in accord with classical physics, where the electron in a lower angular momentum state is described by orbits more elliptic in shape.

8-29   To find Δr we first compute $\langle r^2 \rangle$ using the radial probability density for the 1s state of

hydrogen: $P_{1s}(r) = \dfrac{4}{a_0^3}r^2 e^{-2r/a_0}$. Then $\langle r^2 \rangle = \int_0^\infty r^2 P_{1s}(r)dr = \dfrac{4}{a_0^3}\int_0^\infty r^4 e^{-2r/a_0}dr$. With $z = \dfrac{2r}{a_0}$, this is

$\langle r^2 \rangle = \dfrac{4}{a_0^3}\left(\dfrac{a_0}{2}\right)^5\int_0^\infty z^4 e^{-z}dz$. The integral on the right is (see Example 8.9) $\int_0^\infty z^4 e^{-z}dz = 4!$ so that

$\langle r^2 \rangle = \dfrac{4}{a_0^3}\left(\dfrac{a_0}{2}\right)^5(4!) = 3a_0^2$ 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.

8-30   The averages $\langle r \rangle$ and $\langle r^2 \rangle$ are found by weighting the probability density for this state

$P_{1s}(r) = 4\left(\dfrac{Z}{a_0^3}\right)r^2 e^{-2Zr/a_0}$ with r and r^2, respectively, in the integral from $r = 0$ to $r = \infty$:

$$\langle r \rangle = \int_0^\infty rP_{1s}(r)dr = 4\left(\dfrac{Z}{a_0^3}\right)\int_0^\infty r^3 e^{-2Zr/a_0}dr$$

$$\langle r^2 \rangle = \int_0^\infty r^2 P_{1s}(r)dr = 4\left(\dfrac{Z}{a_0^3}\right)\int_0^\infty r^4 e^{-2rZ/a_0}dr$$

Substituting $z = \dfrac{2Zr}{a_0}$ gives

$$\langle r \rangle = 4\left(\dfrac{Z}{a_0}\right)^3\left(\dfrac{a_0}{2Z}\right)^4\int_0^\infty z^3 e^{-z}dz = \dfrac{3!}{4}\left(\dfrac{a_0}{Z}\right) = \dfrac{3}{2}\left(\dfrac{a_0}{Z}\right)$$

$$\langle r^2 \rangle = 4\left(\dfrac{Z}{a_0}\right)^3\left(\dfrac{a_0}{2Z}\right)^5\int_0^\infty z^4 e^{-z}dz = \dfrac{4!}{8}\left(\dfrac{a_0}{Z}\right)^2 = 3\left(\dfrac{a_0}{Z}\right)^2$$

and $\Delta r = \left(\langle r^2 \rangle - \langle r \rangle^2\right)^{1/2} = \dfrac{a_0}{Z}\left[3 - \dfrac{9}{4}\right]^{1/2} = 0.866\left(\dfrac{a_0}{Z}\right)$. The momentum uncertainty is deduced

from the average potential energy

$$\langle U \rangle = -kZe^2\int_0^\infty \dfrac{1}{r}P_{1s}(r)dr = -4kZe^2\left(\dfrac{Z}{a_0}\right)^3\int_0^\infty re^{-2Zr/a_0} = -4kZe^2\left(\dfrac{Z}{a_0}\right)^3\left(\dfrac{a_0}{2Z}\right)^2 = -\dfrac{k(Ze)^2}{a_0}\,.$$

Then, since $E = -\dfrac{k(Ze)^2}{2a_0}$ for the 1s level, and $a_0 = \dfrac{\hbar^2}{m_e ke^2}$, we obtain

$$\langle p^2 \rangle = 2m_e \langle K \rangle = 2m_e \left(E - \langle U \rangle \right) = \frac{2m_e k(Ze)^2}{2a_0} = \left(\frac{Z\hbar}{a_0} \right)^2 .$$

With $\langle \mathbf{p} \rangle = 0$ from symmetry, we get $\Delta p = \left(\langle p^2 \rangle \right)^{1/2} = \dfrac{Z\hbar}{a_0}$ and $\Delta r \Delta p = 0.866\hbar$ for any Z, consistent with the uncertainty principle.

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

$2\left(9.27 \times 10^{-24}\ \text{J/T}\right)\!\left(0.35\ \text{T}\right) = \left(6.63 \times 10^{-34}\ \text{Js}\right)\!f$ so $f = 9.79 \times 10^9$ Hz

9-4   (a)   3d subshell $\Rightarrow l = 2 \Rightarrow m_l = -2,\ -1,\ 0,\ 1,\ 2$ and $m_s = \pm\dfrac{1}{2}$ 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)   3p 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 $\pm\dfrac{1}{2}$.

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

$$\Delta U = g\mu_B B = (2)(9.273 \times 10^{-24} \text{ J/T})(0.5 \text{ T}) = 9.273 \times 10^{-24} \text{ J} = 5.80 \times 10^{-5} \text{ eV}.$$

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

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

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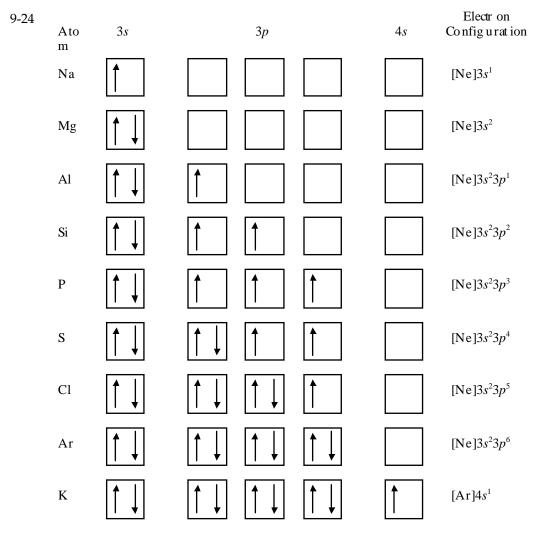
$$E_{112} = E_{121} = E_{211} = (9.4 \text{ eV})\left(1^2 + 1^2 + 2^2\right) = 56.4 \text{ eV}$$
$$E_{\min} = 2 \times \left(E_{111} + E_{112} + E_{121} + E_{211}\right) = 2\left(28.2 + 3 \times 56.4\right) = 398.4 \text{ eV}$$

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

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

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

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

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

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

9-24

Atom	3s	3p			4s	Electron Configuration
Na	↑					$[Ne]3s^1$
Mg	↑↓					$[Ne]3s^2$
Al	↑↓	↑				$[Ne]3s^23p^1$
Si	↑↓	↑	↑			$[Ne]3s^23p^2$
P	↑↓	↑	↑	↑		$[Ne]3s^23p^3$
S	↑↓	↑↓	↑	↑		$[Ne]3s^23p^4$
Cl	↑↓	↑↓	↑↓	↑		$[Ne]3s^23p^5$
Ar	↑↓	↑↓	↑↓	↑↓		$[Ne]3s^23p^6$
K	↑↓	↑↓	↑↓	↑↓	↑	$[Ar]4s^1$

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

9-26 (a) From Equation 9.26, the energy of a K_α photon is $E[K_\alpha] = \dfrac{ke^2}{2a_0}\ \dfrac{3(Z-1)^2}{4}$. Writing

$E = hf$ and noting that $\dfrac{ke^2}{2a_0} = 13.6$ eV , this relation may be solved for the photon

frequency f to get $f = \left(\dfrac{13.6\text{ eV}}{h}\right)\left(\dfrac{3(Z-1)^2}{4}\right)$. Taking the square root of this last

equation gives the desired result: $\sqrt{f} = \sqrt{\left(\dfrac{3}{4}\right)\left(\dfrac{13.6\text{ eV}}{h}\right)}(Z-1)$.

(b) According to part (a), the plot of $\sqrt{f}$ against Z should have unit intercept and slope

$\sqrt{\left(\dfrac{3}{4}\right)\left(\dfrac{13.6\text{ eV}}{h}\right)} = \sqrt{\dfrac{3(13.6\text{ eV})}{4\left(1.14\times10^{-15}\text{ eV s}\right)}} = 0.496\times10^8$ 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 $\dfrac{22-8}{45-17} = 0.50\times10^8$ 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 $Z-1$.