

# CHAPTER 1

## ATOMS: THE QUANTUM WORLD

**1.2** radio waves < infrared radiation < visible light < ultraviolet radiation

**1.4** (a)  $2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1} = (\lambda)(7.1 \times 10^{14} \text{ s}^{-1})$

$$\begin{aligned}\lambda &= \frac{2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{7.1 \times 10^{14} \text{ s}^{-1}} \\ &= 4.2 \times 10^{-7} \text{ m} = 420 \text{ nm}\end{aligned}$$

(b)  $2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1} = (\lambda)(2.0 \times 10^{18} \text{ s}^{-1})$

$$\begin{aligned}\lambda &= \frac{2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{2.0 \times 10^{18} \text{ s}^{-1}} \\ &= 1.5 \times 10^{-10} \text{ m} = 150 \text{ pm}\end{aligned}$$

**1.6** From Wien's law:  $T\lambda_{\text{max}} = 2.88 \times 10^{-3} \text{ K} \cdot \text{m}$ .

$$(T)(715 \times 10^{-9} \text{ m}) = 2.88 \times 10^{-3} \text{ K} \cdot \text{m}$$

$$T \approx 4.03 \times 10^3 \text{ K}$$

**1.8** (a)  $E = h\nu$

$$\begin{aligned}&= (6.626\,08 \times 10^{-34} \text{ J} \cdot \text{s})(1.2 \times 10^{17} \text{ s}^{-1}) \\ &= 8.0 \times 10^{-17} \text{ J}\end{aligned}$$

(b) The energy per mole will be  $6.022 \times 10^{23}$  times the energy of one atom.

$$\begin{aligned}E &= (2.00 \text{ mol})(6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}) \\ &\quad \times (6.626\,08 \times 10^{-34} \text{ J} \cdot \text{s})(1.2 \times 10^{17} \text{ s}^{-1}) \\ &= 9.6 \times 10^7 \text{ J or } 9.6 \times 10^4 \text{ kJ}\end{aligned}$$

$$\begin{aligned}
 \text{(c)} \quad E &= \left( \frac{2.00 \text{ g Cu}}{63.54 \text{ g} \cdot \text{mol}^{-1} \text{ Cu}} \right) \\
 &\quad \times (6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1})(8.0 \times 10^{-17} \text{ J} \cdot \text{atom}^{-1}) \\
 &= 1.5 \times 10^6 \text{ J or } 1.5 \times 10^3 \text{ kJ}
 \end{aligned}$$

**1.10** From  $c = \nu\lambda$  and  $E = h\nu$ ,  $E = hc\lambda^{-1}$ .

$$\begin{aligned}
 E \text{ (for one atom)} &= \frac{(6.62608 \times 10^{-34} \text{ J} \cdot \text{s})(2.99792 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{470 \times 10^{-9} \text{ m}} \\
 &= 4.23 \times 10^{-19} \text{ J} \cdot \text{atom}^{-1} \\
 E \text{ (for 1.00 mol)} &= (6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1})(4.23 \times 10^{-19} \text{ J} \cdot \text{atom}^{-1}) \\
 &= 2.55 \times 10^5 \text{ J} \cdot \text{mol}^{-1} \text{ or } 255 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

**1.12** (a) false. UV photons have higher energy than infrared photons. (b) false. The kinetic energy of the electron is directly proportional to the energy (and hence frequency) of the radiation in excess of the amount of energy required to eject the electron from the metal surface. (c) true.

**1.14** The wavelength of radiation needed will be the sum of the energy of the work function plus the kinetic energy of the ejected electron.

$$\begin{aligned}
 E_{\text{work function}} &= (4.37 \text{ eV})(1.6022 \times 10^{-19} \text{ J} \cdot \text{eV}^{-1}) = 7.00 \times 10^{-19} \text{ J} \\
 E_{\text{kinetic}} &= \frac{1}{2} mv^2 \\
 &= \frac{1}{2} (9.10939 \times 10^{-31} \text{ kg})(1.5 \times 10^6 \text{ m} \cdot \text{s}^{-1})^2 \\
 &= 1.02 \times 10^{-18} \text{ J} \\
 E_{\text{total}} &= E_{\text{work function}} + E_{\text{kinetic}} \\
 &= 7.00 \times 10^{-19} \text{ J} + 1.02 \times 10^{-18} \text{ J} \\
 &= 1.72 \times 10^{-18} \text{ J}
 \end{aligned}$$

To obtain the wavelength of radiation we use the relationships between  $E$ , frequency, wavelength, and the speed of light:

From  $E = h\nu$  and  $c = \nu\lambda$  we can write

$$\begin{aligned}\lambda &= \frac{hc}{E} \\ &= \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{1.72 \times 10^{-18} \text{ J}} \\ &= 1.16 \times 10^{-7} \text{ m or } 116 \text{ nm}\end{aligned}$$

- 1.16** Use the de Broglie relationship,  $\lambda = hp^{-1} = h(mv)^{-1}$ .  
 $(200 \text{ km} \cdot \text{h}^{-1})(1000 \text{ m/km})(1 \text{ h}/3600 \text{ s}) = 55.6 \text{ m} \cdot \text{s}^{-1}$

$$\begin{aligned}\lambda &= h(mv)^{-1} \\ &= (6.626 \text{ } 08 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1})[(1550 \text{ kg})(55.6 \text{ m} \cdot \text{s}^{-1})]^{-1} \\ &= 7.69 \times 10^{-39} \text{ m}\end{aligned}$$

- 1.18** The mass of one He atom is given by the molar mass of He divided by Avogadro's constant:

$$\begin{aligned}\text{mass of He atom} &= \frac{4.00 \text{ g} \cdot \text{mol}^{-1}}{6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}} \\ &= 6.64 \times 10^{-24} \text{ g or } 6.64 \times 10^{-27} \text{ kg}\end{aligned}$$

From the de Broglie relationship,  $p = h\lambda^{-1}$  or  $h = mv\lambda$ , we can calculate wavelength.

$$\begin{aligned}\lambda &= h(mv)^{-1} \\ &= \frac{6.626 \text{ } 08 \times 10^{-34} \text{ J} \cdot \text{s}}{(6.64 \times 10^{-27} \text{ kg})(1230 \text{ m} \cdot \text{s}^{-1})} \\ &= \frac{6.626 \text{ } 08 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}}{(6.64 \times 10^{-27} \text{ kg})(1230 \text{ m} \cdot \text{s}^{-1})} \\ &= 8.11 \times 10^{-11} \text{ m}\end{aligned}$$

- 1.20** Yes, degeneracies are allowed. The lowest energy states which are degenerate in energy are the  $n_1 = 1, n_2 = 4$  state and the  $n_1 = 2, n_2 = 2$  state.

- 1.22** The observed line is the third lowest energy line.

The frequency of the given line

$$\text{is: } \nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^8 \text{ m s}^{-1}}{5910 \times 10^{-9} \text{ m}} = 5.073 \times 10^{13} \text{ s}^{-1}$$

This frequency is closest to the frequency resulting from the  $n = 9$  to  $n = 6$  transition:

$$\nu = \mathfrak{R} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) = 3.29 \times 10^{15} \text{ Hz} \left( \frac{1}{6^2} - \frac{1}{9^2} \right) = 5.08 \times 10^{13} \text{ Hz}$$

- 1.24** (a) The Rydberg equation gives  $\nu$  when  $\mathfrak{R} = 3.29 \times 10^{15} \text{ s}^{-1}$ , from which one can calculate  $\lambda$  from the relationship  $c = \nu\lambda$ .

$$\nu = \mathfrak{R} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

$$\text{and } c = \nu\lambda = 2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1}$$

$$c = \mathfrak{R} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \lambda$$

$$2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1} = (3.29 \times 10^{15} \text{ s}^{-1}) \left( \frac{1}{1} - \frac{1}{25} \right) \lambda$$

$$\lambda = 9.49 \times 10^{-8} \text{ m} = 94.9 \text{ nm}$$

(b) Lyman series

(c) This absorption lies in the ultraviolet region.

- 1.26** Here we are searching for a transition of  $\text{He}^+$  whose frequency matches that of the  $n = 2$  to  $n = 1$  transition of H. The frequency of the H transition is:

$$\nu_{\text{H}} = \mathfrak{R} \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = \left( \frac{3}{4} \right) \mathfrak{R}$$

A transition of the  $\text{He}^+$  ion with the same frequency is the  $n = 2$  to  $n = 4$  transition:

$$\nu_{\text{He}^+} = (Z^2) \mathfrak{R} \left( \frac{1}{2^2} - \frac{1}{4^2} \right) = (2^2) \mathfrak{R} \left( \frac{3}{16} \right) = \left( \frac{3}{4} \right) \mathfrak{R}$$

- 1.28** (a) The highest energy photon is the one that corresponds to the ionization energy of the atom, the energy required to produce the condition in which the electron and nucleus are “infinitely” separated. This energy corresponds to the transition from the highest energy level for which  $n = 1$  to the highest energy level for which  $n = \infty$ .

$$E = h\mathfrak{R} \left( \frac{1}{n_{\text{lower}}^2} - \frac{1}{n_{\text{upper}}^2} \right) = (6.626\,08 \times 10^{-34} \text{ J} \cdot \text{s}) \\ \times (3.29 \times 10^{15} \text{ s}^{-1}) \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right) \\ = 2.18 \times 10^{-18} \text{ J}$$

- (b) The wavelength is obtained from

$$c = \nu\lambda \text{ and } E = h\nu, \text{ or } E = hc\lambda^{-1}, \text{ or } \lambda = hcE^{-1}.$$

$$\lambda = \frac{(6.626\,08 \times 10^{-34} \text{ J} \cdot \text{s})(2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{2.18 \times 10^{-18} \text{ J}} \\ = 9.11 \times 10^{-8} \text{ m} = 91.1 \text{ nm}$$

- (c) ultraviolet

- 1.30** Because the line is in the visible part of the spectrum, it belongs to the Balmer series for which the ending  $n$  is 2. We can use the following equation to solve for the starting value of  $n$ :

$$\nu = \frac{c}{\lambda} = \frac{2.99792 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{434 \times 10^{-9} \text{ m}} = 6.91 \times 10^{14} \text{ s}^{-1}$$

$$\nu = (3.29 \times 10^{15} \text{ s}^{-1}) \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$6.91 \times 10^{14} \text{ s}^{-1} = (3.29 \times 10^{15} \text{ s}^{-1}) \left( \frac{1}{2^2} - \frac{1}{n_2^2} \right)$$

$$0.210 = 0.250 - \frac{1}{n_2^2}$$

$$\frac{1}{n_2^2} = 0.04$$

$$n_2^2 = \frac{1}{0.04}$$

$$n_2 = 5$$

This transition is from the  $n = 5$  to the  $n = 2$  level.

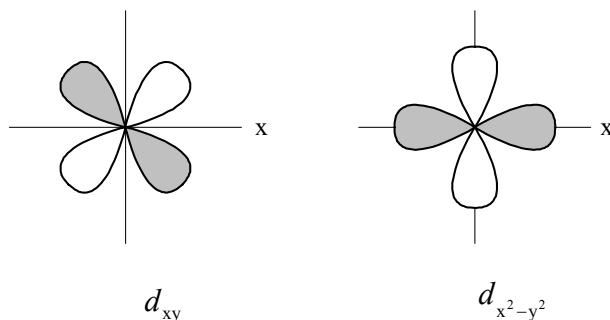
- 1.32** (a) The easiest way to approach this problem is to plot the radial probability distribution,  $P(r) = r^2 \cdot R_{3s}^2$ , ( $R_{3s}$  is given in Table 1.2) and, using the plot, determine the position of the nodes. Another approach is to take the derivative of this probability distribution with respect to  $r$  and set this derivative equal to zero to find the position of the extrema of the curve. Taking the latter approach, one finds that the minima are at

$$\left( \frac{9 + (3 \cdot \sqrt{3})}{2} \right) a_o \text{ and } \left( \frac{9 - (3 \cdot \sqrt{3})}{2} \right) a_o, \text{ or } 7.10 \cdot a_o \text{ and } 1.90 \cdot a_o.$$

(b)  $R_{4d} = 1/96\sqrt{5} \left( 6 - \frac{Zr}{2a_o} \right) \left( \frac{Zr}{2a_o} \right)^2 Z^{\frac{3}{2}} e^{\frac{-Zr}{4a_o}}$  As in part (a) above, the easiest

way to find the node is to plot the probability distribution function and find the position of the node by inspection. Taking the derivative of the probability distribution function and setting it equal to zero, one finds three extrema for the 4d distribution:  $12a_o$ ,  $2(7 + \sqrt{13})a_o$ , and  $2(7 - \sqrt{13})a_o$ . The first of these three is the position of the node while the latter two are the positions of the maxima in the distribution.

- 1.34** The  $d_{xy}$  orbital will have its lobes pointing *between* the x and y axes, while the  $d_{x^2-y^2}$  orbital will have its lobes pointing *along* the x and y axes.



**1.36** The equation demonstrated in example 1.8 can be used:

$$\frac{\psi^2(r = 0.65a_0, \theta, \phi)}{\psi^2(0, \theta, \phi)} = \frac{e^{-2(0.65a_0)/a_0}}{\left(\frac{1}{\pi a_0^3}\right)} = 0.27$$

**1.38** The radial probability distribution may be found by integrating the full wavefunction,  $\psi(r, \theta, \phi)$ , over all possible values of  $\theta$  and  $\phi$ . Since s-orbitals are spherically symmetric and are not a function of  $\theta$  or  $\phi$ , integration of any s-orbital over all  $\theta$  and  $\phi$  always gives the same result:

$$\begin{aligned} \int_0^\pi \int_0^{2\pi} \psi(r)^2 \sin \theta \, d\theta \, d\phi &= \psi(r)^2 \left[ \int_0^\pi \int_0^{2\pi} \sin \theta \, d\theta \, d\phi \right] \\ &= \psi(r)^2 \left[ \int_0^{2\pi} 2 \, d\phi \right] = \psi(r)^2 (4\pi) \end{aligned}$$

The  $\sin \theta$  term in the equation above is needed to correct for the differential volume element in spherical polar coordinates. Likewise, to integrate over all possible values of  $r$  one must evaluate the integral:

$$\int_0^\infty (4\pi) \psi(r)^2 r^2 \, dr$$

where again the  $r^2$  term corrects for the differential volume element in spherical polar coordinates. From this expression it is clear that the probability distribution is  $(4\pi) \psi(r)^2 r^2$ .

- 1.40** (a) To find the maximum in the radial probability distribution function for the  $3d$ -orbital, one can take the derivative of the distribution with respect to  $r$ , set the result equal to zero and solve for  $r$ :

$$P = r^2 R_{3d}^2 = C^2 \cdot r^6 \cdot e^{-\frac{2r}{3a_0}} \quad \text{where } C = \frac{4}{81 \cdot \sqrt{30}} \left( \frac{1}{a_0} \right)^{\frac{7}{2}}$$

$$\frac{dP}{dr} = C^2 \left[ r^6 \left( \frac{-2}{3a_0} \right) \cdot e^{-\frac{2r}{3a_0}} + 6 r^5 \cdot e^{-\frac{2r}{3a_0}} \right] = C^2 \cdot e^{-\frac{2r}{3a_0}} \left[ r^6 \left( \frac{-2}{3a_0} \right) + 6 r^5 \right] \equiv 0$$

The non-trivial solution to this equation is found when:

$$r^6 \left( \frac{-2}{3a_0} \right) + 6 r^5 = 0$$

Dividing both sides by  $r^5$ :

$$r \left( \frac{-2}{3a_0} \right) + 6 = 0 \quad \text{and, therefore, } r = 9a_0$$

The position of the maximum in the distribution for the  $3d$ -orbital occurs when  $r = 9a_0$ .

- (b) The radial wavefunction for the  $4s$ -orbital is:

$$R_{4s} = C \left( 1 - \frac{3}{4 \cdot a_0} r + \frac{1}{8 \cdot a_0^2} r^2 - \frac{1}{192 \cdot a_0^3} r^3 \right) e^{-\frac{r}{4a_0}} \quad \text{where } C = \frac{1}{4} \left( \frac{1}{a_0} \right)^{\frac{3}{2}}$$

The derivative of the radial probability distribution,  $P = r^2 R_{4s}^2$ , with respect to  $r$  is:

$$\frac{dP}{dr} = C^2 e^{-\frac{r}{2a_0}} \left[ r^2 - \frac{3}{2 \cdot a_0} r^3 + \frac{13}{16 \cdot a_0^2} r^4 - \frac{19}{96 \cdot a_0^3} r^5 + \frac{3}{128 \cdot a_0^4} r^6 - \frac{1}{768 \cdot a_0^5} r^7 + \frac{1}{36864 \cdot a_0^6} r^8 \right]$$

The non-trivial solutions to this equation are found when the polynomial in brackets is equal to zero. The roots are most easily found using a computer and are:  $0.732a_0$ ,  $1.872 a_0$ ,  $4 a_0$ ,  $6.611 a_0$ ,  $10.65 a_0$ ,  $15.52 a_0$ , and  $24.62 a_0$ . The last of these roots,  $24.62 a_0$ , is the position of the maximum of the probability distribution for the  $4s$ -orbital.



**1.42** (a) 5:  $l = 0, 1, 2, 3, 4$ ; (b)  $5s, 5p, 5d, 5f, 5g$ ; (c)  $1 + 3 + 5 + 7 + 9 = 25$  orbitals

**1.44** (a) 6 values: 0, 1, 2, 3, 4, 5; (b) 7 values: -3, -2, -1, 0, 1, 2, 3; (c) 1 value: 0; (d) 3 subshells:  $3s, 3p$ , and  $3d$

**1.46** (a)  $n = 2; l = 0$ ; (b)  $n = 6; l = 3$ ; (c)  $n = 4; l = 2$ ; (d)  $n = 5; l = 1$

**1.48** (a) 0; (b) -3, -2, -1, 0, 1, 2, 3; (c) -2, -1, 0, 1, 2; (d) -1, 0, 1

**1.50** (a) 2; (b) 6; (c) 10; (d) 14

**1.52** (a)  $3d, 10$ ; (b)  $5s, 2$ ; (c)  $7p, 6$ ; (d)  $4f, 14$

**1.54** (a) 6; (b) 2; (c) 2; (d) 98

**1.56** (a) cannot exist; (b) cannot exist; (c) exists; (d) cannot exist

**1.58** (a) The total Coulomb potential energy  $V(r)$  is the sum of the individual coulombic attractions and repulsions. There will be one attraction between the nucleus and each electron plus a repulsive term to represent the interaction between each pair of electrons. For beryllium, there are four protons in the nucleus and four electrons. Each attractive force will be equal to

$$\frac{(-e)(+4e)}{4\pi\epsilon_0 r} = \frac{-4e^2}{4\pi\epsilon_0 r} = -\frac{e^2}{\pi\epsilon_0 r}$$

where  $-e$  is the charge on the electron and  $+4e$  is the charge on the nucleus,  $\epsilon_0$  is the vacuum permittivity, and  $r$  is the distance from the electron to the nucleus. The total attractive potential will thus be

$$-\frac{e^2}{\pi\epsilon_0 r_1} - \frac{e^2}{\pi\epsilon_0 r_2} - \frac{e^2}{\pi\epsilon_0 r_3} - \frac{e^2}{\pi\epsilon_0 r_4} = -\frac{e^2}{\pi\epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} + \frac{1}{r_4} \right)$$

The first four terms are the attractive terms between the nucleus and each electron, and the last six terms are the repulsive interactions between all the possible combinations of electrons taken in pairs.

(b) The number of attractive terms is straightforward. There should be one term representing the attraction between the nucleus and each electron, so there should be a total of  $n$  terms representing attractions. The number of repulsive terms goes up with the number of electrons.

Examining the progression, we see that

$n =$	1	2	3	4	5	6	7
# of repulsive terms =	0	1	3	6	10	15	21

Hence, the addition of an electron adds one  $r_{ab}$  term for each electron already present; so the difference in the number of repulsive terms increases by  $n - 1$  for each additional electron. This relation can be written as a summation to give the total number of repulsive terms:

$$\text{number of repulsive terms} = \sum_{1 \rightarrow n} (n - 1)$$

The repulsive terms will have the form

$$\frac{(-e)(-e)}{4\pi\epsilon_0 r_{ab}} = \frac{e^2}{4\pi\epsilon_0 r_{ab}}$$

where  $r_{ab}$  represents the distance between the two electrons a and b. The total repulsive term will thus be

$$\begin{aligned} & \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{14}} + \frac{e^2}{4\pi\epsilon_0 r_{23}} + \frac{e^2}{4\pi\epsilon_0 r_{24}} + \frac{e^2}{4\pi\epsilon_0 r_{34}} \\ & \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{14}} + \frac{1}{r_{23}} + \frac{1}{r_{24}} + \frac{1}{r_{34}} \right) \end{aligned}$$

This gives

$$V(r) = \left( \frac{-e^2}{\pi\epsilon_0} \right) \left( \frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} + \frac{1}{r_4} \right) + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{14}} + \frac{1}{r_{23}} + \frac{1}{r_{24}} + \frac{1}{r_{34}} \right)$$

The total number of attractive and repulsive terms will thus be equal to

$$n + \sum_{l \rightarrow n} (n - 1)$$

The point of this exercise is to show that, with each added electron, we add an increasingly larger number of  $e-e$  repulsive terms.

- 1.60** (a) false. The  $2s$ -electrons will be shielded by the electrons in the  $1s$ -orbital and will thus experience a lower  $Z_{\text{eff}}$ . (b) false. Because the  $2p$ -orbitals do not penetrate to the nucleus as the  $2s$ -orbitals do, they will experience a lower  $Z_{\text{eff}}$ . (c) false. The ability of the electrons in the  $2s$ -orbital to penetrate to the nucleus will make that orbital lower in energy than the  $2p$ . (d) false. There are three  $p$ -orbitals, and the electron configuration for C will be  $1s^2 2s^2 2p^2$ . There will be two electrons in the  $p$ -orbitals, but each will go into a separate orbital and, as per quantum mechanics and Hund's rule, they will be in these orbitals with the spins parallel (i.e., the spin magnetic quantum numbers will have the same sign) for the ground-state atom. (e) false. Because the electrons are in the same orbital, they must have opposite spin quantum numbers,  $m_s$ , because the Pauli exclusion principle states that no two electrons in an atom can have the same four quantum numbers.

- 1.62** The atom with a  $4s^2 4p^2$  valence-shell configuration is germanium, Ge. The ground-state configuration is given by (d); the other configurations represent excited states.

- 1.64** (a) This configuration is not possible because the maximum value  $l$  can have is  $n - 1$ ; because  $n = 2$ ,  $l_{\text{max}} = 1$ . (b) This configuration is possible.

(c) This configuration is not possible because, for  $l = 4$ ,  $m_l$  can only be an integer from  $-3$  to  $+3$ , i.e.,  $m_l$  can only equal  $0, \pm 1, \pm 2$ , or  $\pm 3$ .

**1.66** (a) sulfur  $[\text{Ne}]3s^2 3p^4$

(b) cesium  $[\text{Xe}]6s^1$

(c) polonium  $[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^4$

(d) palladium  $[\text{Kr}]4d^{10}$

(e) rhenium  $[\text{Xe}]4f^{14} 5d^5 6s^2$

(f) vanadium  $[\text{Ar}]3d^3 4s^2$

**1.68** (a) Ga; (b) Na; (c) Sr; (d) Eu

**1.70** (a)  $4s$ ; (b)  $3p$ ; (c)  $3p$ ; (d)  $4s$

**1.72** (a) 5; (b) 2; (c) 7; (d) 12

For (d), note that the filled  $3d$ -orbitals become core electrons, which are not available. The chemistry of Zn is dominated by its +2 oxidation number; and, consequently, Zn, Cd, and Hg are often grouped with the  $p$ -block elements and referred to collectively as the *post transition metals*.

**1.74** (a) 2; (b) 3; (c) 1; (d) 0

**1.76** (a)  $ns^2 np^5$ ; (b)  $ns^2 np^4$ ; (c)  $nd^3 (n+1)s^2$ ; (d)  $ns^2 np^2$

**1.78** (a) As one goes across a period, a proton and an electron are added to each new atom. The electrons, however, are not completely shielded from the nucleus by other electrons in the same subshell, so the set of electrons experience an overall greater nuclear charge. (b) The ionization energies of the Group 16 elements of O, S, and Se lie somewhat lower than those of the Group 15 elements that precede them. This exception may be

explained by observing that, as the three *p*-orbitals up through Group 15 are filled, each electron goes into a separate orbital. The next electron (for Group 16) goes into an orbital already containing an electron, so electron-electron repulsions are higher. This increased repulsion makes it easier to remove the additional electron from the Group 16 elements.

**1.80** While Na has a smaller effective nuclear charge than K, the outermost electron occupies a 3*s*-orbital. In potassium atoms, the outermost electron occupies a 4*s*-orbital and so on average is much further from the nucleus than the electron in the 3*s*-orbital of sodium. Despite the larger effective nuclear charge, the electron in potassium is more easily removed because it is, on average, further from the nucleus.

**1.82** (a) silicon (118 pm) > sulfur (104 pm) > chlorine (99 pm);  
(b) titanium (147 pm) > chromium (129 pm) > cobalt (125 pm);  
(c) mercury (155 pm) > cadmium (152 pm) > zinc (137 pm);  
(d) bismuth (182 pm) > antimony (141 pm) > phosphorus (110 pm)

**1.84** (a) Ba<sup>2+</sup>; (b) As<sup>3-</sup>; (c) Sn<sup>2+</sup>

**1.86** (a) Al; (b) Sb; (c) Si

**1.88** From Appendix 2D, the radii (in pm) are

Ge	122	Sb	141
Ge <sup>2+</sup>	90	Sb <sup>3+</sup>	89

The diagonal relationship between elements can often be attributed to the fact that the most common oxidation states for these elements give rise to ions of similar size, which consequently often show similar reaction chemistry.

**1.90** (a) Ga and Si and (c) As and Sn. Note: (b) Be and Al exhibit a diagonal relationship. Because diagonal relationships often exist as a result of similarities in ionic radii, they can exist across the *s* and *p* blocks.

**1.92** (c) hafnium and (d) niobium

**1.94** (a) metal; (b) nonmetal; (c) metalloid; (d) metalloid; (e) nonmetal; (f) metalloid

**1.96** (a)  $\lambda = 0.20 \text{ nm}$ ;  $E = h\nu$  or  $E = hc\lambda^{-1}$

$$E = \frac{(6.626\,08 \times 10^{-34} \text{ J} \cdot \text{s})(2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{0.20 \times 10^{-9} \text{ m}}$$

$$= 9.9 \times 10^{-16} \text{ J}$$

This radiation is in the x-ray region of the electromagnetic spectrum. For comparison, the  $K_{\alpha}$  radiation from Cu is 0.154 439 0 nm and that from Mo is 0.0709 nm. X-rays produced from these two metals are those most commonly employed for determining structures of molecules in single crystals.

(b) From the de Broglie relationship  $p = h\lambda^{-1}$ , we can write  $h\lambda^{-1} = mv$ , or  $v = h m^{-1} \lambda^{-1}$ . For an electron,  $m_e = 9.109\,39 \times 10^{-28} \text{ g}$ . (Convert units to kg and m.)

$$v = \frac{(6.626\,08 \times 10^{-34} \text{ J} \cdot \text{s})}{(9.109\,39 \times 10^{-31} \text{ kg})(200 \times 10^{-12} \text{ m})}$$

$$= \frac{(6.626\,08 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1})}{(9.109\,39 \times 10^{-31} \text{ kg})(200 \times 10^{-12} \text{ m})}$$

$$= 3.6 \times 10^6 \text{ m} \cdot \text{s}^{-1}$$

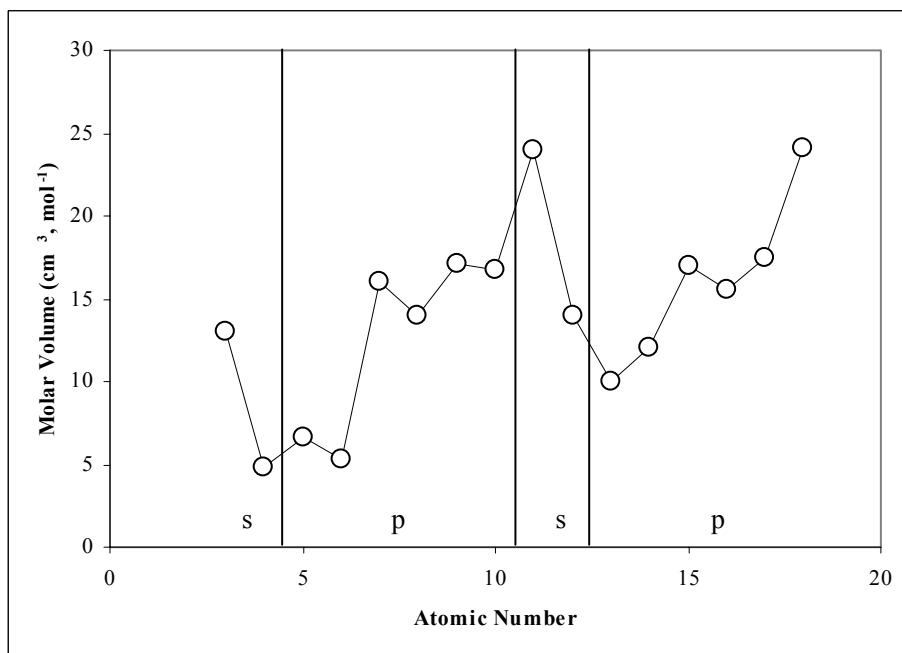
(c) Solve similarly to (b). For a neutron,  $m_n = 1.674\,93 \times 10^{-24} \text{ g}$ . (Convert units to kg and m.)

$$\begin{aligned}
 \nu &= \frac{(6.626\,08 \times 10^{-34} \text{ J} \cdot \text{s})}{(1.674\,93 \times 10^{-27} \text{ kg})(200 \times 10^{-12} \text{ m})} \\
 &= \frac{(6.626\,08 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1})}{(1.67493 \times 10^{-27} \text{ kg})(200 \times 10^{-12} \text{ m})} \\
 &= 2.0 \times 10^3 \text{ m} \cdot \text{s}^{-1}
 \end{aligned}$$

**1.98** A ground-state oxygen atom has four electrons in the  $p$ -orbitals. This configuration means that as one goes across the periodic table in Period 2, oxygen is the first element encountered in which the  $p$ -electrons must be paired. This added electron-electron repulsion energy causes the ionization potential to be lower.

**1.100** molar volume ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ) = molar mass ( $\text{g} \cdot \text{mol}^{-1}$ )/density ( $\text{g} \cdot \text{cm}^{-3}$ )

Element	Molar vol.	Element	Molar vol.
Li	13	Na	24
Be	4.87	Mg	14.0
B	4.62	Al	9.99
C	5.31	Si	12.1
N	16	P	17.0
O	14.0	S	15.5
F	17.1	Cl	17.5
Ne	16.7	Ar	24.1



The molar volume roughly parallels atomic size (volume), which increases as the *s*-sublevel begins to fill and subsequently decreases as the *p*-sublevel fills (refer to the text discussion of periodic variation of atomic radii). In the above plot, this effect is most clearly seen in passing from Ne(10) to Na(11) and Mg(12), then to Al(13) and Si(14). Ne has a filled *2p*-sublevel; the *3s*-sublevel fills with Na and Mg; and the *3p*-sublevel begins to fill with Al.

**1.102** In general, as the principal quantum number increases, the energy spacing between orbitals becomes smaller. This trend indicates that it doesn't take very much change in electronic structure to cause the normal orbital energy pattern to rearrange.

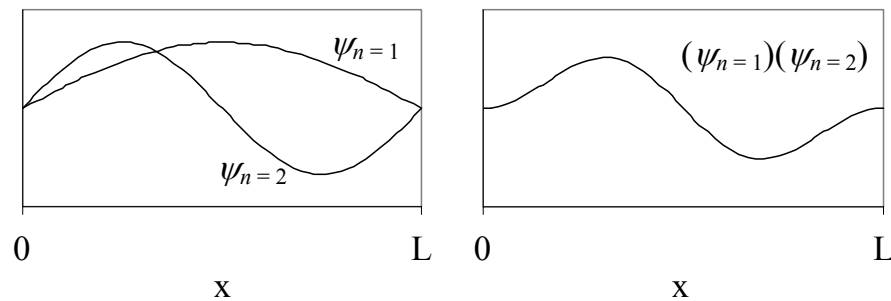
**1.104** (a)

$$\int_0^L \left( \sin \frac{\pi \cdot x}{L} \right) \cdot \left( \sin \frac{2\pi \cdot x}{L} \right) dx$$

$$= \frac{L}{2\pi} \left( \sin \frac{\pi \cdot x}{L} \right) - \frac{L}{6\pi} \left( \sin \frac{3\pi \cdot x}{L} \right) \Big|_0^L = 0$$



(b) Below is a plot of the first two wavefunctions describing the one-dimensional particle-in-a-box and the product of these two wavefunctions. Notice that the area above zero in the product exactly cancels the area below zero, making the integral of the product zero. This happens whenever a wavefunction that is unaltered by a reflection through the center of the box (wavefunctions with odd  $n$ ) is multiplied by a wavefunction that changes sign everywhere when reflected through the center of the box (wavefunctions with even  $n$ ).



**1.106** (a)  $\Delta p \Delta x \geq \frac{1}{2} \hbar$

where  $\hbar = \frac{h}{2\pi} = \frac{6.626\,08 \times 10^{-34} \text{ J} \cdot \text{s}}{2\pi} = 1.054\,57 \times 10^{-34} \text{ J} \cdot \text{s}$

$$\Delta p \Delta x \geq \frac{1}{2} (1.054\,57 \times 10^{-34} \text{ J} \cdot \text{s}) = 5.272\,85 \times 10^{-35} \text{ J} \cdot \text{s}$$

The minimum uncertainty occurs at the point where this relationship is an equality (i.e., using = rather than  $\geq$ ).

The uncertainty in position will be taken as the 200 nm corresponding to the length of the box:

$$\Delta p \Delta x = 5.272\,85 \times 10^{-35} \text{ J} \cdot \text{s}$$

$$\Delta p = \frac{5.272\,85 \times 10^{-35} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}}{200 \times 10^{-9} \text{ m}} = 2.64 \times 10^{-28} \text{ kg} \cdot \text{m} \cdot \text{s}^{-1}$$

$$= \Delta(mv) = m \Delta v = 2.64 \times 10^{-28} \text{ kg} \cdot \text{m} \cdot \text{s}^{-1}$$

Because the mass of an electron is

$$9.109\,39 \times 10^{-28} \text{ g or } 9.109\,39 \times 10^{-31} \text{ kg, the uncertainty in velocity will}$$

be given by

$$\Delta v = (2.63 \times 10^{-28} \text{ kg} \cdot \text{m} \cdot \text{s}^{-1})(9.109\,39 \times 10^{-31} \text{ kg})^{-1}$$

$$= 289 \text{ m} \cdot \text{s}^{-1}$$

The calculation is then repeated for a 1.00 mm wire where 1.00 mm is considered the uncertainty in position.

$$\Delta p = \frac{5.272\,85 \times 10^{-35} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}}{1.00 \times 10^{-3} \text{ m}} = 5.27 \times 10^{-32} \text{ kg} \cdot \text{m} \cdot \text{s}^{-1}$$

$$\Delta v = (5.27 \times 10^{-32} \text{ kg} \cdot \text{m} \cdot \text{s}^{-1})(9.109\,39 \times 10^{-31} \text{ kg})^{-1}$$

$$= 0.0578 \text{ m} \cdot \text{s}^{-1}$$

The uncertainty in velocity is much less in the macroscopic wire.

(b) The problem is solved as in (a), but now the mass is that of a  $\text{Li}^+$  ion, which is roughly  $(6.94 \text{ g} \cdot \text{mol}^{-1}) / (6.022 \times 10^{23} \text{ ions} \cdot \text{mol}^{-1})$   
 $= 1.15 \times 10^{-23} \text{ g} \cdot \text{ion}^{-1}$  or  $1.15 \times 10^{-26} \text{ kg} \cdot \text{ion}^{-1}$ . Technically, the mass of the  $\text{Li}^+$  ion should be the mass of the atom less the mass of one electron, but because the mass of an electron is five orders of magnitude smaller than the mass of a neutron or a proton, the loss is insignificant in the overall mass of the lithium ion.

$$\Delta v = \frac{2.64 \times 10^{-28} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}}{1.15 \times 10^{-26} \text{ kg}} = 0.0230 \text{ m} \cdot \text{s}^{-1}$$

(c) From the calculations, it is clear that the larger particle will have less uncertainty in the measurement of its speed and could theoretically be measured more accurately, as would be anticipated from quantum mechanics.

**1.108** (a) Evaluating the integral for an  $n = 1$  to  $n = 3$  transition:

$$\begin{aligned}
& \int_0^L \sin\left(\frac{\pi x}{L}\right) \cdot x \cdot \sin\left(\frac{3\pi x}{L}\right) \\
&= \frac{L^2}{8\pi^2} \left( \cos\left(\frac{2\pi x}{L}\right) + \frac{2\pi x}{L} \sin\frac{2\pi x}{L} \right) - \\
&\quad \frac{L^2}{32\pi^2} \left( \cos\left(\frac{4\pi x}{L}\right) + \frac{4\pi x}{L} \sin\frac{4\pi x}{L} \right) \Bigg|_0^L \\
&= \frac{L^2}{8\pi^2} (1+0) - \frac{L^2}{32\pi^2} (1+0) - \left[ \frac{L^2}{8\pi^2} (1+0) - \frac{L^2}{32\pi^2} (1+0) \right] \\
&= 0
\end{aligned}$$

Because the integral is zero, one would not expect to observe a transition between the  $n = 1$  and  $n = 3$  states.

(b) Again, evaluating the integral:

$$\begin{aligned}
& \int_0^L \sin\left(\frac{\pi x}{L}\right) \cdot x \cdot \sin\left(\frac{2\pi x}{L}\right) \\
&= \frac{L^2}{\pi^2} \left( \frac{1}{2} \left( \cos\left(\frac{\pi x}{L}\right) + \frac{\pi x}{L} \sin\left(\frac{\pi x}{L}\right) \right) - \frac{1}{18} \left( \cos\left(\frac{3\pi x}{L}\right) + \frac{3\pi x}{L} \sin\left(\frac{3\pi x}{L}\right) \right) \right) \Bigg|_0^L
\end{aligned}$$

Given the  $L^2$  term, we see that the integral, and therefore  $I$ , will increase as the length of the box increases.