

CHAPTER 1

ATOMS: THE QUANTUM WORLD

- 1.3** (a) If wavelength is known, the frequency can be obtained from the relation

$$c = \nu\lambda:$$

$$2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1} = (\nu) (925 \times 10^{-9} \text{ m})$$

$$\begin{aligned}\nu &= \frac{2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{925 \times 10^{-9} \text{ m}} \\ &= 3.24 \times 10^{14} \text{ s}^{-1}\end{aligned}$$

(b) $2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1} = (\nu) (4.15 \times 10^{-3} \text{ m})$

$$\begin{aligned}\nu &= \frac{2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{4.15 \times 10^{-3} \text{ m}} \\ &= 7.22 \times 10^{10} \text{ s}^{-1}\end{aligned}$$

- 1.5** Wien's law states that $T\lambda_{\text{max}} = \text{constant} = 2.88 \times 10^{-3} \text{ K} \cdot \text{m}$.

If $T/\text{K} = 1540^\circ\text{C} + 273^\circ\text{C} = 1813 \text{ K}$, then $\lambda_{\text{max}} = \frac{2.88 \times 10^{-3} \text{ K} \cdot \text{m}}{1813 \text{ K}}$

$$\lambda_{\text{max}} = 1.59 \times 10^{-6} \text{ m, or } 1590 \text{ nm}$$

- 1.7** (a) From $c = \nu\lambda$ and $E = h\nu$, we can write

$$\begin{aligned}E &= hc\lambda^{-1} \\ &= (6.626\,08 \times 10^{-34} \text{ J} \cdot \text{s}) (2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1}) (589 \times 10^{-9} \text{ m})^{-1} \\ &= 3.37 \times 10^{-19} \text{ J}\end{aligned}$$

$$\begin{aligned}
 \text{(b)} \quad E &= \left(\frac{5.00 \times 10^{-3} \text{ g Na}}{22.99 \text{ g} \cdot \text{mol}^{-1} \text{ Na}} \right) (6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}) \\
 &\quad \times (3.37 \times 10^{-19} \text{ J} \cdot \text{atom}^{-1}) \\
 &= 44.1 \text{ J}
 \end{aligned}$$

$$\begin{aligned}
 \text{(c)} \quad E &= (6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1})(3.37 \times 10^{-19} \text{ J} \cdot \text{atom}^{-1}) \\
 &= 2.03 \times 10^5 \text{ J or } 203 \text{ KJ}
 \end{aligned}$$

1.9 The energy is first converted from eV to joules:

$$E = (140.511 \times 10^3 \text{ eV}) (1.6022 \times 10^{-19} \text{ J} \cdot \text{eV}^{-1}) = 2.2513 \times 10^{-14} \text{ J}$$

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

$$\begin{aligned}
 \lambda &= \frac{hc}{E} \\
 &= \frac{(6.626 \ 09 \times 10^{-34} \text{ J} \cdot \text{s}) (2.997 \ 92 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{2.2513 \times 10^{-14} \text{ J}} \\
 &= 8.8236 \times 10^{-12} \text{ m or } 8.8236 \text{ pm}
 \end{aligned}$$

1.11 (a) false. The total intensity is proportional to T^4 . (Stefan-Boltzmann Law) (b) true; (c) false. Photons of radio-frequency radiation are lower in energy than photons of ultraviolet radiation.

1.13 (a) Use the de Broglie relationship, $\lambda = hp^{-1} = h(mv)^{-1}$.

$$\begin{aligned}
 m_e &= (9.109 \ 39 \times 10^{-28} \text{ g}) (1 \text{ kg}/1000 \text{ g}) = 9.109 \ 39 \times 10^{-31} \text{ kg} \\
 (3.6 \times 10^3 \text{ km} \cdot \text{s}^{-1}) (1000 \text{ m} \cdot \text{km}^{-1}) &= 3.6 \times 10^6 \text{ m} \cdot \text{s}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \lambda &= h(mv)^{-1} \\
 &= \frac{6.626 \ 08 \times 10^{-34} \text{ J} \cdot \text{s}}{(9.109 \ 39 \times 10^{-31} \text{ kg}) (3.6 \times 10^6 \text{ m} \cdot \text{s}^{-1})} \\
 &= 2.0 \times 10^{-10} \text{ m}
 \end{aligned}$$

$$\begin{aligned}
 \text{(b)} \quad E &= h\nu \\
 &= (6.626 \ 08 \times 10^{-34} \text{ J} \cdot \text{s}) (2.50 \times 10^{16} \text{ s}^{-1}) \\
 &= 1.66 \times 10^{-17} \text{ J}
 \end{aligned}$$

(c) The photon needs to contain enough energy to eject the electron from the surface as well as to cause it to move at $3.6 \times 10^3 \text{ km} \cdot \text{s}^{-1}$. The energy involved is the kinetic energy of the electron, which equals $\frac{1}{2}mv^2$.

$$\begin{aligned} E_{\text{photon}} &= 1.66 \times 10^{-17} \text{ J} + \frac{1}{2}mv^2 \\ &= 1.66 \times 10^{-17} \text{ J} + \frac{1}{2}(9.109\,39 \times 10^{-31} \text{ kg})(3.6 \times 10^6 \text{ m} \cdot \text{s}^{-1})^2 \\ &= 1.66 \times 10^{-17} \text{ J} + 5.9 \times 10^{-18} \text{ J} \\ &= 2.3 \times 10^{-17} \text{ J} \end{aligned}$$

But we are asked for the wavelength of the photon, which we can get from

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

$$\begin{aligned} 2.3 \times 10^{-17} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} &= (6.626\,08 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}) \\ &\times (2.997\,92 \cdot 10^8 \text{ m} \cdot \text{s}^{-1})\lambda^{-1} \\ \lambda &= 6.8 \times 10^{-8} \text{ m} \\ &= 8.8 \text{ nm} \end{aligned}$$

(d) 8.8 nm is in the x-ray/gamma ray region.

1.15 To answer this question, we need to convert the quantities to a consistent set of units, in this case, SI units.

$$\begin{aligned} (5.15 \text{ ounce})(28.3 \text{ g} \cdot \text{ounce}^{-1})(1 \text{ kg}/1000 \text{ g}) &= 0.146 \text{ kg} \\ \left(\frac{92 \text{ mi}}{\text{h}}\right)\left(\frac{1 \text{ h}}{3600 \text{ s}}\right)\left(\frac{1 \text{ km}}{0.6214 \text{ mi}}\right)\left(\frac{1000 \text{ m}}{1 \text{ km}}\right) &= 41 \text{ m} \cdot \text{s}^{-1} \end{aligned}$$

Use the de Broglie relationship.

$$\begin{aligned} \lambda &= hp^{-1} = h(mv)^{-1} \\ &= h(mv)^{-1} \\ &= \frac{6.626\,08 \times 10^{-34} \text{ J} \cdot \text{s}}{(0.146 \text{ kg})(0.041 \text{ km} \cdot \text{s}^{-1})} \\ &= \frac{6.626\,08 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}}{(0.146 \text{ kg})(41 \text{ m} \cdot \text{s}^{-1})} \\ &= 1.1 \times 10^{-34} \text{ m} \end{aligned}$$

- 1.17** From the de Broglie relationship, $p = h\lambda^{-1}$ or $h = mv\lambda$, we can calculate the velocity of the neutron:

$$\begin{aligned} v &= \frac{h}{m\lambda} \\ &= \frac{(6.626\,08 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1})}{(1.674\,93 \times 10^{-27} \text{ kg}) (100 \times 10^{-12} \text{ m})} \text{ (remember that } 1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2}) \\ &= 3.96 \times 10^3 \text{ m} \cdot \text{s}^{-1} \end{aligned}$$

- 1.19** Yes there are degenerate levels. The first three cases of degenerate levels are:

$$n_1 = 2, n_2 = 3 \text{ is degenerate with } n_1 = 3, n_2 = 2$$

$$n_1 = 1, n_2 = 3 \text{ is degenerate with } n_1 = 3, n_2 = 1$$

$$n_1 = 2, n_2 = 3 \text{ is degenerate with } n_1 = 3, n_2 = 2$$

- 1.21** (a) Integrate over the “left half of the box” or from 0 to $\frac{1}{2}L$:

$$\begin{aligned} \int_0^{\frac{L}{2}} \Psi^2 &= \frac{2}{L} \int_0^{\frac{L}{2}} \left(\sin \frac{n\pi x}{L} \right)^2 dx \\ &= \frac{2}{L} \left[\left(\frac{-1}{2n\pi} \cdot \cos \frac{n\pi x}{L} \cdot \sin \frac{n\pi x}{L} + \frac{x}{2} \right) \right]_0^{\frac{L}{2}} \end{aligned}$$

given n is an integer:

$$= \frac{2}{L} \left[\left(\frac{L/2}{2} \right) - 0 \right] = \frac{1}{2}$$

- (b) Integrate over the “left third of the box” or from 0 to $\frac{1}{3}L$:

$$\begin{aligned} \int_0^{\frac{L}{3}} \Psi^2 &= \frac{2}{L} \int_0^{\frac{L}{3}} \left(\sin \frac{n\pi x}{L} \right)^2 dx \\ &= \frac{2}{L} \left[\left(\frac{-1}{2n\pi} \cdot \cos \frac{n\pi x}{L} \cdot \sin \frac{n\pi x}{L} + \frac{x}{2} \right) \right]_0^{\frac{L}{3}} \\ &= \frac{-1}{L \cdot n \cdot \pi} \cos \frac{n\pi}{3} \cdot \sin \frac{n\pi}{3} + \frac{1}{3} \end{aligned}$$

if n is a multiple of 3, the first term in this sum is zero and the probability of finding an electron in the left third of the box is $1/3$. Also, as n becomes large the probability of finding the electron in the left third of the box approaches $1/3$.

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

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

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

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

$$2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1} = (3.29 \times 10^{15} \text{ s}^{-1}) \left(\frac{1}{4} - \frac{1}{16} \right) \lambda$$

$$\lambda = 4.86 \times 10^{-7} \text{ m} = 486 \text{ nm}$$

(b) Balmer series

(c) visible, green

1.25
$$\nu = Z^2 R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

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

$$= 9.87 \times 10^{15} \text{ Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{2.9979 \times 10^8 \frac{\text{m}}{\text{s}}}{9.87 \times 10^{15} \text{ Hz}} = 3.04 \times 10^{-8} \text{ m or } 30.4 \text{ nm}$$

- 1.27** (a) This problem is the same as that solved in Example 1.5, but the electron is moving between different energy levels. For movement between energy levels separated by a difference of 1 in principal quantum number, the expression is

$$\Delta E = E_{n+1} - E_n = \frac{(n+1)^2 h^2}{8mL^2} - \frac{n^2 h^2}{8mL^2} = \frac{(2n+1)h^2}{8mL^2}$$

For $n = 2$ and $n + 1 = 3$, $\Delta E = \frac{5h^2}{8mL^2}$

Then $\lambda_{3,2} = \frac{hc}{E} = \frac{8mhcL^2}{5h^2} = \frac{8mcL^2}{5h}$

For an electron in a 150-pm box, the expression becomes

$$\begin{aligned}\lambda_{3,2} &= \frac{8(9.109\,39 \times 10^{-31} \text{ kg}) (2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1}) (150 \times 10^{-12} \text{ m})^2}{5(6.626\,08 \times 10^{-34} \text{ J} \cdot \text{s})} \\ &= 1.5 \times 10^{-8} \text{ m}\end{aligned}$$

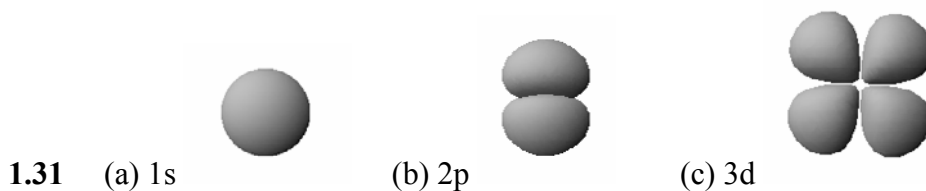
(b) We need to remember that the equation for ΔE was originally determined for energy separations between successive energy levels, so the expression needs to be altered to make it general for energy levels two units apart:

$$\begin{aligned}\Delta E &= E_{n+2} - E_n = \frac{(n+2)^2 h^2}{8mL^2} - \frac{n^2 h^2}{8mL^2} = \frac{(n^2 + 4n + 4 - n^2)h^2}{8mL^2} = \frac{(4n + 4)h^2}{8mL^2} \\ \lambda &= \frac{hc}{\Delta E} = \frac{hc(8mL^2)}{h^2[4n + 4]} = \frac{8mcL^2}{h^2[4n + 4]}\end{aligned}$$

For $n = 2$, the expression becomes

$$\begin{aligned}\lambda &= \frac{8mcL^2}{h[(4 \times 2) + 4]} = \frac{8mcL^2}{9h} \\ &= \frac{8(9.109\,39 \times 10^{-31} \text{ kg}) (2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1}) (150 \times 10^{-12} \text{ m})^2}{12(6.626\,08 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1})} \\ &= 6.2 \times 10^{-9} \text{ m}\end{aligned}$$

1.29 In each of these series, the principal quantum number for the lower energy level involved is the same for each absorption line. Thus, for the Lyman series, the lower energy level is $n = 1$; for the Balmer series, $n = 2$; for Paschen series, $n = 3$; and for the Brackett series, $n = 4$.



(b) A node is a region in space where the wavefunction ψ passes through 0. (c) The simplest s -orbital has 0 nodes, the simplest p -orbital has 1 nodal plane, and the simplest d -orbital has 2 nodal planes. (d) Given the increase in number of nodes, an f -orbital would be expected to have 3 nodal planes.

1.33 The p_x orbital will have its lobes oriented along the x axis, the p_y orbital will have its lobes oriented along the y axis, and the p_z orbital will have its lobes oriented along the z axis.

1.35 The equation derived in Illustration 1.4 can be used:

$$\frac{\psi^2(r = 0.55a_0, \theta, \phi)}{\psi^2(0, \theta, \phi)} = \frac{e^{-2(0.55a_0)/a_0}}{\left(\frac{1}{\pi a_0^3}\right)} = 0.33$$

1.37 To show that three p orbitals taken together are spherically symmetric, sum the three probability distributions (the wavefunctions squared) and show that the magnitude of the sum is not a function of θ or ϕ .

$$p_x = R(r)C \sin \theta \cos \phi$$

$$p_y = R(r)C \sin \theta \sin \phi$$

$$p_z = R(r)C \cos \theta$$

$$\text{where } C = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}}$$

Squaring the three wavefunctions and summing them:

$$\begin{aligned}
& R(r)^2 C^2 \sin^2 \theta \cos^2 \phi + R(r)^2 C^2 \sin^2 \theta \sin^2 \phi + R(r)^2 C^2 \cos^2 \theta \\
&= R(r)^2 C^2 (\sin^2 \theta \cos^2 \phi + \sin^2 \theta \sin^2 \phi + \cos^2 \theta) \\
&= R(r)^2 C^2 (\sin^2 \theta (\cos^2 \phi + \sin^2 \phi) + \cos^2 \theta)
\end{aligned}$$

Using the identity $\cos^2 x + \sin^2 x = 1$ this becomes

$$R(r)^2 C^2 (\sin^2 \theta + \cos^2 \theta) = R(r)^2 C^2$$

With one electron in each p orbital, the electron distribution is not a function of θ or ϕ and is, therefore, spherically symmetric.

- 1.39** (a) The probability (P) of finding an electron within a sphere of radius a_o may be determined by integrating the appropriate wavefunction squared from 0 to a_o :

$$P = \frac{4}{a_o^2} \int_0^{a_o} r^2 \exp\left(-\frac{2r}{a_o}\right) dr$$

This integral is easier to evaluate if we allow the following change of variables:

$$z = \frac{2r}{a_o} \quad \therefore z = 2 \text{ when } r = a_o, z = 0 \text{ when } r = 0, \text{ and } dr = \left(\frac{a_o}{2}\right) dz$$

$$\begin{aligned}
P &= \frac{1}{2} \int_0^2 z^2 \exp(-z) dz = -\frac{1}{2} (z^2 + 2z + 2) \exp(-z) \Big|_0^2 \\
&= -\frac{1}{2} [(4 + 4 + 2) \exp(-2) - 2] \\
&= 0.323 \text{ or } 32.3\%
\end{aligned}$$

- (b) Following the answer developed in (a) changing the integration limits to 0 to $2 a_o$:

$$z = 4 \text{ when } r = 2a_o, z = 0 \text{ when } r = 0, \text{ and } dr = \left(\frac{a_o}{2}\right) dz$$

$$\begin{aligned}
P &= \frac{1}{2} \int_0^4 z^2 \exp(-z) dz = -\frac{1}{2} (z^2 + 2z + 2) \exp(-z) \Big|_0^4 \\
&= -\frac{1}{2} [(26 \exp(-4)) - 2] \\
&= 0.761 \text{ or } 76.1\%
\end{aligned}$$

- 1.41 (a) 1 orbital; (b) 5 orbitals; (c) 3 orbitals; (d) 7 orbitals
- 1.43 (a) 7 values: 0, 1, 2, 3, 4, 5, 6; (b) 5 values: $-2, -1, 0, 1, 2$; (c) 3 values: $-1, 0, 1$; (d) 4 subshells: $4s, 4p, 4d$, and $4f$
- 1.45 (a) $n = 6; l = 1$; (b) $n = 3; l = 2$; (c) $n = 2; l = 1$; (d) $n = 5; l = 3$
- 1.47 (a) 0; (b) $-3, -2, -1, 0, 1, 2, 3$; (c) $-2, -1, 0, 1, 2$; (d) $-1, 0, 1$
- 1.49 (a) 6 electrons; (b) 10 electrons; (c) 2 electrons; (d) 14 electrons
- 1.51 (a) $5d$, five; (b) $1s$, one; (c) $6f$, seven; (d) $2p$, three
- 1.53 (a) six; (b) two; (c) eight; (d) two
- 1.55 (a) cannot exist; (b) exists; (c) cannot exist; (d) exists
- 1.57 (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 lithium, there are three protons in the nucleus and three electrons. Each attractive Coulomb potential will be equal to

$$\frac{(-e)(+3e)}{4\pi\epsilon_0 r} = \frac{-3e^2}{4\pi\epsilon_0 r}$$

where $-e$ is the charge on the electron and $+3e$ is the charge on the nucleus, ϵ_0 is the vacuum permittivity, and r is the distance from the electron to the nucleus. The total attractive potential will thus be

$$\left(\frac{-3e^2}{4\pi\epsilon_0 r_1}\right) + \left(\frac{-3e^2}{4\pi\epsilon_0 r_2}\right) + \left(\frac{-3e^2}{4\pi\epsilon_0 r_3}\right) = \left(\frac{-3e^2}{4\pi\epsilon_0}\right)\left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3}\right)$$

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 two electrons a and b. The total repulsive term will thus be

$$\frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{23}} = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right)$$

This gives

$$V(r) = \left(\frac{-3e^2}{4\pi\epsilon_0} \right) \left(\frac{1}{r_2} + \frac{1}{r_2} + \frac{1}{r_3} \right) + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right)$$

(b) The first term represents the coulombic attractions between the nucleus and each electron, and the second term represents the coulombic repulsions between each pair of electrons.

- 1.59** (a) false. Z_{eff} is considerably affected by the total number of electrons present in the atom because the electrons in the lower energy orbitals will “shield” the electrons in the higher energy orbitals from the nucleus. This effect arises because the $e-e$ repulsions tend to offset the attraction of the electron to the nucleus. (b) true; (c) false. The electrons are increasingly less able to penetrate to the nucleus as l increases. (d) true.
- 1.61** Only (d) is the configuration expected for a ground-state atom; the others all represent excited-state configurations.
- 1.63** (a) This configuration is possible. (b) This configuration is not possible because $l = 0$ here, so m_l must also equal 0. (c) This configuration is not possible because the maximum value l can have is $n - 1$; $n = 4$, so $l_{\text{max}} = 3$.

- 1.65** (a) silver $[\text{Kr}]4d^{10}5s^1$
 (b) beryllium $[\text{He}]2s^2$
 (c) antimony $[\text{Kr}]4d^{10}5s^25p^3$
 (d) gallium $[\text{Ar}]3d^{10}4s^24p^1$
 (e) tungsten $[\text{Xe}]4f^{14}5d^46s^2$
 (f) iodine $[\text{Kr}]4d^{10}5s^25p^5$

1.67 (a) tellurium; (b) vanadium; (c) carbon; (d) thorium

1.69 (a) $4p$; (b) $4s$; (c) $6s$; (d) $6s$

1.71 (a) 5; (b) 11; (c) 5; (d) 20

1.73 (a) 3; (b) 2; (c) 3; (d) 2

1.75 (a) ns^1 ; (b) ns^2np^1 ; (c) $(n-1)d^5ns^2$; (d) $(n-1)d^{10}ns^1$

1.77 (a) oxygen ($1310 \text{ kJ} \cdot \text{mol}^{-1}$) > selenium ($941 \text{ kJ} \cdot \text{mol}^{-1}$) > tellurium ($870 \text{ kJ} \cdot \text{mol}^{-1}$); ionization energies generally decrease as one goes down a group. (b) gold ($890 \text{ kJ} \cdot \text{mol}^{-1}$) > osmium ($840 \text{ kJ} \cdot \text{mol}^{-1}$) > tantalum ($761 \text{ kJ} \cdot \text{mol}^{-1}$); ionization energies generally decrease as one goes from right to left in the periodic table. (c) lead ($716 \text{ kJ} \cdot \text{mol}^{-1}$) > barium ($502 \text{ kJ} \cdot \text{mol}^{-1}$) > cesium ($376 \text{ kJ} \cdot \text{mol}^{-1}$); ionization energies generally decrease as one goes from right to left in the periodic table.

1.79 The atomic radii (in pm) are

| | | | |
|----|-----|----|-----|
| Sc | 164 | Fe | 124 |
| Ti | 147 | Co | 125 |

| | | | |
|----|-----|----|-----|
| V | 135 | Ni | 125 |
| Cr | 129 | Cu | 128 |
| Mn | 137 | Zn | 137 |

The major trend is for decreasing radius as the nuclear charge increases, with the exception that Cu and Zn begin to show the effects of electron-electron repulsions and become larger as the *d*-subshell becomes filled.

Mn is also an exception as found for other properties; this may be attributed to having the *d*-shell half-filled.

1.81 (a) Sb^{3+} , Sb^{5+} (b) As^{3+} , As^{5+} (c) Tl^{1+} , Tl^{3+} (d) only forms one positive ion

1.83 $\text{P}^{3-} > \text{S}^{2-} > \text{Cl}^{-}$

1.85 (a) sulfur; (b) germanium (c) germanium; (d) bromine

1.87 A diagonal relationship is a similarity in chemical properties between an element in the periodic table and one lying one period lower and one group to the right. It is caused by the similarity in size of the ions. The lower-right element in the pair would generally be larger because it lies in a higher period, but it also will have a higher oxidation state, which will cause the ion to be smaller. For example, Al^{3+} and Ge^{4+} compounds show the diagonal relationship, as do Li^{+} and Mg^{2+} .

1.89 (a) N and S; (b) Li and Mg

1.91 The ionization energies of the *s*-block metals are considerably lower, thus making it easier for them to lose electrons in chemical reactions.

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

1.95 (a) $\frac{\nu}{c} = 3600 \text{ cm}^{-1}$

$$\nu = c(3600 \text{ cm}^{-1})$$

$$\nu = (2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1})(3600 \text{ cm}^{-1})$$

$$\nu = (2.997\,92 \times 10^{10} \text{ cm} \cdot \text{s}^{-1})(3600 \text{ cm}^{-1})$$

$$\nu = 1.1 \times 10^{14} \text{ s}^{-1}$$

(b) From $E = h\nu$: $E = (6.626\,08 \times 10^{-34} \text{ J} \cdot \text{s})(1.079 \times 10^{14} \text{ s}^{-1})$

$$= 7.2 \times 10^{-20} \text{ J}.$$

(c) 1.00 mol of molecules = 6.022×10^{23} molecules, so the energy absorbed by 1.00 mol will be

$$(7.151 \times 10^{-20} \text{ J} \cdot \text{molecule}^{-1})(6.022 \times 10^{23} \text{ molecules} \cdot \text{mol}^{-1})$$

$$= 4.3 \times 10^4 \text{ J} \cdot \text{mol}^{-1} \text{ or } 43 \text{ kJ} \cdot \text{mol}^{-1}.$$

1.97 In copper it is energetically favorable for an electron to be promoted from the 4s orbital to a 3d orbital, giving a completely filled 3d subshell. In the case of Cr, it is energetically favorable for an electron to be promoted from the 4s orbital to a 3d orbital to exactly $\frac{1}{2}$ fill the 3d subshell.

1.99 This trend is attributed to the inert-pair effect, which states that the *s*-electrons are less available for bonding in the heavier elements. Thus, there is an increasing trend as we descend the periodic table for the preferred oxidation number to be 2 units lower than the maximum one. As one descends the periodic table, ionization energies tend to decrease. For Tl, however, the values are slightly higher than those of its lighter analogues.

1.101 (a) The relation is derived as follows: the energy of the photon entering, E_{total} , must be equal to the energy to eject the electron, E_{ejection} , plus the energy that ends up as kinetic energy, E_{kinetic} , in the movement of the electron:

$$E_{\text{total}} = E_{\text{ejection}} + E_{\text{kinetic}}$$

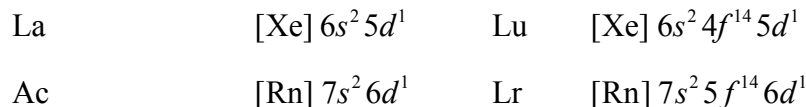
But E_{total} for the photon $= h\nu$ and $E_{\text{kinetic}} = \left(\frac{1}{2}\right)mv^2$, where m is the mass of the object and v is its velocity. E_{ejection} corresponds to the ionization energy, I , so we arrive at the final relationship desired.

$$\begin{aligned} \text{(b)} \quad E_{\text{total}} &= h\nu = hc\lambda^{-1} \\ &= (6.626\,08 \times 10^{-34} \text{ J} \cdot \text{s}) (2.997\,92 \times 10^8 \text{ m} \cdot \text{s}^{-1}) (58.4 \times 10^{-9} \text{ m})^{-1} \\ &= 3.40 \times 10^{-18} \text{ J} \\ &= E_{\text{ejection}} + E_{\text{kinetic}} \end{aligned}$$

$$\begin{aligned} E_{\text{kinetic}} &= \left(\frac{1}{2}\right)mv^2 = \left(\frac{1}{2}\right) (9.109\,39 \times 10^{-28} \text{ g}) (2450 \text{ km} \cdot \text{s}^{-1})^2 \\ &= \left(\frac{1}{2}\right) (9.109\,39 \times 10^{-31} \text{ kg}) (2.450 \times 10^6 \text{ m} \cdot \text{s}^{-1})^2 \\ &= 2.73 \times 10^{-18} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = 2.73 \times 10^{-18} \text{ J} \end{aligned}$$

$$\begin{aligned} 3.40 \times 10^{-18} \text{ J} &= E_{\text{ejection}} + 2.73 \times 10^{-18} \text{ J} \\ E_{\text{ejection}} &= 6.7 \times 10^{-19} \text{ J} \end{aligned}$$

1.103 By the time we get to the lanthanides and actinides—the two series of f -orbital filling elements—the energy levels become very close together and minor changes in environment cause the different types of orbitals to switch in energy-level ordering. For the elements mentioned, the electronic configurations are



As can be seen, all these elements have one electron in a d -orbital, so placement in the third column of the periodic table could be considered appropriate for either, depending on what aspects of the chemistry of these elements we are comparing. The choice is not without argument, and it is discussed by W. B. Jensen (1982), *J. Chem. Ed.* **59**, 634.

- 1.105** (a)—(c) We can use the hydrogen $2s$ wavefunction found in Table 1.2. Remember that the probability of locating an electron at a small region in space is proportional to ψ^2 , not ψ .

$$\begin{aligned}\psi_{2s} &= \frac{1}{4} \left(\frac{1}{2\pi a_0^3} \right)^{\frac{1}{2}} \left(2 - \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}} \\ \psi_{2s}^2 &= \left(\frac{1}{32\pi a_0^3} \right) \left(2 - \frac{r}{a_0} \right)^2 e^{-\frac{r}{a_0}} \\ \frac{\psi_{2s}^2(r, \theta, \phi)}{\psi_{2s}^2(0, \theta, \phi)} &= \frac{\left(\frac{1}{32\pi a_0^3} \right) \left(2 - \frac{r}{a_0} \right)^2 e^{-\frac{r}{a_0}}}{\left(\frac{1}{32\pi a_0^3} \right) 2^2 e^{-\frac{0}{a_0}}} \\ &= \frac{\left(2 - \frac{r}{a_0} \right)^2 e^{-\frac{r}{a_0}}}{4}\end{aligned}$$

Because r will be equal to some fraction x times a_0 , the expression will simplify further:

$$\frac{\psi_{2s}^2(r, \theta, \phi)}{\psi_{2s}^2(0, \theta, \phi)} = \frac{\left(2 - \frac{xa_0}{a_0} \right)^2 e^{-\frac{xa_0}{a_0}}}{4} = \frac{(2-x)^2 e^{-x}}{4}$$

Carrying out this calculation for the other points, we obtain:

| x | relative probability |
|-----|----------------------|
| 0.1 | 0.82 |
| 0.2 | 0.66 |
| 0.3 | 0.54 |
| 0.4 | 0.43 |
| 0.5 | 0.34 |
| 0.6 | 0.27 |
| 0.7 | 0.21 |
| 0.8 | 0.16 |
| 0.9 | 0.12 |

| | |
|-----|---------|
| 1 | 0.092 |
| 1.1 | 0.067 |
| 1.2 | 0.048 |
| 1.3 | 0.033 |
| 1.4 | 0.022 |
| 1.5 | 0.014 |
| 1.6 | 0.0081 |
| 1.7 | 0.0041 |
| 1.8 | 0.0017 |
| 1.9 | 0.0004 |
| 2 | 0.0000 |
| 2.1 | 0.00031 |
| 2.2 | 0.0011 |
| 2.3 | 0.0023 |
| 2.4 | 0.0036 |
| 2.5 | 0.0051 |
| 2.6 | 0.0067 |
| 2.7 | 0.0082 |
| 2.8 | 0.0097 |
| 2.9 | 0.011 |
| 3 | 0.012 |

This can be most easily carried out graphically by simply plotting the

function $f(x) = \frac{(2-x)^2 e^{-x}}{4}$ from 0 to 3.

The node occurs when $x = 2$, or when $r = 2a_0$. This is exactly what is obtained by setting the radial part of the equation equal to 0.

1.107 The approach to showing that this is true involves integrating the probability function over all space. The probability function is given by the square of the wave function, so that for the particle in the box we have

$$\psi = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{n\pi x}{L}\right)$$

and the probability function will be given by

$$\psi^2 = \left(\frac{2}{L}\right) \sin^2\left(\frac{n\pi x}{L}\right)$$

Because x can range from 0 to L (the length of the box), we can write the integration as

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

for the entire box, we write

probability of finding the particle somewhere in the box =

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

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

$$\begin{aligned} \int_0^L \Psi^2 &= \frac{2}{L} \int_0^L \left(\sin \frac{n\pi x}{L}\right)^2 dx \\ &= \frac{2}{L} \left[\left(\frac{-1}{2n\pi} \cdot \cos \frac{n\pi x}{L} \cdot \sin \frac{n\pi x}{L} + \frac{x}{2} \right) \right]_0^L \\ &= \frac{2}{L} \left[\left(\frac{-1}{2n\pi} \cdot \cos n\pi \cdot \sin n\pi + \frac{L}{2} \right) - 0 \right] \end{aligned}$$

if n is an integer, $\sin n\pi$ will always be zero and

$$probability = \frac{2}{L} \left[\frac{L}{2} \right] = 1$$