The mole ratio of C:H:O is 3.67:4.67:1 or 11:14:3, so the empirical formula is $C_{11}H_{14}O_3$.

(b) The molar mass of the empirical formula is 194 g/mol, which is half of 388.46 g/mol. Therefore, the molecular formula of the compound is $C_{22}H_{28}O_6$.

FOCUS 1

ATOMS

1A.1 (a) Radiation may pass through a metal foil. (b) All light (electromagnetic radiation) travels at the same speed; the slower speed supports the particle model. (c) This observation supports the radiation model. (d) This observation supports the particle model; electromagnetic radiation has no mass and no charge.

1A.3 All of these can be determined using $E = h\nu$ and $c = \nu\lambda$.

(a) No; speed is constant (c). (b) No; $\nu \propto \lambda^{-1}$. (c) Yes. The electrical field corresponds to the amplitude; as the frequency decreases the waves broaden and the extent of the change (the slope of the wave) decreases. (d) No; $E \propto \nu$.

1A.5 microwaves < visible light < ultraviolet light < x-rays < γ-rays

1A.7 (a) $\lambda = \dfrac{c}{\nu} = \dfrac{2.998\times10^{8}\ \text{m}\cdot\text{s}^{-1}}{7.1\times10^{14}\ \text{s}^{-1}} = 4.2\times10^{-7}\ \text{m} = 420\ \text{nm}$

(b) $\lambda = \dfrac{c}{\nu} = \dfrac{2.998\times10^{8}\ \text{m}\cdot\text{s}^{-1}}{2.0\times10^{18}\ \text{s}^{-1}} = 1.5\times10^{-10}\ \text{m} = 150\ \text{pm}$

1A.9 All of these can be determined using $E = h\nu$ and $c = \nu\lambda$. For example, in the first entry frequency is given, so:

$$\lambda = \frac{c}{\nu} = \frac{2.998\times10^{8}\ \text{m}\cdot\text{s}^{-1}}{8.7\times10^{14}\ \text{s}^{-1}} = 3.4\times10^{-7}\ \text{m} = 340\ \text{nm};$$

and $E = h\nu = (6.626\times10^{-34}\ \text{J}\cdot\text{s})(8.7\times10^{14}\ \text{s}^{-1}) = 5.8\times10^{-19}\ \text{J}$

Frequency (2 s.f.)	Wavelength (2 s.f.)	Energy of photon (2 s.f.)	Event
8.7×10^{14} Hz	340 nm	5.8×10^{-19} J	Suntan
5.0×10^{14} Hz	600 nm	3.3×10^{-19} J	Reading
300 MHz	1 m	2×10^{-25} J	Microwave popcorn
1.2×10^{17} Hz	2.5 nm	7.9×10^{-17} J	Dental x-ray

1A.11 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, $n = 4$.

1A.13 (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 $c = \nu\lambda$.

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

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

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

$$2.99\ 792 \times 10^8\ m \cdot s^{-1} = (3.29 \times 10^{15}\ s^{-1})\left(\frac{1}{1} - \frac{1}{4}\right)\lambda$$

$$\lambda = 1.21 \times 10^{-7}\ m = 121\ nm$$

(b) Lyman series

(c) This absorption lies in the ultraviolet region.

1A.15 The ultraviolet spectrum of atomic hydrogen (known as the Lyman series) has $n_1 = 1$; so, for a line at 102.6 nm:

$$\upsilon = \frac{c}{\lambda} = \frac{2.998 \times 10^8\ \text{m} \cdot \text{s}^{-1}}{102.6 \times 10^{-9}\ \text{m}} = 2.922 \times 10^{15}\ \text{s}^{-1};$$

using the Rydberg equation we can now solve for n_2:

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

$$\frac{1}{n_2^2} = 1 - \frac{2.922 \times 10^{15}\ \text{s}^{-1}}{3.29 \times 10^{15}\ \text{s}^{-1}} = 0.112$$

$$n_2^2 = 9;\ n_2 = 3$$

The transition is $n_1 = 1$ to $n_2 = 3$.

1A.17 For hydrogenlike one-electron ions, we use the Z-dependent Rydberg relation with the relationship $c = \lambda\nu$ to determine the transition wavelength. For He$^+$, $Z = 2$.

$$\nu = Z^2\mathfrak{R}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = (2^2)(3.29 \times 10^{15}\ \text{s}^{-1})\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = 9.87 \times 10^{15}\ \text{Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{2.997\ 92 \times 10^8\ \text{m} \cdot \text{s}^{-1}}{9.87 \times 10^{15}\ \text{s}^{-1}} = 3.04 \times 10^{-8}\ \text{m} = 30.4\ \text{nm}$$

1B.1 (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.

1B.3 The photoelectric effect (d) best supports the idea that EMR has the properties of particles. To explain the photoelectric effect, Einstein proposed that EMR consists of particles (or packets) of energy called photons, each photon having a fixed energy equal to $h\nu$.

1B.5 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

$$\lambda = \frac{hc}{E}$$
$$= \frac{(6.626\,08\times10^{-34}\ \text{J}\cdot\text{s})\,(2.997\,92\times10^{8}\ \text{m}\cdot\text{s}^{-1})}{2.2513\times10^{-14}\ \text{J}}$$
$$= 8.8237\times10^{-12}\ \text{m or } 8.8237\ \text{pm}$$

1B.7 (a) From $c = \nu\lambda$ and $E = h\nu$, we can write

$$E = hc\lambda^{-1}$$
$$= (6.626\,08\times10^{-34}\ \text{J}\cdot\text{s})\,(2.997\,92\times10^{8})\,(589\times10^{-9}\ \text{m})^{-1}$$
$$= 3.37\times10^{-19}\ \text{J}$$

(b) $$E = \left(\frac{5.00\times10^{-3}\ \text{g Na}}{22.99\ \text{g}\cdot\text{mol}^{-1}\ \text{Na}}\right)(6.022\times10^{23}\ \text{atoms}\cdot\text{mol}^{-1})$$
$$\times\,(3.37\times10^{-19}\ \text{J}\cdot\text{atom}^{-1})$$
$$= 44.1\ \text{J}$$

(c) $$E = (6.022\times10^{23}\ \text{atoms}\cdot\text{mol}^{-1})(3.37\times10^{-19}\ \text{J}\cdot\text{atom}^{-1})$$
$$= 2.03\times10^{5}\ \text{J or } 203\ \text{kJ}$$

1B.9 $32\ \text{W} = 32\ \text{J}\cdot\text{sec}^{-1}$, so in 2 seconds 64 J will be emitted.

For violet light $(\lambda = 420\ \text{nm} = 420\times10^{-9}\ \text{m})$ the energy per photon is:

$$E = hc\lambda^{-1}$$
$$= (6.626\,08\times10^{-34}\ \text{J}\cdot\text{s})\,(2.997\,92\times10^{8})\,(420\times10^{-9}\ \text{m})^{-1}$$
$$= 4.7\times10^{-19}\ \text{J}\cdot\text{photon}^{-1}$$

$$\text{number of photons} = (64\ \text{J})\,(4.7\times10^{-19}\ \text{J}\cdot\text{photon}^{-1})^{-1}$$
$$= 1.4\times10^{20}\ \text{photons}$$

$$\text{moles of photons} = (1.4\times10^{20}\ \text{photons})\left(\frac{1\ \text{mol}}{6.022\times10^{23}\ \text{photons}}\right)$$
$$= 2.3\times10^{-4}\ \text{mol photons}$$

1B.11 Using Wien's law: $T\lambda_{\text{max}} = \text{constant} = 2.88\times10^{-3}\ \text{K}\cdot\text{m}$.

$$\lambda_{\text{max}} = 850\ \text{nm} = 8.5\times10^{-7}\ \text{m},$$
$$\text{then } T = \frac{2.88\times10^{-3}\ \text{K}\cdot\text{m}}{8.5\times10^{-7}\ \text{m}} = 3400\ \text{K}$$

1B.13 Wien's law states that $T\lambda_{\text{max}} = \text{constant} = 2.88\times10^{-3}\ \text{K}\cdot\text{m}$.

If $T/\text{K} = 1540°\text{C} + 273°\text{C} = 1813\ \text{K}$, then $\lambda_{\text{max}} = \dfrac{2.88\times10^{-3}\ \text{K}\cdot\text{m}}{1813\ \text{K}}$

$\lambda_{\text{max}} = 1.59\times10^{-6}\ \text{m, or } 1590\ \text{nm}$

This wavelength falls in the infrared region.

1B.15 (a) Use the de Broglie relationship, $\lambda = hp^{-1} = h(mv)^{-1}$.

$$m_{\text{e}} = (9.109\,39\times10^{-28}\ \text{g})\,(1\ \text{kg}/1000\ \text{g}) = 9.109\,39\times10^{-31}\ \text{kg}$$
$$(3.6\times10^{3}\ \text{km}\cdot\text{s}^{-1})\,(1000\ \text{m}\cdot\text{km}^{-1}) = 3.6\times10^{6}\ \text{m}\cdot\text{s}^{-1}$$
$$\lambda = h(mv)^{-1}$$
$$= \frac{6.626\,08\times10^{-34}\ \text{J}\cdot\text{s}}{(9.109\,39\times10^{-31}\ \text{kg})\,(3.6\times10^{6}\ \text{m}\cdot\text{s}^{-1})}$$
$$= 2.0\times10^{-10}\ \text{m}$$

(b) $$E = h\nu$$
$$= (6.626\,08\times10^{-34}\ \text{J}\cdot\text{s})\,(2.50\times10^{16}\ \text{s}^{-1})$$
$$= 1.66\times10^{-17}\ \text{J}$$

(c) The photon needs to contain enough energy to eject the electron from the surface as well as to cause it to move at $3.6\times10^{3}\ \text{km}\cdot\text{s}^{-1}$. The energy involved is the kinetic energy of the electron, which equals $\frac{1}{2}mv^{2}$.

$$E_{\text{photon}} = 1.66 \times 10^{-17}\ \text{J} + \frac{1}{2}mv^2$$
$$= 1.66 \times 10^{-17}\ \text{J} + \frac{1}{2}(9.109\ 39 \times 10^{-31}\ \text{kg})\,(3.6 \times 10^6\ \text{m}\cdot\text{s}^{-1})^2$$
$$= 1.66 \times 10^{-17}\ \text{J} + 5.9 \times 10^{-18}\ \text{J}$$
$$= 2.25 \times 10^{-17}\ \text{J}$$

But we are asked for the wavelength of the photon, which we can get from $E = h\nu$ and $c = \nu\lambda$ or $E = hc\lambda^{-1}$.

$$2.25 \times 10^{-17}\ kg \cdot m^2 \cdot s^{-2} = (6.626\ 08 \times 10^{-34}\ kg \cdot m^2 \cdot s^{-1})$$
$$\times (2.997\ 92 \times 10^8\ m \cdot s^{-1})\lambda^{-1}$$
$$\lambda = 8.8 \times 10^{-9}\ m$$
$$= 8.8\ nm$$

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

1B.17 The de Broglie relationship, $\lambda = hp^{-1} = h(mv)^{-1}$, states that the wavelength of a particle is inversely proportional to its mass. Therefore, the heavier person (80 kg) should have a shorter wavelength than the lighter person (60 kg) if they are moving at the same speed.

1B.19 The wavelength for both a proton and a neutron can be calculated using the de Broglie relationship; thus:

$$\lambda_{proton} = h(m_{proton}v)^{-1}$$
$$= \frac{6.626\ 08 \times 10^{-34}\ \text{J}\cdot\text{s}}{(1.673 \times 10^{-27}\ \text{kg})\,(2.75 \times 10^5\ \text{m}\cdot\text{s}^{-1})}$$
$$= 1.44 \times 10^{-12}\ \text{m} = 1.44\ \text{pm}.$$
$$\lambda_{neutron} = h(m_{neutron}v)^{-1}$$
$$= \frac{6.626\ 08 \times 10^{-34}\ \text{J}\cdot\text{s}}{(1.675 \times 10^{-27}\ \text{kg})\,(2.75 \times 10^5\ \text{m}\cdot\text{s}^{-1})}$$
$$= 1.44 \times 10^{-12}\ \text{m} = 1.44\ \text{pm}.$$

The wavelength of a proton and a neutron are identical to 3 significant figures.

1B.21 To answer this question, we need to convert the quantities to a consistent set of units, in this case, SI units.

$$(5.15\ \text{ounce})\,(28.3\ \text{g}\cdot\text{ounce}^{-1})\,(1\ \text{kg}/1000\ \text{g}) = 0.146\ \text{kg}$$

$$\left(\frac{92\ \text{mi}}{\text{h}}\right)\left(\frac{1\ \text{h}}{3600\ \text{s}}\right)\left(\frac{1\ \text{km}}{0.6214\ \text{mi}}\right)\left(\frac{1000\ \text{m}}{1\ \text{km}}\right) = 41\ \text{m}\cdot\text{s}^{-1}$$

Use the de Broglie relationship.

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

1B.23 From the de Broglie relationship, $p = h\lambda^{-1}$ or $h = mv\lambda$, we can calculate the velocity of the neutron:

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

1B.25 The uncertainty principle states that $\Delta p\Delta x = \frac{1}{2}\hbar$; so, for an electron $\Delta p = m_e\Delta v$, then $m_e\Delta v\Delta x = \frac{1}{2}\hbar$ and $\Delta v = \frac{1}{2}\frac{\hbar}{m_e\Delta x}$; if we assume that the uncertainty in the position of the electron is equal to the diameter of the lead atom $\Delta x = 350\ \text{pm} = 350 \times 10^{-12}\ \text{m}$.

Remembering that $1\ \text{J} = 1\ \text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}$, gives

$$\hbar = \left(1.054\ \ 457 \times 10^{-34}\ J\cdot s\right)\left(\frac{1\ kg\cdot m^2\cdot s^{-2}}{J}\right) = 1.054\ \ 457 \times 10^{-34}\ kg\cdot m^2\cdot s^{-1}$$

Then

$$\Delta v = \frac{1}{2}\left(\frac{1.054\ 457\times10^{-34}\,\text{kg}\cdot\text{m}^2\cdot\text{s}^{-1}}{(9.109\ 38\times10^{-31}\,\text{kg})(350\times10^{-12}\ \text{m})}\right)$$

$$\Delta v = 1.65\times10^{5}\,\text{m}\cdot\text{s}^{-1}$$

1B.27 The minimum uncertainty in the position of the bowling ball can be calculated using the uncertainty principle:

$$\Delta x = \frac{1}{2}\left(\frac{\hbar}{m\Delta v}\right) = \frac{1}{2}\left(\frac{1.054\ 457\times10^{-34}\,\text{kg}\cdot\text{m}^2\cdot\text{s}^{-1}}{(8.00\ \text{kg})(5.0\ \text{m}\cdot\text{s}^{-1})}\right)$$

$$\Delta x = 1.3\times10^{-36}\,\text{m}$$

1C.1 (a) For movement between energy levels separated by a difference of 1 in principal quantum number, the expression is

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

For $n = 4$ and $n+1 = 5$, $\Delta E = \dfrac{9h^2}{8mL^2}$

Then $\lambda_{5,4} = \dfrac{hc}{E} = \dfrac{8mhcL^2}{9h^2} = \dfrac{8mcL^2}{9h}$

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

$$\lambda_{5,4} = \frac{8(9.109\ 39\times10^{-31}\ \text{kg})\,(2.997\ 92\times10^{8}\ \text{m}\cdot\text{s}^{-1})\,(150\times10^{-12}\ \text{m})^2}{9(6.626\ 08\times10^{-34}\ \text{J}\cdot\text{s})}$$

$$= 8.24\times10^{-9}\ \text{m} = 8.24\ \text{nm}.$$

(b) Do the same as in (a):

$n = 3$ and $n+1 = 4$, $\Delta E = \dfrac{7h^2}{8mL^2}$

$$\lambda_{4,3} = \frac{hc}{E} = \frac{8mhcL^2}{7h^2} = \frac{8mcL^2}{7h}$$

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

$$\lambda_{4,3} = \frac{8(9.109\ 39\times10^{-31}\ \text{kg})\,(2.997\ 92\times10^{8}\ \text{m}\cdot\text{s}^{-1})\,(150\times10^{-12}\ \text{m})^2}{7(6.626\ 08\times10^{-34}\ \text{J}\cdot\text{s})}$$

$$= 1.06\times10^{-8}\ \text{m} = 10.6\ \text{nm}.$$

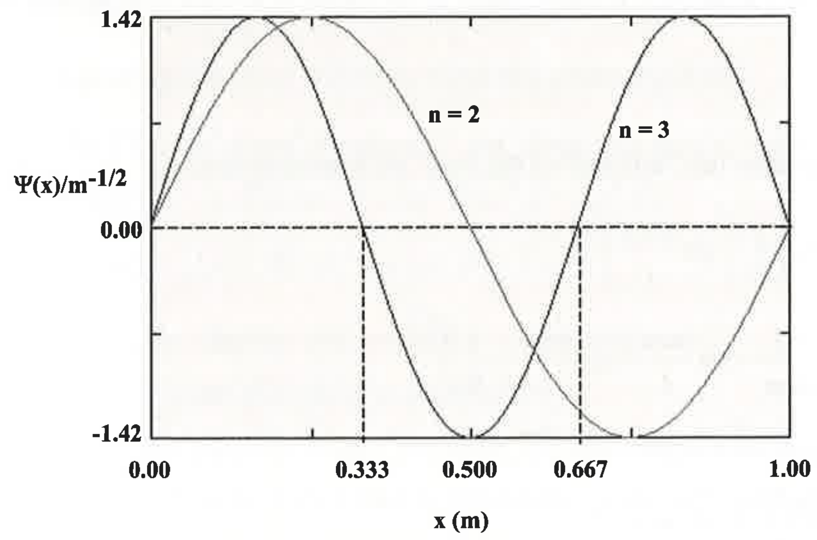
1C.3 Yes, there are degenerate levels. The first three cases of degenerate levels are:

$n_1 = 1,\ n_2 = 2$ is degenerate with $n_1 = 2,\ n_2 = 1$

$n_1 = 1,\ n_2 = 3$ is degenerate with $n_1 = 3,\ n_2 = 1$

$n_1 = 2,\ n_2 = 3$ is degenerate with $n_1 = 3,\ n_2 = 2$

1C.5 (a) Refer to the plot below for parts (a) thru (d); nodes are where the wavefunction is zero:

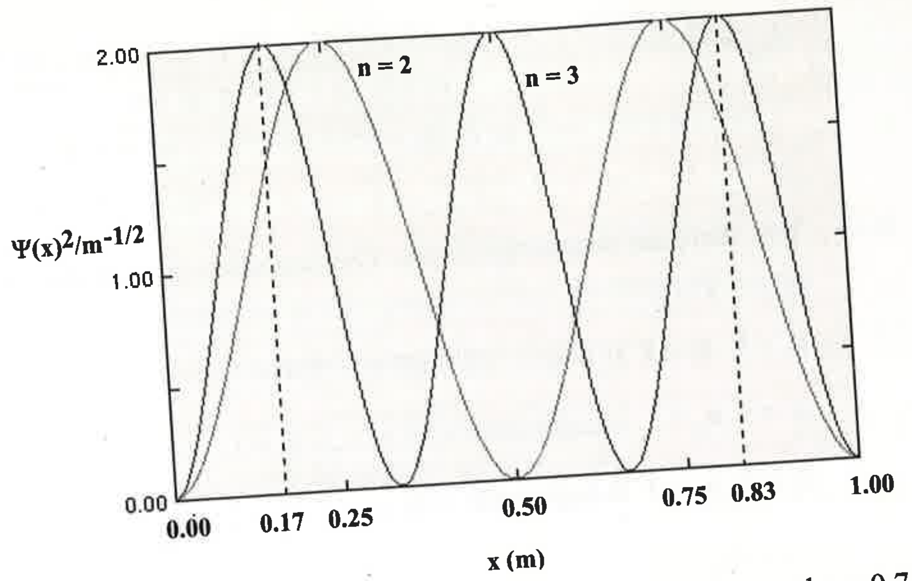


(b) for $n = 2$ there is one node at $x = 0.500$ m.

(c) for $n = 3$ there are two nodes, one at $x = 0.333$ and 0.667 m.

(d) the number of nodes is equal to $n - 1$

Refer to the plot below for parts (e) and (f):



(e) for $n = 2$ a particle is most likely to be found at $x = 0.25$ m and $x = 0.75$ m.

(f) for $n = 3$ a particle is most likely to be found at $x = 0.17, 0.50$, and 0.83 m.

1C.7 Integrate over the "left half of the box" or from 0 to ½ L:

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

$$= \frac{2}{L}\left[\left(\frac{-1}{2n\pi}\cdot\cos\frac{n\pi x}{L}\cdot\sin\frac{n\pi x}{L}+\frac{x}{2}\right)\Bigg|_0^{\frac{L}{2}}\right]$$

given n is an integer:

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

1D.1 (a) Energy will increase (energy is a function of n). (b) n increases (from $n = 1$ to $n = 2$). (c) l increases (from $l = 0$ for s to $l = 1$ for p). (d) radius increases (radius is a function of n).

1D.3 The equation derived in Example 1D.1 can be used:

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

1D.5 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.

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

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

Squaring the three wavefunctions and summing them:

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

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

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

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

1D.7 (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:

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

$$P=\frac{1}{2}\int_0^2 z^2\exp(-z)dz=-\frac{1}{2}(z^2+2z+2)\exp(-z)\Big|_0^2$$

$$=-\frac{1}{2}\left[((4+4+2)\exp(-2))-2\right]$$

$$=0.323 \text{ or } 32.3\%$$

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

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

$$P=\frac{1}{2}\int_0^4 z^2\exp(-z)dz=-\frac{1}{2}(z^2+2z+2)\exp(-z)\Big|_0^4$$

$$=-\frac{1}{2}\left[(26\exp(-4))-4\right]$$

$$=0.761 \text{ or } 76.1\%$$

1D.9 (a) 1s

2p

3d

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

1D.11 (a) one orbital; (b) five orbitals; (c) three orbitals; (d) seven orbitals

1D.13 (a) seven values: 0, 1, 2, 3, 4, 5, 6; (b) five values; −2, −1, 0, 1, 2; (c) three values: −1, 0, 1; (d) four subshells: $4s, 4p, 4d$, and $4f$

1D.15 (a) $n=6; l=1$; (b) $n=3; l=2$; (c) $n=2; l=1$; (d) $n=5; l=3$

1D.17 (a) −1, 0, +1; (b) −2, −1, 0, +1, +2; (c) −1, 0, +1;
(d) −3, −2, −1, 0, +1, +2, +3.

1D.19 (a) three orbitals; (b) five orbitals; (c) one orbital; (d) seven orbitals

1D.21 (a) 5d, five; (b) 1s, one; (c) 6f, seven; (d) 2p, three

1D.23 (a) 3; (b) 1; (c) 4; (d) 1

1D.25 (a) cannot exist; (b) exists; (c) cannot exist; (d) exists

1E.1 (a) Energy increases; (b) n increases; (c) l increases; (d) radius increases. All of these are the same for a hydrogen atom. (Exercise 1D.1)

1E.3 (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

$$\frac{(-e)(+3e)}{4\pi\varepsilon_0 r}=\frac{-3e^2}{4\pi\varepsilon_0 r}$$

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

$$\left(\frac{-3e^2}{4\pi\varepsilon_0 r_1}\right)+\left(\frac{-3e^2}{4\pi\varepsilon_0 r_2}\right)+\left(\frac{-3e^2}{4\pi\varepsilon_0 r_3}\right)=\left(\frac{-3e^2}{4\pi\varepsilon_0}\right)\left(\frac{1}{r_1}+\frac{1}{r_2}+\frac{1}{r_3}\right)$$

The repulsive terms will have the form

$$\frac{(-e)(-e)}{4\pi\varepsilon_0 r_{\text{ab}}}=\frac{e^2}{4\pi\varepsilon_0 r_{\text{ab}}}$$

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

$$\frac{e^2}{4\pi\varepsilon_0 r_{12}}+\frac{e^2}{4\pi\varepsilon_0 r_{13}}+\frac{e^2}{4\pi\varepsilon_0 r_{23}}=\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}}+\frac{1}{r_{13}}+\frac{1}{r_{23}}\right)$$

This gives

$$V(r)=\left(\frac{-3e^2}{4\pi\varepsilon_0}\right)\left(\frac{1}{r_1}+\frac{1}{r_2}+\frac{1}{r_3}\right)+\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}}+\frac{1}{r_{13}}+\frac{1}{r_{23}}\right)$$

(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.

1E.5 (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.

1E.7 Only (d) is the configuration expected for a ground-state atom; the others all represent excited-state configurations.

1E.9 (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 $l_{\text{max}} = 3$.

1E.11

(a) sodium	[Ne] $3s^1$
(b) silicon	[Ne] $3s^2 3p^2$
(c) chlorine	[Ne] $3s^2 3p^5$
(d) rubidium	[Kr] $5s^1$

1E.13

(a) silver	[Kr] $4d^{10} 5s^1$
(b) beryllium	[He] $2s^2$
(c) antimony	[Kr] $4d^{10} 5s^2 5p^3$
(d) gallium	[Ar] $3d^{10} 4s^2 4p^1$
(e) tungsten	[Xe] $4f^{14} 5d^4 6s^2$
(f) iodine	[Kr] $4d^{10} 5s^2 5p^5$

1E.15 (a) tellurium; (b) vanadium; (c) carbon; (d) thorium

1E.17 (a) 4p; (b) 4s; (c) 6s; (d) 6s

1E.19 (a) 5; (b) 11; (c) 5; (d) 20

1E.21 (a) 3; (b) 2; (c) 3; (d) 2

1E.23

Element	*Electron Configuration*	*Unpaired Electrons*
Ga	[Ar] $3d^{10}4s^2 4p^1$	1
Ge	[Ar] $3d^{10}4s^2 4p^2$	2
As	[Ar] $3d^{10}4s^2 4p^3$	3
Se	[Ar] $3d^{10}4s^2 4p^4$	2
Br	[Ar] $3d^{10}4s^2 4p^5$	1

1E.25 (a) ns^1; (b) ns^2np^3; (c) $(n-1)d^3ns^2$; (d) $(n-1)d^{10}ns^1$

1F.1 (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)

1F.3 $P^{3-} > S^{2-} > Cl^-$

1F.5 (a) Ca; (b) Na; (c) Na

1F.7 (a) oxygen (1310 $kJ \cdot mol^{-1}$) > selenium (941 $kJ \cdot mol^{-1}$) > tellurium (870 $kJ \cdot mol^{-1}$); ionization energies generally decrease as one goes down a group. (b) gold (890 $kJ \cdot mol^{-1}$) > osmium (840 $kJ \cdot mol^{-1}$) > tantalum (761 $kJ \cdot mol^{-1}$); ionization energies generally decrease as one goes from right to left in the periodic table. (c) lead (716 $kJ \cdot mol^{-1}$) > barium (502 $kJ \cdot mol^{-1}$) > cesium (376 $kJ \cdot mol^{-1}$); ionization energies generally decrease as one goes from right to left in the periodic table.

1F.9 The first ionization energy for sulfur and phosphorus atoms are nearly the same, despite sulfur having a larger Z_{eff}; this is due to greater electron-electron repulsions in S, making the energy of the outermost electrons higher than predicted. Once the first electron is removed, the Z_{eff} becomes the predominant factor and the remaining electrons are held tighter due to the smaller size of the S^+ ion as compared with the P^+ ion; this is reflected in the much greater second ionization energy of sulfur as compared with phosphorus.

1F.11 (a) iodine; (b) they are equal; (c) sulfur; (d) they are equal

1F.13 (a) The inert-pair effect is the term used to describe the fact that heavy (period 5 and greater) p-block elements have a tendency to form ions that are two units lower in charge than that expected based on their group number. (b) The inert-pair effect is presumed to only be observed for heavy elements because of the poor shielding ability of the d electrons in these elements, enhancing the ability of the s electrons to penetrate to the nucleus and therefore be bound tighter than expected.

1F.15 (a) 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. (b) 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. (c) For example, Al^{3+} and Ge^{4+} compounds show the diagonal relationship, as do Li^+ and Mg^{2+}.

1F.17 Only (b) Li and Mg exhibit a diagonal relationship.

1F.19 The ionization energies of the s-block metals are considerably lower, thus making it easier for them to lose electrons in chemical reactions.

1F.21 (a) metal; (b) nonmetal; (c) metal; (d) metalloid; (e) metalloid; (f) metal

1.1 For the Balmer Series $n_1 = 2$, so the fifth line in the spectrum should be $n_2 = 7$. Using the Rydberg equation we get

$$\nu = \Re\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \left(3.29 \times 10^{15}\ \text{s}^{-1}\right)\left(\frac{1}{2^2} - \frac{1}{7^2}\right) = 7.55 \times 10^{14}\ \text{s}^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{2.99792 \times 10^{8}\ \text{m}\cdot\text{s}^{-1}}{7.55 \times 10^{14}\ \text{s}^{-1}} = 3.97 \times 10^{-7}\ \text{m} = 397\ \text{nm}$$

1.3 For light with a wavelength of 633 nm the energy per photon is:

$$\begin{aligned} E &= hc\lambda^{-1} \\ &= (6.626\,08 \times 10^{-34}\ \text{J}\cdot\text{s})\,(2.997\,92 \times 10^{8}\ \text{m}\cdot\text{s}^{-1})\,(633 \times 10^{-9}\ \text{m})^{-1} \\ &= 3.14 \times 10^{-19}\ \text{J}\cdot\text{photon}^{-1}. \end{aligned}$$

The total energy produced is

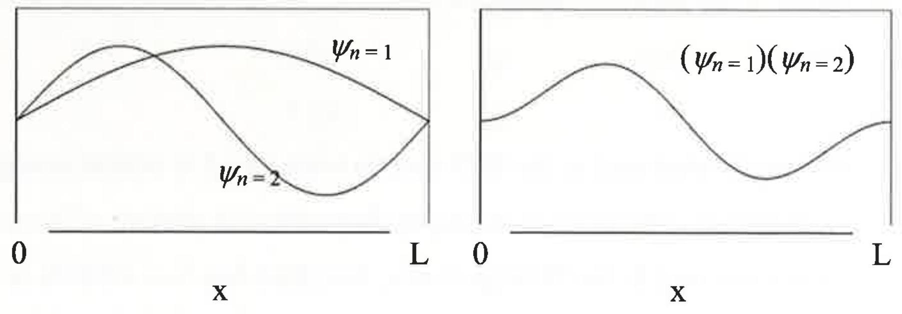
$$(3.14 \times 10^{-19}\ \text{J}\cdot\text{photon}^{-1})\,(2.4 \times 10^{21}\ \text{photons}) = 750\ \text{J}.$$

1.5 (a)

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

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

(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).



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

$$\int_0^L \sin\left(\frac{\pi x}{L}\right)\cdot x\cdot\sin\left(\frac{3\pi x}{L}\right)$$

$$= \frac{L^2}{8\pi^2}\left(\cos\left(\frac{2\pi x}{L}\right) + \frac{2\pi x}{L}\sin\frac{2\pi x}{L}\right) - \frac{L^2}{32\pi^2}\left(\cos\left(\frac{4\pi x}{L}\right) + \frac{4\pi x}{L}\sin\frac{4\pi x}{L}\right)\Bigg|_0^L$$

$$= \frac{L^2}{8\pi^2}(1+0) - \frac{L^2}{32\pi^2}(1+0) - \left[\frac{L^2}{8\pi^2}(1+0) - \frac{L^2}{32\pi^2}(1+0)\right]$$

$$= 0$$

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:

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

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

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

1.9 A $2p_x$ orbital has two lobes, one that has a wavefunction with a positive sign and one with a wavefunction with a negative sign. Thus there is a ½ or 0.50 probability that an electron excited to the $2p_x$-orbital would be found in the region of space for which the wavefunction has a positive sign.

1.11 The peaks observed in the PES spectra correspond to orbital energies; for each energy value seen, a corresponding orbital is present. Thus, if two values are seen in the PES spectrum, that atom has two orbitals (a 1s and a 2s); each PES value observed corresponds to the ejection of *all* electrons from that orbital. The PES value observed is approximately equal to the ionization energy of the first electron to be removed from that orbital; differences that are seen are due to the differences in how the various measurements are made. See Figure 1F.10 and Appendix 2 for the successive ionization energies of the elements.

(a) The observed values

75.7 eV ($7.30\ \text{MJ}\times\text{mol}^{-1}$) and 5.38 eV ($0.519\ \text{MJ}\times\text{mol}^{-1}$) correspond respectively to the second ($7300\ \text{kJ}\cdot\text{mol}^{-1}$) and first ($519\ \text{kJ}\cdot\text{mol}^{-1}$) ionization energies of Li ($1s^2 2s^1$).

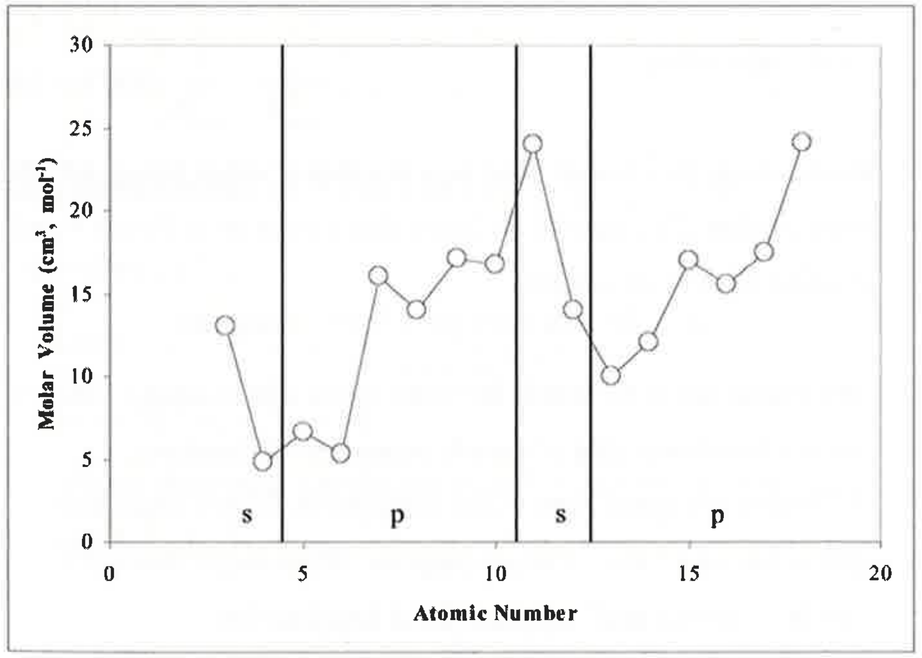
(b) The PES values observed

153 eV ($14.8\ \text{MJ}\cdot\text{mol}^{-1}$) and 9.33 eV ($0.90\ \text{MJ}\cdot\text{mol}^{-1}$) correspond respectively to the third ($14800\ \text{kJ}\cdot\text{mol}^{-1}$) and first ($900\ \text{kJ}\cdot\text{mol}^{-1}$) ionization energies of Be ($1s^2 2s^2$).

1.13 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.

1.15 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	4.38	Al	9.99
C	5.29	Si	12.1
N	16	P	17.0
O	14.0	S	15.3
F	17.1	Cl	21.4
Ne	16.7	Ar	24.1



The molar volume roughly parallels atomic size (volume), which decreases as the s-sublevel begins to fill and subsequently increases 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.

1.17 (a) 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 ½ fill the 3d subshell.

(b) From Appendix 2C, the other elements for which anomalous electron configurations exist are Nb, Mo, Ru, Rh, Pd, Ag, Pt and Au. Of these, the explanation used for chromium and copper is valid for Mo, Pd, Ag and Au.

(c) Because the *n*p orbitals are so much lower in energy than the (*n*+1)s orbitals no elements are known where the (*n*+1)s orbitals fill in preference to the *n*p orbitals.

1.19 Based on (a) the element must be a member of either Group 4/IVB (the titanium family). From (b) we know that it must be in Period 5 and thus the element must be Zirconium.

1.21 By examining at the trends followed by the other Group 1 elements, one can arrive at estimates of various properties of francium:

(a) radius of neutral atom = 285 pm (approx. 20 pm larger than Cs);

(b) radius of +1 ion = 194 pm (approx. 20 pm larger than Cs^+);

(c) IE_1 = 356 kJ·mol^{-1} (approx. 20 kJ less than Cs)

1.23 **<u>A</u>** = Na; **<u>B</u>** = Cl; **<u>C</u>** = Na^+; **<u>D</u>** = Cl^-

The assignments can be made by looking at neutral atom and ionic radii (Figures 1F.4 and 1F.6)

1.25 (a) $1s^4 2s^1$; (b) +1; (c) One would expect the second inert gas in the other universe to still have the 1s, 2s, and 2p levels completely filled. Based on this the electron configuration of the neutral atom should be $1s^4 2s^4 2p^{12}$; therefore it should have $Z = 20$.

1.27 (a) $\lambda = \dfrac{c}{\nu} = \dfrac{2.997\ 92 \times 10^8\ \text{m} \cdot \text{s}^{-1}}{6.27 \times 10^{14}\ \text{s}^{-1}} = 4.78 \times 10^{-7}\ \text{m} = 478\ \text{nm}$

(b) $\nu = \dfrac{c}{\lambda} = \dfrac{2.997\ 92 \times 10^8\ \text{m} \cdot \text{s}^{-1}}{421 \times 10^{-9}\ \text{m}} = 7.12 \times 10^{14}\ \text{s}^{-1}$

1.29 Neon ($Z = 10$) would have to lose a 2p electron to ionize; to accomplish this it would need to be exposed to radiation with sufficient energy to do so. Using the Rydberg equation (with $n_{lower} = 2$ and $n_{upper} = \infty$):

$$\Delta E = Z^2 h\mathfrak{R}\left(\frac{1}{n_{lower}^2} - \frac{1}{n_{upper}^2}\right)$$

$$\Delta E = 10^2(6.626\ 08 \times 10^{-34}\ \text{J} \cdot \text{s})(3.29 \times 10^{15}\ \text{s}^{-1})\left(\frac{1}{2^2} - \frac{1}{\infty^2}\right)$$

$$\Delta E = 5.45 \times 10^{-17}\ \text{J}$$

$$\lambda = hc\Delta E^{-1} = \frac{(6.626\ 08 \times 10^{-34}\ \text{J} \cdot \text{s})(2.997\ 92 \times 10^8\ \text{m} \cdot \text{s}^{-1})}{5.45 \times 10^{-17}\ \text{J}}$$

$$\lambda = 3.64 \times 10^{-9}\ \text{m}\ =\ 3.64\ \text{nm}.$$

The longest detectable wavelength would be 3.64 nm, which is in the x-ray region.

1.31 (a) An electron can be driven out of a metal only if a photon possessing a minimum energy equal to that of the work function for that metal strikes it. Here, to eject the electron from lithium we need

$E_{work\ function} = (2.93\ \text{eV})\ (1.602\ 18 \times 10^{-19}\ \text{J} \cdot \text{eV}^{-1}) = 4.69 \times 10^{-19}\ \text{J}.$

For the ruby-red laser (694 nm):

$$\begin{aligned} E_{694} &= hc\lambda^{-1} \\ &= (6.626\ 08 \times 10^{-34}\ \text{J}\cdot\text{s})(2.997\ 92 \times 10^{8}\ \text{m}\cdot\text{s}^{-1})(694 \times 10^{-9}\ \text{m})^{-1} \\ &= 2.86 \times 10^{-19}\ \text{J}. \end{aligned}$$

For the violet GaN laser (405 nm):

$$\begin{aligned} E_{405} &= hc\lambda^{-1} \\ &= (6.626\ 08 \times 10^{-34}\ \text{J}\cdot\text{s})(2.997\ 92 \times 10^{8}\ \text{m}\cdot\text{s}^{-1})(405 \times 10^{-9}\ \text{m})^{-1} \\ &= 4.90 \times 10^{-19}\ \text{J}. \end{aligned}$$

The violet GaN laser will provide enough energy to eject the electron.

(b) The kinetic energy (E_K) of the ejected electron can be determined by subtracting the work function from the energy supplied by the laser:

$$\begin{aligned} E_K &= hc\lambda^{-1} - E_{work\ function} \\ &= (4.90 \times 10^{-19}\ \text{J}) - (4.69 \times 10^{-19}\ \text{J}) \\ &= 2.10 \times 10^{-20}\ \text{J}. \end{aligned}$$

1.33 The allowed energies of a particle of mass m in a one-dimensional box of length L are determined using $E_n = \dfrac{n^2h^2}{8mL^2}$.

(a) if $L = 139\ \text{pm} = 1.39 \times 10^{-10}$ m for a C – C bond, and $m_e = 9.109 \times 10^{-31}$ kg, then

$$\Delta E = \frac{(6.626\ 08 \times 10^{-34}\ \text{J}\cdot\text{s})^2}{8(9.109 \times 10^{-31}\ \text{kg})(1.39 \times 10^{-10}\ \text{m})^2}(2^2 - 1^2)$$

$$= 9.35 \times 10^{-18}\ \text{J}$$

(b) This energy corresponds to a wavelength of 2.13×10^{-8} m or 21.3 nm. This falls within the x-ray region.

(c) If the chain is 10 carbons long, then there would be nine C – C bonds. If a wavefunction extends over two adjacent carbon atoms then the minimum number of wavefunctions would be nine.

(d) For the chain of 10 carbons long, the $L = 1251\ \text{pm} = 1.251 \times 10^{-9}$ m (the length of nine C – C bonds). For the $n = 5$ to $n = 6$ transition, we get:

$$\Delta E = \frac{(6.626\ 08 \times 10^{-34}\ \text{J}\cdot\text{s})^2}{8(9.109 \times 10^{-31}\ \text{kg})(1.251 \times 10^{-9}\ \text{m})^2}(6^2 - 5^2)$$

$$= 4.25 \times 10^{-19}\ \text{J}$$

(e) This energy corresponds to a wavelength of 4.69×10^{-7} m or 469 nm. This falls within the visible region.

(f) A wavelength of 696 nm corresponds to an energy of 2.85×10^{-19} J being required for the promotion of an electron from the $n = 6$ to $n = 7$ level. Rearranging the equation from part (a) to solve for L we get

$$L^2 = \frac{h^2}{8m_e\Delta E}(n_2^2 - n_1^2) = \frac{(6.626\ 08 \times 10^{-34}\ \text{J}\cdot\text{s})^2}{8(9.109 \times 10^{-31}\ \text{kg})(2.85 \times 10^{-19}\ \text{J})}(7^2 - 6^2)$$

$$= 2.75 \times 10^{-18}\ \text{m}^2$$

This will give $L = 1.658 \times 10^{-9}\ \text{m} = 1658$ pm. Since each C – C bond is 139 pm long, this length corresponds to the chain of carbon atoms having 12 C – C.