FOCUS 1

ATOMS

1A.2 In an evacuated tube, we expect these particles to be electrons from the metal cathode. In that case, the ratio of charge to mass is

$$\frac{Q}{m} = \frac{-1.602\ 18 \times 10^{-19}\text{C}}{9.109\ 39 \times 10^{-31}\text{kg}} = -1.759 \times 10^{11}\text{C} \cdot \text{kg}^{-1}.$$ Since this ratio for an electron is much larger than the one given for the canal rays in this helium-filled tube, we can reason that these particles are about 10,000 times as massive as an electron. It turns out that He^+ has the right mass:

$$\frac{Q}{m} = \frac{1.602\ 18 \times 10^{-19}\text{C}}{(4.00)(1.660\ 54 \times 10^{-27}\text{kg})} = 2.41 \times 10^{7}\text{C} \cdot \text{kg}^{-1}$$

1A.4 All of these can be determined using $\nu\lambda = c$.

(a) False. The speed of EMR is constant. (b) False. Blue light has a wavelength of 470 nm, green light a wavelength of 530 nm; the wavelength is increasing. (c) False. Since $\nu\lambda = c$ for all EMR, $\lambda_{IR}\nu_{IR} = \lambda_{radio}\nu_{radio}$. Therefore,

$$\frac{\nu_{IR}}{\nu_{radio}} = \frac{\lambda_{radio}}{\lambda_{IR}} = \frac{1.0 \times 10^{6}\text{ nm}}{1.0 \times 10^{3}\text{ nm}};$$ this means $\nu_{IR} = 1000\ \nu_{radio}$, not half.

(d) False. Same reasoning as for (c).

1A.6 radio waves < infrared radiation < visible light < ultraviolet radiation

1A.8 $1\text{ MHz} = 1 \times 10^{6}\text{ Hz} = 1 \times 10^{6}\text{ s}^{-1}$.

(a) $\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8}\text{m} \cdot \text{s}^{-1}}{99.3 \times 10^{6}\text{ s}^{-1}} = 3.0\text{ m}$

(b) $\lambda = \dfrac{c}{\nu} = \dfrac{2.998 \times 10^{8}\,\text{m}\cdot\text{s}^{-1}}{1420 \times 10^{6}\,\text{s}^{-1}} = 0.211\ \text{m} = 211\ \text{mm}$

1A.10 All of these can be determined using $E = h\nu$ and $\nu\lambda = c$. For example: in the first entry, energy is given, so:

$$\nu = \frac{E}{h} = \frac{2.7\times10^{-19}J}{6.626\times10^{-34}J\cdot s} = 4.1\times10^{14}s^{-1} = 4.1\times10^{14}Hz$$

$$and;\ \lambda = \frac{c}{\nu} = \frac{2.998\times10^{8}m\cdot s^{-1}}{4.1\times10^{14}s^{-1}} = 7.4\times10^{-7}m = 740nm$$

Frequency	**Wavelength**	**Energy of photon**	**Event**
4.1×10^{14} Hz	740 nm	2.7×10^{-19} J	Traffic light
3.00×10^{14} Hz	999 nm	1.99×10^{-19} J	IR heated food
5×10^{19} Hz	6 pm	3×10^{-14} J	Cosmic ray
1.93×10^{8} Hz	155 cm	1.28×10^{-25} J	Listen to radio

1A.12 Given that $\Delta E \propto \left(\dfrac{1}{n_2^2} - \dfrac{1}{n_1^2}\right)$, this quantity will be (a) 0.012 for $n = 6$ to $n = 5$, (b) 0.049 for $n = 4$ to $n = 3$, and (c) 0.75 for $n = 2$ to $n = 1$. Therefore (c) will have the most energy.

1A.14 (a) The Rydberg equation gives ν when $\Re = 3.29 \times 10^{15}\ \text{s}^{-1}$, from which one can calculate λ from the relationship $c = \nu\lambda$.

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

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

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

$$2.997\,92 \times 10^{8}\ \text{m}\cdot\text{s}^{-1} = (3.29 \times 10^{15}\ \text{s}^{-1})\left(\frac{1}{1} - \frac{1}{9}\right)\lambda$$

$$\lambda = 1.03 \times 10^{-7}\ \text{m} = 103\ \text{nm}$$

(b) Lyman series

(c) This absorption lies in the ultraviolet region.

1A.16 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*:

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

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

$$6.91 \times 10^{14}\ \text{s}^{-1} = (3.29 \times 10^{15}\ \text{s}^{-1})\left(\frac{1}{2^2} - \frac{1}{n_1^2}\right)$$

$$0.210 = 0.250 - \frac{1}{n_1^2}$$

$$\frac{1}{n_1^2} = 0.04$$

$$n_1^2 = \frac{1}{0.04}$$

$$n_1 = 5$$

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

1A.18 Here we are searching for a transition of He^+ whose frequency matches that of the *n* = 2 to *n* = 1 transition of H. The frequency of the H transition:

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

A transition of the He^+ ion with the same frequency is the *n* = 2 to *n* = 4 transition:

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

1B.2 (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.

1B.4 Electron diffraction (b) best supports the idea that particles have wave properties. Diffraction was thought to be purely a wave property; however electrons also exhibit diffraction when reflected from a crystal.

1B.6 From $c = \nu\lambda$ and $E = h\nu$, $E = hc\lambda^{-1}$.

$$E\text{ (for one atom)} = \frac{(6.626\,08\times10^{-34}\text{ J}\cdot\text{s})(2.997\,92\times10^{8}\text{ m}\cdot\text{s}^{-1})}{865\times10^{-9}\text{ m}}$$

$$= 2.30\times10^{-19}\text{ J}\cdot\text{atom}^{-1}$$

$$E\text{ (for 1.00 mol)} = (6.022\times10^{23}\text{ atoms}\cdot\text{mol}^{-1})(2.30\times10^{-19}\text{ J}\cdot\text{atom}^{-1})$$

$$= 1.38\times10^{5}\text{ J}\cdot\text{mol}^{-1}\text{ or }138\text{ kJ}\cdot\text{mol}^{-1}$$

1B.8 (a) $E = h\nu$

$$= (6.626\,08\times10^{-34}\text{ J}\cdot\text{s})(1.2\times10^{17}\text{ s}^{-1})$$

$$= 8.0\times10^{-17}\text{ J}$$

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

$$E = (2.00\text{ mol})(6.022\times10^{23}\text{ atoms}\cdot\text{mol}^{-1})$$

$$\times(6.626\,08\times10^{-34}\text{ J}\cdot\text{s})(1.2\times10^{17}\text{ s}^{-1})$$

$$= 9.6\times10^{7}\text{ J or }9.6\times10^{4}\text{ kJ}$$

(c) $$E = \left(\frac{2.00\text{ g Cu}}{63.54\text{ g}\cdot\text{mol}^{-1}}\right)$$

$$\times(6.022\times10^{23}\text{ atoms}\cdot\text{mol}^{-1})(8.0\times10^{-17}\text{ J}\cdot\text{atom}^{-1})$$

$$= 1.5\times10^{6}\text{ J or }1.5\times10^{3}\text{ kJ}$$

1B.10 40 W = 40 J·sec^{-1}, so in 2 seconds 80 J will be emitted.

For blue light $(\lambda = 470\text{ nm} = 470\times10^{-9}\text{ m})$ the energy per photon is:

$$\begin{aligned}E &= hc\lambda^{-1}\\ &= \left(6.626\ 08\times10^{-34}\,\mathrm{J\cdot s}\right)\left(2.997\ 92\times10^{8}\,\mathrm{m\cdot s^{-1}}\right)\left(470\times10^{-9}\,\mathrm{m}\right)^{-1}\\ &= 4.2\times10^{-19}\,\mathrm{J\cdot photons^{-1}}\end{aligned}$$

$$\begin{aligned}\text{number of photons} &= (80.\ \mathrm{J})\,(4.7\times10^{-19}\ \mathrm{J\cdot photon^{-1}})^{-1}\\ &= 1.7\times10^{20}\ \text{photons}\\ \text{moles of photons} &= (1.7\times10^{20}\ \text{photons})\,(6.022\times10^{23}\ \mathrm{mol\cdot photons^{-1}})^{-1}\\ &= 2.8\times10^{-4}\ \text{mol photons}\end{aligned}$$

1B.12 From Wien's law: $T\lambda_{\max} = 2.88\times10^{-3}\ \mathrm{K\cdot m}$.

$$\lambda_{\max} = \frac{2.88\times10^{-3}\ \mathrm{K\cdot m}}{2.3\times10^{4}\ \mathrm{K}}$$

$$\lambda_{\max} = 1.3\times10^{-7}\ \mathrm{m} = 130\ \mathrm{nm}.$$

1B.14 From Wien's law: $T\lambda_{\max} = 2.88\times10^{-3}\ \mathrm{K\cdot m}$.

$$(T)(632\times10^{-9}\ \mathrm{m}) = 2.88\times10^{-3}\ \mathrm{K\cdot m}$$

$$T \approx 4.56\times10^{3}\ \mathrm{K}$$

1B.16 The wavelength of radiation needed will be the sum of the energy of the work function plus the kinetic energy of the ejected electron.

$$E_{\text{work function}} = (4.37\ \mathrm{eV})(1.6022\times10^{-19}\ \mathrm{J\cdot eV^{-1}}) = 7.00\times10^{-19}\ \mathrm{J}$$

$$\begin{aligned}E_{\text{kinetic}} &= \frac{1}{2}mv^{2}\\ &= \frac{1}{2}(9.10939\times10^{-31}\ \mathrm{kg})(1.5\times10^{6}\ \mathrm{m\cdot s^{-1}})^{2}\\ &= 1.02\times10^{-18}\ \mathrm{J}\\ E_{\text{total}} &= E_{\text{work function}} + E_{\text{kinetic}}\\ &= 7.00\times10^{-19}\ \mathrm{J} + 1.02\times10^{-18}\ \mathrm{J}\\ &= 1.72\times10^{-18}\ \mathrm{J}\end{aligned}$$

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

$$\begin{aligned}\lambda &= \frac{hc}{E}\\ &= \frac{(6.626\times10^{-34}\ \mathrm{J\cdot s})(3.00\times10^{8}\ \mathrm{m\cdot s^{-1}})}{1.72\times10^{-18}\ \mathrm{J}}\\ &= 1.16\times10^{-7}\ \mathrm{m\ or\ 116\ nm}\end{aligned}$$

1B.18 (a) Mass of one hydrogen atom:

$$1.008\ \mathrm{g\cdot mol^{-1}}\left(\frac{1\ \mathrm{mol}}{6.022\times10^{23}\ \mathrm{atoms}}\right)\left(\frac{1\times10^{-3}\ \mathrm{kg}}{1\ \mathrm{g}}\right) = 1.674\times10^{-27}\ \mathrm{kg}$$

Using the de Broglie relationship, we get

$$\begin{aligned}\lambda &= h(mv)^{-1}\\ &= (6.626\,08\times10^{-34}\ \mathrm{kg\cdot m^2\cdot s^{-1}})[(1.675\times10^{-27}\ \mathrm{kg})(10.\ \mathrm{m\cdot s^{-1}})]^{-1}\\ &= 4.0\times10^{-8}\ \mathrm{m} = 40.\ \mathrm{nm}.\end{aligned}$$

(b) Since $\lambda \propto$ speed, decreasing the speed should cause the wavelength to decrease.

1B.20 Let x = wavelength; then $v = x\ \mathrm{m\cdot s^{-1}}$. Now use the de Broglie relationship:

$$\begin{aligned}\lambda = x &= h(m_e v)^{-1}\\ &= (6.626\,08\times10^{-34}\ \mathrm{kg\cdot m^2\cdot s^{-1}})[(9.1094\times10^{-31}\ \mathrm{kg})(x\ \mathrm{m\cdot s^{-1}})]^{-1}\end{aligned}$$

$$x^2 = 7.27\times10^{-4}\ \mathrm{m^2}$$

$$x = 2.70\times10^{-2}\ \mathrm{m} = 2.70\ \mathrm{cm}.$$

1B.22 Use the de Broglie relationship, $\lambda = hp^{-1} = h(mv)^{-1}$.

$$(175\ \mathrm{km\cdot h^{-1}})(1000\ \mathrm{m/km})(1\ \mathrm{h}/3600\ \mathrm{s}) = 48.6\ \mathrm{m\cdot s^{-1}}$$

$$\begin{aligned}\lambda &= h(mv)^{-1}\\ &= (6.626\,08\times10^{-34}\ \mathrm{kg\cdot m^2\cdot s^{-1}})[(1531\ \mathrm{kg})(48.6\ \mathrm{m\cdot s^{-1}})]^{-1}\\ &= 8.90\times10^{-39}\ \mathrm{m}\end{aligned}$$

1B.24 The mass of one He atom is given by the molar mass of He divided by Avogadro's constant:

$$\text{mass of He atom} = \frac{4.00\ \text{g}\cdot\text{mol}^{-1}}{6.022\times10^{23}\ \text{atoms}\cdot\text{mol}^{-1}}$$
$$= 6.64\times10^{-24}\ \text{g or } 6.64\times10^{-27}\ \text{kg}$$

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

$$\lambda = h(mv)^{-1}$$
$$= \frac{6.626\,08\times10^{-34}\ \text{J}\cdot\text{s}}{(6.64\times10^{-27}\ \text{kg})(1230\ \text{m}\cdot\text{s}^{-1})}$$
$$= \frac{6.626\,08\times10^{-34}\ \text{kg}\cdot\text{m}^2\cdot\text{s}^{-1}}{(6.64\times10^{-27}\ \text{kg})(1230\ \text{m}\cdot\text{s}^{-1})}$$
$$= 8.11\times10^{-11}\ \text{m}$$

1B.26 The uncertainty principle states that $\Delta p\Delta x = \frac{1}{2}\hbar$; so for a hydrogen, $\Delta p = m_H\Delta v$, then $m_H\Delta v\Delta x = \frac{1}{2}\hbar$ and $\Delta x = \frac{1}{2}\frac{\hbar}{m_H\Delta v}$; if we assume that the uncertainty in the velocity of the hydrogen atom is $\Delta v = 5.0\ \text{m}\cdot\text{s}^{-1}$, knowing that the mass of a hydrogen atom is

$$m_H = 1.0079\ \text{g}\cdot\text{mol}^{-1}\times\frac{1\ \text{mol}}{6.022\times10^{23}\ \text{atoms}}\times\frac{1\ \text{kg}}{1000\ \text{g}} = 1.6737\times10^{-27}\ \text{kg},$$

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

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

Then

$$\Delta x = \frac{1}{2}\left(\frac{1.054\ 457\times10^{-34}\,\text{kg}\cdot\text{m}^2\cdot\text{s}^{-1}}{(1.67\ 37\times10^{-27}\,\text{kg})(5.0\ \text{m}\cdot\text{s}^{-1})}\right)$$
$$\Delta x = 6.3\times10^{-9}\,\text{m} = 6.3\ \text{nm}.$$

1B.28 The uncertainty principle states that $m\Delta v\Delta x = \frac{1}{2}\hbar$; so, $\Delta v = \frac{1}{2}\frac{\hbar}{m\Delta x}$.

(a) For an electron confined in a nanoparticle of diameter 2.00×10^2 nm:

$$\Delta v = \frac{1}{2}\frac{\hbar}{m_e\Delta x} = \frac{1}{2}\left(\frac{1.054\ 457 \times 10^{-34}\,\text{kg}\cdot\text{m}^2\cdot\text{s}^{-1}}{(9.1094 \times 10^{-31}\,\text{kg})(2.00 \times 10^{-7}\ \text{m})}\right)$$
$$= 289\ \text{m}\cdot\text{s}^{-1}$$

(b) For a Li^+ ion confined to the same nanoparticle:

$$m_{Li^+} = 6.94\ \text{g}\cdot\text{mol}^{-1} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{atoms}} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 1.15 \times 10^{-26}\ \text{kg}$$

$$\Delta v = \frac{1}{2}\frac{\hbar}{m_e\Delta x} = \frac{1}{2}\left(\frac{1.054\ 457 \times 10^{-34}\,\text{kg}\cdot\text{m}^2\cdot\text{s}^{-1}}{(1.15 \times 10^{-26}\,\text{kg})(2.00 \times 10^{-7}\ \text{m})}\right)$$
$$= 0.0229\ \text{m}\cdot\text{s}^{-1}$$

(c) Because the Li^+ ion has a smaller deviation in its speed, it can be defined more accurately.

1C.2 (a) For movement between the energy levels the energy must be determined for each level and then the difference calculated

$$\Delta E = E_4 - E_1 = \frac{4^2h^2}{8mL^2} - \frac{1^2h^2}{8mL^2} = \frac{15h^2}{8mL^2}$$

Then $\lambda_{4,1} = \frac{hc}{E} = \frac{8mhcL^2}{15h^2} = \frac{8mcL^2}{15h}$

For an electron in a 100.–pm box, the expression becomes

$$\lambda_{4,1} = \frac{8(9.109\,39 \times 10^{-31}\ \text{kg})\,(2.997\,92 \times 10^8\ \text{m}\cdot\text{s}^{-1})\,(100. \times 10^{-12}\ \text{m})^2}{15(6.626\,08 \times 10^{-34}\ \text{J}\cdot\text{s})}$$
$$= 2.20 \times 10^{-9}\ \text{m} = 2.20\ \text{nm}.$$

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

$$\Delta E = E_4 - E_2 = \frac{4^2h^2}{8mL^2} - \frac{2^2h^2}{8mL^2} = \frac{12h^2}{8mL^2}$$

$$\lambda_{4,2} = \frac{hc}{E} = \frac{8mhcL^2}{12h^2} = \frac{2mcL^2}{3h}$$

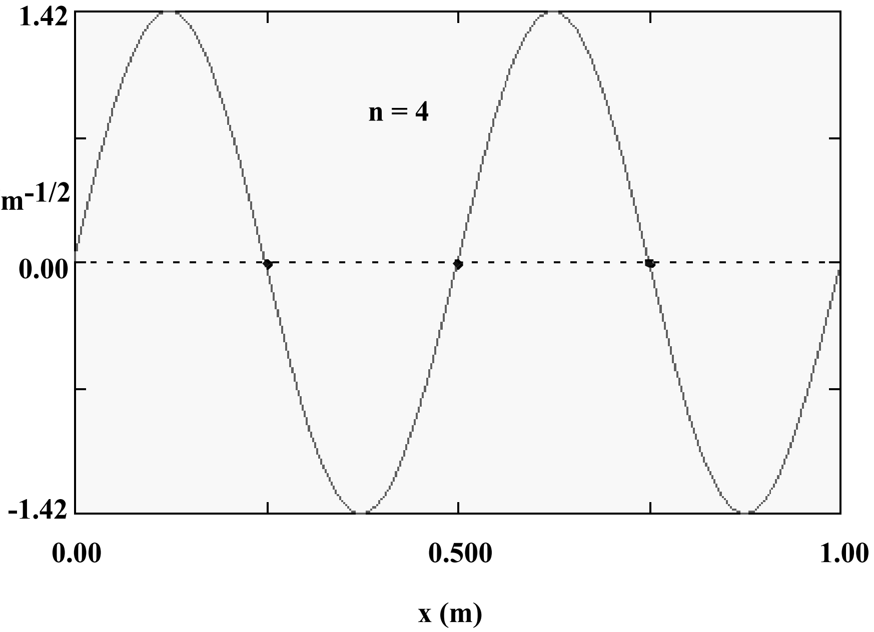
For an electron in a 100.–pm box, the expression becomes

$$\lambda_{4,1} = \frac{2(9.109\,39\times10^{-31}\ \text{kg})\,(2.997\,92\times10^{8}\ \text{m}\cdot\text{s}^{-1})\,(100.\times10^{-12}\ \text{m})^2}{3(6.626\,08\times10^{-34}\ \text{J}\cdot\text{s})}$$

$$= 2.75\times10^{-9}\ \text{m} = 2.75\ \text{nm}.$$

1C.4 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.

1C.6 When $n = 4$, three nodes are seen (marked with a •):



1C.8 The observed line is the third lowest energy line.

The frequency of the given line is:

$$\nu = \frac{c}{\lambda} = \frac{2.9979\times10^{8}\ \text{m s}^{-1}}{5910\times10^{-9}\ \text{m}} = 5.073\times10^{13}\ \text{s}^{-1}$$

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

$$\nu = \Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = 3.29\times10^{15}\ \text{Hz}\left(\frac{1}{6^2} - \frac{1}{9^2}\right) = 5.08\times10^{13}\ \text{Hz}$$

1D.2 (a) Energy will remain the same; energy is a function of *n*. (b) *n* remains the same (from $n = 2$). (c) *l* increases (from $l = 0$ for *s* to $l = 1$ for *p*).
(d) Radius remains the same (radius is a function of *n*).

1D.4 The equation demonstrated in Example 1D.1 can be used:

$$\frac{\psi^2\,(r = 0.83a_0,\theta,\phi)}{\psi^2(0,\theta,\phi)} = \frac{\dfrac{e^{-2(0.83a_0)/a_0}}{\pi a_0^3}}{\left(\dfrac{1}{\pi a_0^3}\right)} = 0.19$$

1D.6 The radial probability distribution may be found by integrating the full wavefunction, $\psi(r,\theta,\phi)$, over all possible values of θ and ϕ. Since s-orbitals are spherically symmetric and are not a function of θ or ϕ, integration of any s-orbital over all θ and ϕ always gives the same result:

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

$$= \psi(r)^2\left[\int_0^{2\pi} 2\ d\phi\right] = \psi(r)^2(4\pi)$$

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 $(4\pi)\ \psi(r)^2 r^2$.

1D.8 (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*:

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

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

The nontrivial solution to this equation is found when:

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

Dividing both sides by r^5:

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

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

(b) The plot of the radial distribution function for the first three s-orbitals of hydrogen is given in Figure 1D.5. We can qualitatively estimate the radius using this plot by looking at the radius with the greatest probability density. This would give an approximate value of $13a_0$. A more advanced approach would be to solve this problem similarly to part (a) of this question. The radial wavefunction for the 3s-orbital is:

$$R_{3s} = C\left(\frac{3}{a_0^{3/2}} - \frac{2}{a_0^{5/2}}r + \frac{2}{9\cdot a_0^{7/2}}r^2\right)e^{-\frac{r}{3a_o}}$$

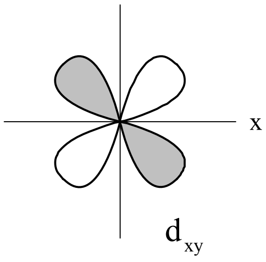
where $C = \dfrac{2}{9\sqrt{3}}$

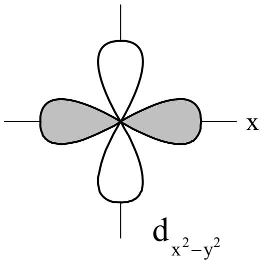
The derivative of the radial probability distribution, $P = r^2 R_{3s}^2$, with respect to r is:

$$\frac{dP}{dr} = C^2 e^{-\frac{2r}{3a_o}}\left[\frac{9}{a_0^3}r^2 + \frac{12}{a_0^4}r^3 + \frac{48}{9\cdot a_0^5}r^4 + \frac{8}{9\cdot a_0^6}r^5 + \frac{4}{81\cdot a_0^7}r^6\right]$$

The nontrivial 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 plotting the solution.

1D.10 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.





1D.12 (a) 6: $l = 0, 1, 2, 3, 4, 5$; (b) 6s, 6p, 6d, 6f, 6g, 6h; (c) 1 + 3 + 5 + 7 + 9 + 11 = 36 orbitals

1D.14 (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

1D.16 (a) $n = 3$; $l = 0$; (b) $n = 4$; $l = 1$; (c) $n = 5$; $l = 2$; (d) $n = 6$; $l = 3$

1D.18 (a) 0; (b) −1, 0, 1 (c) −2, −1, 0, 1, 2; (d) −3, −2, −1, 0, 1, 2, 3;

1D.20 (a) 1; (b) 3; (c) 5; (d) 7

1D.22 (a) 4p, 3; (b) 5*s*, 1; (c) 6d, 5; (d) 7f, 7

1D.24 (a) 3; (b) 1; (c) 1; (d) 49

1D.26 (a) cannot exist; (b) exists; (c) exists; (d) exists

1E.2 (a) Energy increases (p orbital is higher in energy than an s in Li); (b) n remains the same; (c) l increases; (d) radius increases. Both (a) and (d) are different from Exercise 1D.2 because of shielding effects of the added electrons, causing Z_{eff} for Li to be smaller than Z; as a result the p-electrons are not held as tightly as the s-electrons, which leads to a larger radius and higher energy for the p-electron.

1E.4 (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

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

where $-e$ is the charge on the electron and $+4e$ is the charge on the nucleus, ε_0 is the vacuum permittivity, and r is the distance from the electron to the nucleus. There will be six repulsive terms between the four electrons of the form:

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

The total potential will be:

$$-\frac{e^2}{\pi\varepsilon_0 r_1}-\frac{e^2}{\pi\varepsilon_0 r_2}-\frac{e^2}{\pi\varepsilon_0 r_3}-\frac{e^2}{\pi\varepsilon_0 r_4}+\frac{e^2}{4\pi\varepsilon_0 r_{12}}+\frac{e^2}{4\pi\varepsilon_0 r_{13}}+\frac{e^2}{4\pi\varepsilon_0 r_{14}}+\frac{e^2}{4\pi\varepsilon_0 r_{23}}+\frac{e^2}{4\pi\varepsilon_0 r_{24}}+\frac{e^2}{4\pi\varepsilon_0 r_{34}}$$
$$=-\frac{e^2}{\pi\varepsilon_0}\left(\frac{1}{r_1}+\frac{1}{r_2}+\frac{1}{r_3}+\frac{1}{r_4}-\frac{1}{4r_{12}}-\frac{1}{4r_{13}}-\frac{1}{4r_{14}}-\frac{1}{4r_{23}}-\frac{1}{4r_{24}}-\frac{1}{4r_{34}}\right)$$

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 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:

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

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

$$n+\sum_{1\to n}(n-1)$$

The point of this exercise is to show that each added electron, increases the number of *e*-*e* repulsive terms.

1E.6 (a) False. The 2s-electrons will be shielded by the electrons in the 1*s*-orbital and will thus have a lower Z_{eff}. (b) False. Because the 2p- orbitals do not penetrate to the nucleus as the 2*s*-orbitals do, they will have a lower Z_{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) to that of 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.

1E.8 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.

1E.10 (a) This configuration is not possible because the maximum value l can have is $n - 1$; because $n = 2$, $l_{\max} = 1$. (b) This configuration is not possible because the maximum value l can have is $n - 1$; because $n = 6$, $l_{\max} = 5$. (c) This configuration is not possible; for $l = 4$, m_l can only be an integer from -4 to $+4$; that is, m_l can only equal 0, ±1, ±2, ±3, or ±4.

1E.12 (a) Titanium: $[\mathrm{Ar}]\, 3d^2 4s^2$

(b) Chromium: $[\mathrm{Ar}]\, 3d^5 4s^1$

(c) Europium: $[\mathrm{Xe}]\, 4f^7 6s^2$

(d) Krypton: $[\mathrm{Ar}]\, 3d^{10} 4s^2 4p^6$

1E.14 (a) Germanium: $[\mathrm{Ar}]\, 3d^{10} 4s^2 4p^2$

(b) Cesium: $[\mathrm{Xe}]\, 6s^1$

(c) Iridium: $[\mathrm{Xe}]\, 4f^{14} 5d^7 6s^2$

(d) Tellurium: $[\mathrm{Kr}]\, 4d^{10} 5s^2 5p^4$

(e) Thallium: $[\mathrm{Xe}]\, 4f^{14} 5d^{10} 6s^2 6p^1$

(f) Plutonium: $[\mathrm{Rn}]\, 5f^6 7s^2$

1E.16 (a) Ga; (b) Na; (c) Sr; (d) Eu

1E.18 (a) 4s; (b) 3p; (c) 3p; (d) 4s

1E.20 (a) 19; (b) 7; (c) 16; (d) 27

1E.22 (a) 2; (b) 3; (c) 1; (d) 0

1E.24

Element	***Electron configuration***	***Unpaired electrons***
N	[He] $2s^2 2p^3$	3
P	[Ne] $3s^2 3p^3$	3
As	[Ar] $3d^{10} 4s^2 4p^3$	3
Sb	[Kr] $4d^{10} 5s^2 5p^3$	3
Bi	[Xe] $4f^{14} 5d^{10} 6s^2 6p^3$	3

1E.26 (a) ns^2np^5; (b) ns^2np^4; (c) $(n-1)d^3ns^2$; (d) ns^2np^2

1F.2 (a) I > Br > Cl; (b) Ga >As > Se; (c) K > Ca > Zn;
(d) Ba > Sr > Ca.

1F.4 (a) In^{3+}; (b) P^{3-}; (c) Pb^{2+}; (d) Ba^{2+}; (e) As^{3-}; (f) Sn^{2+}

1F.6 (a) Ca (b) Mg; (c) Al

1F.8 (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 takes on 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.

1F.10 The first ionization energy for chlorine is much greater than that of sulfur due to the Z_{eff} of Cl being greater than that of S; as a result, the valence electrons are held tighter, and shielding effects here due to *e-e* repulsions have a minimal effect on electron energies. Based solely on Z_{eff} we would expect chlorine to have a much higher second ionization energy than sulfur; however, S and Cl have nearly the same value. This can be explained by the orbital box diagrams for the two ions:

$$S^+ : \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow} \qquad Cl^+ : \boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$$

Here, spin pairing causes the electron in Cl^+ already to be at a higher energy than expected and results in the energy required to remove it to be lower than expected, bringing it down to nearly the same as that required to remove the second electron from S^+.

1F.12 (a) selenium; (b) carbon; (c) arsenic

1F.14 (a) Sb^{3+}, Sb^{5+}; (c) Tl^+, Tl^{3+}; (b) and (d) only form one positive ion each.

1F.16 From Appendix 2D, the radii (in picometers) are

Ge	123	Sb	182
Ge^{2+}	90	Sb^{3+}	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.

1F.18 (b) As and Sn do not exhibit a diagonal relationship. Note: (a) Be and Al as well as Ga and Sn exhibit diagonal relationships. Because diagonal relationships often are a result of similarities in ionic radii, they can persist across the s and p blocks.

1F.20 (c) hafnium, (d) niobium, and (e) cadmium are transition metals.

1F.22 (a) metal; (b) nonmetal; (c) metalloid; (d) metalloid;
(e) nonmetal; (f) metalloid

1.2 (a) We would expect to see the excited electron in the hydrogen atom fall from the $n_1 = 5$ level to each of levels below it: $n_2 = 4,\ 3,\ 2,$ and 1; therefore, we would expect to see four lines in its atomic spectrum.

(b) The range of wavelengths should span from $n_1 = 5,\ n_2 = 4$ to $n_1 = 5,\ n_2 = 1$. Thus:

$$\nu_{5,4} = \Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = 3.29 \times 10^{15}\ \text{Hz}\left(\frac{1}{4^2} - \frac{1}{5^2}\right) = 7.40 \times 10^{13}\ \text{Hz}$$

$$\lambda_{5,4} = \frac{c}{\nu_{5,4}} = \frac{2.9979 \times 10^{8}\ \text{m s}^{-1}}{7.40 \times 10^{13}\ \text{m}^{-1}} = 4.05 \times 10^{-6}\ \text{m} = 4050\ \text{nm}.$$

Likewise, for the $n_1 = 5,\ n_2 = 1$ transition, we get

$\nu_{5,1} = 3.16 \times 10^{15}$ Hz and $\lambda_{5,1} = 9.49 \times 10^{-8}$ m = 94.9 nm.

The wavelengths are expected to range from 94.9 nm to 4050 nm.

1.4 If each droplet observed had contained an even number of electrons, the technicians would have reported the charge of an electron to be twice as large as it really is.

1.6 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:

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

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:

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

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

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

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

$$= \frac{2}{L}\left[\left(\frac{-1}{2n\pi} \cdot \cos n\pi \cdot \sin n\pi + \frac{L}{2}\right) - 0\right]$$

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

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

1.8 (a) The smallest increment of charge between droplets will be the charge on one electron, 4.8 x 10^{-10} esu;

(b) $\frac{6.72 \times 10^{-9}\text{esu}}{4.8 \times 10^{-10}\text{esu/electron}} = 14$ electrons

(c) Both are a measure of the charge of an electron and their relationship can be found by:

$(4.8 \times 10^{-10}\text{esu})(\text{relationship}) = 1.602 \times 10^{-19}\text{C}$

relationship = $3.3\text{x}10^{-10}$C/esu

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

1.12 The peaks observed in the PES spectra correspond to orbital energies; for each energy value seen, a corresponding orbital is present. Thus, if three values are seen in the PES spectrum, that atom has three orbitals (a 1s, 2s, and a 2p); 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 reflect 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) Because three PES energies are observed, the elements must have 1s-, 2s-, and 2p- electrons. The observed values:

257eV ($24.8\ \text{MJ}\times\text{mol}^{-1}$), 25.2 eV ($2.43\ \text{MJ}\times\text{mol}^{-1}$), and 8.29 eV ($0.800\ \text{MJ}\times\text{mol}^{-1}$) correspond most closely to the fourth ($25{,}000\ \text{kJ}\cdot\text{mol}^{-1}$), second ($2427\ \text{kJ}\cdot\text{mol}^{-1}$), and first ($799\ \text{kJ}\cdot\text{mol}^{-1}$) ionization energies of B ($1s^2 2s^2 2p^1$). See Figure 1F.10.

(b) The PES values observed:

301 eV ($29.0\ \text{MJ}\times\text{mol}^{-1}$), 47.8 eV ($4.61\ \text{MJ}\times\text{mol}^{-1}$), and 11.4 eV ($1.10\ \text{MJ}\times\text{mol}^{-1}$) correspond most closely to the first ($1090\ \text{kJ}\cdot\text{mol}^{-1}$) and third ($4620\ \text{kJ}\cdot\text{mol}^{-1}$) ionization energies of C ($1\text{s}^2 2\text{s}^2 2\text{p}^2$). The remaining value ($29\ \text{MJ}\cdot\text{mol}^{-1}$) should correspond to the energy necessary to remove an electron from a 1s- orbital in an atom with Z = 6. The fifth

ionization energy for this value is not given in the Appendix, it is consistent with the value of the fourth ionization energy for boron (25,000 $\text{kJ}\cdot\text{mol}^{-1}$). This corresponds to the removal of an electron from a 1s- orbital in an atom with Z = 5, presumably an energy-similar process when compared to carbon.

1.14 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 analog.

1.16 (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, so $E_{\text{total}} = E_{\text{ejection}} + E_{\text{kinetic}}$.

But $E_{\text{total}} = h\nu$ for the photon and $E_{\text{kinetic}} = \left(\frac{1}{2}\right) m\text{v}^2$ 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.

(b) $E_{\text{total}} = h\nu = hc\lambda^{-1}$

$$= (6.62608 \times 10^{-34}\ J\cdot s)(2.99792 \times 10^{8}\ m\cdot s^{-1})(58.4 \times 10^{-9}\ m)^{-1}$$

$$= 3.401 \times 10^{-18}\ J$$

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

$$E_{\text{kinetic}} = \left(\frac{1}{2}mv^2\right) = \left(\frac{1}{2}\right)(9.10939 \times 10^{-28}\ \text{g})(2450\ \text{km}\cdot\text{s}^{-1})^2$$
$$= \left(\frac{1}{2}\right)(9.10939 \times 10^{-31}\ \text{kg})(2.450 \times 10^{6}\ \text{m}\cdot\text{s}^{-1})^2$$
$$= 2.734 \times 10^{-18}\ \text{kg}\cdot\text{m}^2\cdot\text{s}^{-2} = 2.734 \times 10^{-18}\ \text{J}$$

$$3.401 \times 10^{-18}\ \text{J} = E_{\text{ejection}} + 2.734 \times 10^{-18}\ \text{J}$$
$$E_{\text{ejection}} = 6.67 \times 10^{-19}\ \text{J}$$

1.18 Given that $E_n = -\dfrac{h\Re}{n^2} = -\dfrac{2.18 \times 10^{-18}\,\text{J}}{n^2}$ and $\Delta E = E_{\text{final}} - E_{\text{initial}}$:

(a) For an electron to fall from the 4d to 1s level, the energy of the photon is $\Delta E = E_1 - E_4 = -2.18 \times 10^{-18}\ \text{J}\left(\frac{1}{1^2} - \frac{1}{4^2}\right) = -2.04 \times 10^{-18}\ \text{J}$. (The negative sign means that energy is released or emitted). (b) Similarly, an electron moving from the 4d to 2p level will emit a photon of 4.09×10^{-19} J; (c) Same as (b); an electron moving from the 4d to 2s emits the same amount of energy as it would if it were moving to the 2p-orbital. This is due to the fact that all orbitals having the same principal quantum number *n* are degenerate (i.e., they have the same energy). (d) In a hydrogen atom, no photon would be emitted on moving between orbitals possessing the same *n* (due to degeneracy of the 4d and the 4s orbitals in hydrogen). (e) Since potassium has more electrons and protons than hydrogen, the individual orbitals within a given shell will have different energies (arising from the attractions and repulsions of electrons with the nucleus and other electrons in the atom). As a result we expect to see emission lines for all the transitions; thus potassium should show four lines while hydrogen only shows two.

1.20 $\lambda = 1064\ \text{nm} = 1.064 \times 10^{-6}\ \text{m}$; The energy of a photon of this wavelength is

$$E = \frac{hc}{\lambda} = \frac{(6.626\,08 \times 10^{-34}\ \text{J}\cdot\text{s})(2.998 \times 10^{8}\text{m})}{1.064 \times 10^{-6}\text{m}} = 1.867 \times 10^{-19}\,\text{J}\text{; the}$$

energy of the ejected electron is 0.137 eV × (1.602 × 10^{-19} J·eV^{-1}) or 2.195 × 10^{-20} J. The difference between these two values is 1.65 × 10^{-19} J, or 1.65 × 10^{-22} kJ per atom of thulium. Converting this number to electron volts will give the electron affinity of thulium:

$$(1.65\times10^{-19}\ \text{J/atom})(1\ \text{eV}/1.602\times10^{-19}\ \text{J}) = 1.03\ \text{eV/atom}$$

We can also give the electron affinity in kJ/mol by multiplying 1.65 × 10^{-22} kJ/atom by Avogadro's number to give 99.4 kJ/mol.

1.22 **A** = Mg; **B** = O; **C** = Mg^{+2}; **D** = O^{-2}. The assignments can be made by looking at neutral atom and ionic radii (Figures 1F.4 and 1F.6).

1.24 The radial distribution of a 3s orbital is given by curve (b), while curve (a) shows the same for a 3p orbital; this can be determined by examining the electron density near the origin (which is the nucleus); the plot with the most electron density closest to (0, 0) arises from the *s* orbital.

1.26 If there were an additional p-orbital for a given shell then the amount of electrons to fill that shell would increase from 8 in our world to 10 in this four-dimensional world. (a) The periodic table would increase in length by the addition of 2 groups (columns). This would shift what were s-block metals in period 3 to the last two groups in period 2. All of which would shift all the elements in period 3 over by 2, and the first four elements in period 4 would shift to period 3. (b) The first two noble gases in this four-dimensional world would have atomic numbers of 2 (helium) and 12 (magnesium).

1.28 (a) $\lambda = \dfrac{c}{\nu} = \dfrac{2.99792\times10^{8}\ \text{m}\cdot\text{s}^{-1}}{7.83\times10^{14}\ \text{s}^{-1}} = 3.83\times10^{-7}\ \text{m} = 383\ \text{nm}$

(b) $\nu = \dfrac{c}{\lambda} = \dfrac{2.99792\times10^{8}\ \text{m}\cdot\text{s}^{-1}}{452\times10^{-9}\ \text{m}} = 6.63\times10^{14}\ \text{s}^{-1}$

1.30 Use $\Delta E = hc\lambda^{-1}$ to determine the change in energy for each wavelength; this will be the change in energy per barium atom. So for 487 nm:

$$\Delta E_{487} = \frac{(6.626\,08 \times 10^{-34}\ \text{J}\cdot\text{s})(2.997\,92 \times 10^{8}\ \text{m}\cdot\text{s}^{-1})}{487 \times 10^{-9}\ \text{m}}$$
$$= 4.08 \times 10^{-19}\ \text{J}\cdot\text{Ba atom}^{-1}$$

(a) To calculate the energy in electronvolts per Ba atom we must take the change in energy and divide it by 1.602×10^{-19} J/eV:

$$\Delta E_{487} = (4.08 \times 10^{-19}\ \text{J}\cdot\text{Ba atom}^{-1})(1\ \text{eV}/1.602\ \times 10^{-19}\ \text{J})$$
$$= 2.55\ \text{eV}\cdot\text{Ba atom}^{-1}$$

Similarly, we obtain the following values for the other wavelengths:

$\Delta E_{524} = 2.37\ \text{eV}\cdot\text{Ba atom}^{-1}$

$\Delta E_{543} = 2.28\ \text{eV}\cdot\text{Ba atom}^{-1}$

$\Delta E_{553} = 2.24\ \text{eV}\cdot\text{Ba atom}^{-1}$

$\Delta E_{578} = 2.15\ \text{eV}\cdot\text{Ba atom}^{-1}$.

(b) To calculate the energy per mole we must multiply the change in by Avogadro's number:

$$\Delta E_{487} = (6.022 \times 10^{23}\ \text{Ba atoms}\cdot\text{mol}^{-1})(4.08 \times 10^{-19}\ \text{J}\cdot\text{Ba atom}^{-1})$$
$$= 2.46 \times 10^{5}\ \text{J}\cdot\text{mol}^{-1}\ \text{or}\ 246\ \text{kJ}\cdot\text{mol}^{-1}$$

Similarly, we obtain the following values for the other wavelengths:

$\Delta E_{524} = 228\ \text{kJ}\cdot\text{mol}^{-1}$

$\Delta E_{543} = 220\ \text{kJ}\cdot\text{mol}^{-1}$

$\Delta E_{553} = 216\ \text{kJ}\cdot\text{mol}^{-1}$

$\Delta E_{578} = 207\ \text{kJ}\cdot\text{mol}^{-1}$.

1.32 (a) Using the Rydberg equation where $n_1 = 2$ and $n_2 = 100$:

$$\nu = \Re\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \left(3.29 \times 10^{15}\ \text{s}^{-1}\right)\left(\frac{1}{2^2} - \frac{1}{100^2}\right) = 8.22 \times 10^{14}\ \text{s}^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{2.99792 \times 10^{8}\ \text{m}\cdot\text{s}^{-1}}{8.22 \times 10^{14}\ \text{s}^{-1}} = 3.65 \times 10^{-7}\ \text{m} = 365\ \text{nm}$$

(b) This transition is found in the Balmer series. (c) The transition from a state with $n = 100$ to one with $n = 90$ would release less energy than the transition from $n = 100$ to $n = 2$. Less energy would mean a longer wavelength, so we would expect a much larger wavelength for this transition than for the transition in part (a).

1.34 (a) The electron configuration of atomic chlorine is [Ne] $3s^2 3p^5$; it has one unpaired electron. The electron configuration of a chloride ion is that of [Ne] $3s^2 3p^6$; this configuration is identical to neutral argon. (b) Assuming a one quantum level jump of an excited chlorine atom should have an electron configuration of [Ne] $3s^2 3p^4 4s^1$. (c) The energy of a given level n in an atom other than hydrogen can be estimated by $E_n = -\dfrac{Z_{eff}^2 h\Re}{n^2} = -\dfrac{Z_{eff}^2(2.18 \times 10^{-18}\text{ J})}{n^2}$. For chlorine, Z_{eff} is approximately equal to 6 (Fig. 1F.3). For an electron to jump from the $n = 3$ to $n = 4$ quantum level the energy needed is:

$$\Delta E = E_4 - E_5,\ \text{so}\ \Delta E = -(6)^2(2.18 \times 10^{-18}\text{ J})\left(\frac{1}{4^2} - \frac{1}{3^2}\right) = 3.82 \times 10^{-18}\text{ J.}$$

This energy corresponds to a wavelength of 52.0 nm (the X-ray region). (d) This amount of energy corresponds to 2.30×10^3 kJ·mol^{-1} or 23.8 eV per chlorine atom. (e) If the proportion of ^{37}Cl in a sample of chlorine atoms is reduced to 37.89% (half of its typical value), the proportion of ^{35}Cl will be increased to 62.11%. Based on this, the average mass of a chlorine atom will be:

$$\text{Cl}_{\text{ave mass}} = \left(\frac{37.89\%}{100}\right)6.139 \times 10^{-23}\text{g} + \left(\frac{62.11\%}{100}\right)5.807 \times 10^{-23}\text{g}$$

$$\text{Cl}_{\text{ave mass}} = 5.933 \times 10^{-23}\text{g/atom} = 35.73\text{ g/mol}$$

(f) through (h):

Compound	***Chlorine oxidation number***	***Name***
ClO_2	+4	Chlorine dioxide
NaClO	+1	Sodium hypochlorite
$KClO_3$	+5	Potassium chlorate
$NaClO_4$	+7	Sodium perchlorate