

Group	3	4	5	6	7	8	9	10	11	12
Oxidation state	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
0	3d4s <sup>2</sup>	3d <sup>2</sup> 4s <sup>2</sup>	3d <sup>3</sup> 4s <sup>2</sup>	3d <sup>5</sup> 4s <sup>2</sup>	3d <sup>5</sup> 4s <sup>2</sup>	3d <sup>6</sup> 4s <sup>2</sup>	3d <sup>7</sup> 4s <sup>2</sup>	3d <sup>8</sup> 4s <sup>2</sup>	3d <sup>10</sup> 4s	3d <sup>10</sup> 4s <sup>2</sup>
+1			☺	☺	☺			☺	☺	
+2		☺	☺	☺	☺	☺	☺	☺	☺	☺
+3	☺	☺	☺	☺	☺	☺	☺	☺		
+4		☺	☺	☺	☺	☺	☺	☺		
+5			☺	☺	☺	☺				
+6				☺	☺	☺				
+7						☺				

Toward the middle of the first transition series (Cr, Mn, and Fe) elements exhibit the widest ranges of oxidation states. This phenomenon is related to the availability of both electrons and orbitals favorable for bonding. Elements to the left (Sc and Ti) of the series have few electrons and relatively low effective nuclear charge leaves d orbitals at high energies that are relatively unsuitable for bonding. To the far right (Cu and Zn) effective nuclear charge may be higher but there are few, if any, orbitals available for bonding. Consequently, it is more difficult to produce a range of compounds that promote a wide range of oxidation states for elements at either end of the series. At the middle and right of the series the +2 oxidation state is very commonly observed because normal reactions can provide the requisite ionization energies for the removal of 4s electrons. The readily available +2 and +3 oxidation states of Mn, Fe, and the +1 and +2 oxidation states of Cu make these cations useful in electron-transfer processes occurring in chains of specialized protein within biological cells. The special size and charge of the Zn<sup>2+</sup> cation makes it useful for the function of some enzymes. The tendency of Fe<sup>2+</sup> and Cu<sup>+</sup> to bind oxygen proves very useful in hemoglobin and electron transport (respiratory) chains, respectively.

### Solutions to exercises

E9.11

- (a) For an electronic transition of known frequency the transition quantum is the corresponding photon energy. Thus,

$$E_{\text{photon}} = h\nu$$

$$= (6.626 \times 10^{-34} \text{ J s}) \times (1.0 \times 10^{15} \text{ s}^{-1}) = 6.6 \times 10^{-19} \text{ J}$$

and for a mole of photons

$$E_m = N_A h\nu$$

$$= (6.022 \times 10^{23} \text{ mol}^{-1}) \times (6.626 \times 10^{-34} \text{ J s}) \times (1.0 \times 10^{15} \text{ s}^{-1}) = 4.0 \times 10^2 \text{ kJ mol}^{-1}$$

- (b) The harmonic oscillator is used as the model for the quantum motion of molecular vibration and eqn 9.29, along with Figure 9.38, indicates that quantum states are separated by the energy quantum  $\Delta E = h\nu = h/T$  where the period T is defined to be the inverse of frequency ( $T = 1/\nu$ ).

$$\Delta E = h/T$$

$$= (6.626 \times 10^{-34} \text{ J s}) / (20 \times 10^{-15} \text{ s}) = 3.3 \times 10^{-20} \text{ J}$$

$$\Delta E_m = N_A E$$

$$= (6.022 \times 10^{23} \text{ mol}^{-1}) \times (3.3 \times 10^{-20} \text{ J}) = 20. \text{ kJ mol}^{-1}$$

(c) The harmonic oscillator is also used as the model for the quantum states of pendulum motion. So, like part (b) eqn 9.29 indicates that quantum states are separated by the energy quantum  $\Delta E = h\nu = h/T$ .

$$\Delta E = h/T$$

$$= (6.626 \times 10^{-34} \text{ J s}) / (0.50 \text{ s}) = 1.3 \times 10^{-33} \text{ J}$$

$$\Delta E_m = N_A E$$

$$= (6.022 \times 10^{23} \text{ mol}^{-1}) \times (1.3 \times 10^{-33} \text{ J}) = 7.8 \times 10^{-13} \text{ kJ mol}^{-1}$$

This extraordinarily small separation is caused by the macroscopic, large mass characteristics of a pendulum. The energy levels are so close together that the pendulum energies appear as a continuum of values that are successfully described by the classical laws of physics.

**E9.12**

The definition of power  $P$  is  $P = E/t$  and the energy transported by  $N$  photons in time  $t$  is  $E = Nh\nu = Nhc/\lambda$ . Thus,  $P = Nhc/\lambda t$ .

$$(a) P = \frac{Nhc}{\lambda t} = \frac{8 \times 10^7 \times 6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{470 \times 10^{-9} \text{ m} \times 3.8 \times 10^{-3} \text{ s}} = 8.9 \times 10^{-9} \text{ W}$$

$$(b) P = \frac{Nhc}{\lambda t} = \frac{8 \times 10^7 \times 6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{780 \times 10^{-9} \text{ m} \times 3.8 \times 10^{-3} \text{ s}} = 5.3 \times 10^{-9} \text{ W}$$

**E9.13**

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad [9.3]$$

$$(a) \lambda = \frac{(6.626 \times 10^{-34} \text{ J s})}{(1.00 \text{ m s}^{-1}) \times (1.0 \times 10^{-3} \text{ kg})} = 6.6 \times 10^{-31} \text{ m}$$

$$(b) \lambda = \frac{(6.626 \times 10^{-34} \text{ J s})}{(1.0 \times 10^8 \text{ m s}^{-1}) \times (1.0 \times 10^{-3} \text{ kg})} = 6.6 \times 10^{-39} \text{ m}$$

$$(c) \lambda = \frac{(6.626 \times 10^{-34} \text{ J s})}{4.003 \times (1.6605 \times 10^{-27} \text{ kg}) \times (1.0 \times 10^3 \text{ m s}^{-1})} = 99.7 \text{ pm}$$

$$(d) m = 85 \text{ kg} \quad v = 8.0 \text{ km h}^{-1}$$

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \text{de Broglie relation [9.3]}$$

$$= \frac{6.626 \times 10^{-34} \text{ J s}}{(85 \text{ kg}) \times (8.0 \times 10^3 \text{ m h}^{-1})} \left( \frac{3600 \text{ s}}{1 \text{ h}} \right) = 3.5 \times 10^{-36} \text{ m}$$

(e) This extraordinarily small wavelength calculated in part (d) is much, much smaller than the diameter of a hydrogen nucleus and that calculation illustrates the hopelessness of measuring the de Broglie wavelength of a macroscopic object. The de Broglie wavelength does increase as the speed of an object decreases and, according to the quantum behavior of a particle in a one-dimensional box of length  $L$ , the de Broglie wavelength may be as long as  $2L$ . For yourself at rest, the de Broglie wavelength would increase to infinity, but what meaning could be attached to this result is unclear.

**E9.14**

$$p = \frac{h}{\lambda} [9.3] \quad E = hv [9.1] = \frac{hc}{\lambda}$$

$$hc = (6.6261 \times 10^{-34} \text{ J s}) \times (2.99792 \times 10^8 \text{ m s}^{-1}) = 1.986 \times 10^{-25} \text{ J m}$$

$$N_A h c = (6.02214 \times 10^{23} \text{ mol}^{-1}) \times (1.986 \times 10^{-25} \text{ J m}) \\ = 0.1196 \text{ J m mol}^{-1}$$

We can therefore draw up the following table

$\lambda$	$p/\text{kg m s}^{-1}$	$E/\text{J}$	$E/(\text{kJ mol}^{-1})$
(a) 600 nm	$1.10 \times 10^{-27}$	$3.31 \times 10^{-19}$	199
(b) 550 nm	$1.20 \times 10^{-27}$	$3.61 \times 10^{-19}$	218
(c) 400 nm	$1.66 \times 10^{-27}$	$4.97 \times 10^{-19}$	299
(d) 200 nm	$3.31 \times 10^{-27}$	$9.93 \times 10^{-19}$	598
(e) 150 pm	$4.41 \times 10^{-24}$	$1.32 \times 10^{-15}$	$7.98 \times 10^3$
(f) 1.00 cm	$6.6 \times 10^{-32}$	$1.99 \times 10^{-23}$	0.012

- E9.15** (a) The shortest wavelength as estimated without relativistic correction is calculated using eqn. 9.3:

$$\begin{aligned}\lambda_{\text{non-relativistic}} &= \frac{h}{p} = \frac{h}{(2m_e E_k)^{1/2}} = \frac{h}{(2m_e eV)^{1/2}} \\ &= \frac{6.626 \times 10^{-34} \text{ J s}}{\{(2(9.109 \times 10^{-31} \text{ kg}) \times (1.602 \times 10^{-19} \text{ C}) \times (50.0 \times 10^3 \text{ V}))\}^{1/2}} \\ &= 5.48 \text{ pm}\end{aligned}$$

$$\begin{aligned}\lambda_{\text{relativistic}} &= \frac{h}{\left\{ 2m_e eV \left( 1 + \frac{eV}{2m_e c^2} \right) \right\}^{1/2}} \\ &= \frac{\lambda_{\text{non-relativistic}}}{\left( 1 + \frac{eV}{2m_e c^2} \right)^{1/2}} = \frac{5.48 \text{ pm}}{\left\{ 1 + \frac{(1.602 \times 10^{-19} \text{ C})(50.0 \times 10^3 \text{ V})}{2(9.109 \times 10^{-31} \text{ kg})(3.00 \times 10^8 \text{ m s}^{-1})^2} \right\}^{1/2}} \\ &= \boxed{5.35 \text{ pm}}\end{aligned}$$

- (b) For an electron accelerated through 50 kV the non-relativistic de Broglie wavelength is calculated to be high by 2.4%. This error may be insignificant for many applications. However, should an accuracy of 1% or better be required, use the relativistic equation at accelerations through a potential above 20.4 V, as demonstrated in the following calculation.

$$\begin{aligned}\frac{\lambda_{\text{non-relativistic}} - \lambda_{\text{relativistic}}}{\lambda_{\text{relativistic}}} &= \frac{\lambda_{\text{non-relativistic}}}{\lambda_{\text{relativistic}}} - 1 = \left( 1 + \frac{eV}{2m_e c^2} \right)^{1/2} - 1 \\ &= 1 + \frac{1}{2} \left( \frac{eV}{2m_e c^2} \right) - \frac{1}{2 \cdot 4} \left( \frac{eV}{2m_e c^2} \right)^2 + \frac{1 \cdot 3}{2 \cdot 4 \cdot 6} \left( \frac{eV}{2m_e c^2} \right)^3 - \dots \quad \text{A} \\ &\approx \frac{1}{2} \left( \frac{eV}{2m_e c^2} \right) \quad \text{because 2nd- and 3rd-order terms are very small.}\end{aligned}$$

The largest value of  $V$  for which the non-relativistic equation yields a value that has less than 1% error:

$$V = 2 \left( \frac{2m_e c^2}{e} \right) \times \left( \frac{\lambda_{\text{non-relativistic}} - \lambda_{\text{relativistic}}}{\lambda_{\text{relativistic}}} \right) = 2 \left( \frac{2m_e c^2}{e} \right) (0.01) = 20.4 \text{ kV}$$

**E9.16**

The momentum per photon of wavelength 650 nm is

$$p_{\text{photon}} = \frac{h}{\lambda} [9.3] = \frac{6.626 \times 10^{-34} \text{ J s}}{650 \times 10^{-9} \text{ m}} = 1.02 \times 10^{-27} \text{ kg m s}^{-1}$$

and this is also the change of momentum per photon absorbed by the fabric. The laser produces a hefty  $N_A$  photons per second and all photons are absorbed by the spacecraft sail. The power  $P$  of this 650 nm laser is

$$\begin{aligned} P &= (N_A \text{ s}^{-1}) \times E_{\text{photon}} = (N_A \text{ s}^{-1}) \times h c / \lambda \\ &= (6.022 \times 10^{23} \text{ s}^{-1}) \times (6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1}) / (650 \times 10^{-9} \text{ m}) = 184 \text{ kW} \end{aligned}$$

- (a) The force  $F$  in SI units on the sail is the change in momentum experienced by the sail per second. This is equal to the photon flux,  $N_A \text{ s}^{-1}$ , multiplied by the momentum lost by a photon.

$$\begin{aligned} F &= (N_A \text{ s}^{-1}) \times p_{\text{photon}} \\ &= (6.022 \times 10^{23} \text{ s}^{-1}) \times (1.02 \times 10^{-27} \text{ kg m s}^{-1}) = 6.14 \times 10^{-4} \text{ N} \end{aligned}$$

- (b) The pressure exerted by the radiation equals the force  $F$  divided by the sail area  $A$ .

$$F/A = (6.14 \times 10^{-4} \text{ N}) / (1.0 \times 10^6 \text{ m}^2) = 614 \text{ pPa}$$

$$(c) t = \left( \frac{mv}{F} \right)_{\text{spacecraft}} = \frac{(1.0 \text{ kg}) \times (1.0 \text{ m s}^{-1})}{6.14 \times 10^{-4} \text{ N}} = 1.63 \times 10^3 \text{ s} = 0.452 \text{ h}$$

**E9.17**

$$\Delta p = 1.00 \times 10^{-4} p \text{ [i.e. } 0.0100\% \text{ of } p] = 1.00 \times 10^{-4} m_p v$$

$$\begin{aligned} \Delta x &= \frac{\hbar}{2\Delta p} [9.5] = \frac{\hbar}{2 \times (1.00 \times 10^{-4}) \times m_p v} \\ &= \frac{(1.055 \times 10^{-34} \text{ J s})}{2 \times (1.00 \times 10^{-4}) \times (1.673 \times 10^{-27} \text{ kg}) \times (3.5 \times 10^5 \text{ m s}^{-1})} \\ &= 9.0 \times 10^{-10} \text{ m, or } 0.90 \text{ nm} \end{aligned}$$

**E9.18**

The minimum uncertainty in position is  $100 \text{ pm}$ . Therefore, because  $\Delta x \Delta p \geq \frac{1}{2}\hbar[9.5]$

$$\Delta p \geq \frac{\hbar}{2\Delta x} = \frac{1.0546 \times 10^{-34} \text{ J s}}{2(100 \times 10^{-12} \text{ m})} = 5.3 \times 10^{-25} \text{ kg m s}^{-1}$$

$$\Delta v = \frac{\Delta p}{m_e} = \frac{5.3 \times 10^{-25} \text{ kg m s}^{-1}}{9.11 \times 10^{-31} \text{ kg}} = 5.8 \times 10^5 \text{ m s}^{-1}$$

**E9.19**

The Born interpretation (Section 9.2(b)) of a normalized wavefunction states that the probability,  $P$ , of finding a particle in a very small region equals  $\psi^2 \delta V$ . When consideration is given to a particle in a one-dimensional box, this becomes  $P = \psi^2 \delta x$  where  $\psi$  is evaluated at the mid-point of the  $\delta x$  range. This method is an estimate for which improvements require the use of calculus.

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

$$(a) P = \left( \frac{2}{10 \text{ nm}} \right) \times \sin^2 \left( \frac{2\pi \times 0.15 \text{ nm}}{10 \text{ nm}} \right) \times (0.2 \text{ nm} - 0.1 \text{ nm}) = \boxed{1.77 \times 10^{-4}}$$

$$(b) P = \left( \frac{2}{10 \text{ nm}} \right) \sin^2 \left( \frac{2\pi \times 5.05 \text{ nm}}{10 \text{ nm}} \right) (5.2 \text{ nm} - 4.9 \text{ nm}) = \boxed{5.92 \times 10^{-5}}$$

**E9.20** When the Born interpretation (Section 9.29b) describes the infinitesimally small probability,  $dP$ , of finding a particle in an infinitely small region  $dV$ , it is written as the differential equation  $dP = \psi^2 dV$ , where the coordinates of  $\psi$  are those of the infinitesimal volume  $dV$ . To find the probability that the particle will be found in the region of  $V$ , integration must be performed over the region.

$$P = \int_{\text{region}} dV = \int_{\text{region}} \psi^2 dV$$

When consideration is given to a particle in a one-dimensional box, where the region is between  $x_1$  and  $x_2$ , this becomes

$$P = \int_{x_1}^{x_2} \psi^2 dx, \quad \text{where } \psi = \left( \frac{2}{L} \right)^{1/2} \sin \left( \frac{2\pi x}{L} \right)$$

$$P = \int_{x_1}^{x_2} \left\{ \left( \frac{2}{L} \right)^{1/2} \sin \left( \frac{2\pi x}{L} \right) \right\}^2 dx = \left( \frac{2}{L} \right) \int_{x_1}^{x_2} \sin^2 \left( \frac{2\pi x}{L} \right) dx$$

Using the standard integral  $\int \sin^2(ax) dx = \frac{x}{2} - \frac{\sin(2ax)}{4a}$ , the working equation becomes

$$P = \left( \frac{2}{L} \right) \left[ \frac{x}{2} - \frac{\sin \left( 2 \left( \frac{2\pi}{L} \right) x \right)}{4 \left( \frac{2\pi}{L} \right)} \right]_{x_1}^{x_2} = \left[ \frac{x}{L} - \frac{1}{4\pi} \sin \left( \frac{4\pi x}{L} \right) \right]_{x_1}^{x_2}$$

$$(a) P = \left[ \frac{x}{10 \text{ nm}} - \frac{1}{4\pi} \sin \left( \frac{4\pi x}{10 \text{ nm}} \right) \right]_{0.1 \text{ nm}}^{0.2 \text{ nm}} = 1.84 \times 10^{-4}$$

$$\text{Error of the Exercise 9.19 approximation: } \frac{1.84 \times 10^{-4} - 1.77 \times 10^{-4}}{1.84 \times 10^{-4}} \times 100 = \boxed{12.9\%}$$

$$(b) P = \left[ \frac{x}{10 \text{ nm}} - \frac{1}{4\pi} \sin \left( \frac{4\pi x}{10 \text{ nm}} \right) \right]_{4.9 \text{ nm}}^{5.2 \text{ nm}} = 2.36 \times 10^{-4}$$

$$\text{Error of the Exercise 9.19 approximation: } \left| \frac{2.36 \times 10^{-4} - 5.92 \times 10^{-5}}{2.36 \times 10^{-4}} \right| \times 100 = \boxed{74.9\%}$$

**E9.21**  $P = \int_{x_1}^{x_2} \psi^2 dx, \quad \text{where } \psi = \left( \frac{2}{L} \right)^{1/2} \sin \left( \frac{\pi x}{L} \right)$

$$P = \int_{x_1}^{x_2} \left\{ \left( \frac{2}{L} \right)^{1/2} \sin \left( \frac{\pi x}{L} \right) \right\}^2 dx = \left( \frac{2}{L} \right) \int_{x_1}^{x_2} \sin^2 \left( \frac{\pi x}{L} \right) dx$$

Using the standard integral  $\int \sin^2(ax) dx = \frac{x}{2} - \frac{\sin(2ax)}{4a}$ , the working equation becomes

$$P = \left( \frac{2}{L} \right) \left[ \frac{x}{2} - \frac{\sin\left(2\left(\frac{\pi}{L}\right)x\right)}{4\left(\frac{\pi}{L}\right)} \right]_{x_1}^{x_2} = \left[ \frac{x}{L} - \frac{1}{2\pi} \sin\left(\frac{2\pi x}{L}\right) \right]_{x_1}^{x_2}$$

(a)  $P = \left[ \frac{x}{L} - \frac{1}{2\pi} \sin\left(\frac{2\pi x}{L}\right) \right]_{0 \cdot L}^{L/3} = \left[ x - \frac{1}{2\pi} \sin(2\pi x) \right]_0^{L/3} = [0.196]$

(b)  $P = \left[ \frac{x}{L} - \frac{1}{2\pi} \sin\left(\frac{2\pi x}{L}\right) \right]_{L/3}^{2L/3} = \left[ x - \frac{1}{2\pi} \sin(2\pi x) \right]_{L/3}^{2L/3} = [0.609]$

(c)  $P = \left[ \frac{x}{L} - \frac{1}{2\pi} \sin\left(\frac{2\pi x}{L}\right) \right]_{2L/3}^L = \left[ x - \frac{1}{2\pi} \sin(2\pi x) \right]_{2L/3}^L = [0.196]$

Note that the probabilities sum to 1.

**E9.22**  $\int_{-\infty}^{\infty} \psi^2 dx = \int_0^L \psi^2 dx = \int_0^L A^2 dx = A^2 \int_0^L dx = A^2 x \Big|_0^L = A^2 L = 1$  [the normalization condition]

Therefore,  $A = \left(\frac{1}{L}\right)^{1/2}$  and the normalized wavefunction is  $\psi = \left(\frac{1}{L}\right)^{1/2}$ .

**E9.23** (a) The energy levels are given by:

$$E_n = \frac{\hbar^2 n^2}{8mL^2},$$

and we are looking for the energy difference between  $n = 6$  and  $n = 7$ :

$$\Delta E = \frac{\hbar^2 (7^2 - 6^2)}{8mL^2}.$$

Since there are 12 atoms on the conjugated backbone, the length of the box is 11 times the bond length:

$$L = 11(140 \times 10^{-12} \text{ m}) = 1.54 \times 10^{-9} \text{ m},$$

$$\text{so } \Delta E = \frac{(6.626 \times 10^{-34} \text{ J s})^2 (49 - 36)}{8(9.11 \times 10^{-31} \text{ kg})(1.54 \times 10^{-9} \text{ m})^2} = [3.30 \times 10^{-19} \text{ J}].$$

(b) The relationship between energy and frequency is:

$$\Delta E = h\nu, \text{ so } \nu = \frac{\Delta E}{h} = \frac{3.30 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = [4.95 \times 10^{14} \text{ s}^{-1}].$$

This frequency corresponds to a wavelength of about 600 nm, which is in the orange region of the spectrum.

**E9.24**

The rate of tunneling is proportional to the transmission probability, so a ratio of tunneling rates is equal to the corresponding ratio of transmission probabilities. The desired factor is  $T_1/T_2$ , where the subscripts denote the tunneling distances in nanometers:

$$\frac{T_1}{T_2} = \frac{1 + \frac{(e^{\kappa L_2} - e^{-\kappa L_2})^2}{16\epsilon(1-\epsilon)}}{1 + \frac{(e^{\kappa L_1} - e^{-\kappa L_1})^2}{16\epsilon(1-\epsilon)}}. \text{ (See } \textit{Physical Chemistry} \text{ 2010 for the full formula used here).}$$

If  $\frac{(e^{\kappa L_2} - e^{-\kappa L_2})^2}{16\epsilon(1-\epsilon)} \gg 1$ , and similarly for  $L_1$ .

then  $\frac{T_1}{T_2} \approx \frac{(e^{\kappa L_2} - e^{-\kappa L_2})^2}{(e^{\kappa L_1} - e^{-\kappa L_1})^2} \approx e^{2\kappa(L_2-L_1)} = e^{2(7/\text{nm})(2.0-1.0)\text{nm}} = 1.2 \times 10^6$ .

That is, the tunneling rate increases about a million-fold. Note: if the first approximation does not hold, we need more information, namely  $\epsilon = E/V$ . If the first approximation is valid, then the second is also likely to be valid, namely that the negative exponential is negligible compared to the positive one.

**E9.25**

(a)  $v = Ae^{-d/l} = (5 \times 10^{14} \text{ s}^{-1})e^{-(750 \text{ pm})/(70 \text{ pm})} = 1.1 \times 10^{10} \text{ s}^{-1}$

(b)  $\frac{v(d_2)}{v(d_1)} = \frac{Ae^{-d_2/l}}{Ae^{-d_1/l}} = e^{-(d_2-d_1)/l} = e^{-(850 \text{ pm}-750 \text{ pm})/(70 \text{ pm})} = 0.24$

Thus, the current is reduced by about a factor of 4.

**E9.26**

With 10 electrons, the five lowest states will be occupied by two electrons each. The energy levels are (eqn. 9.13b)

$$\begin{aligned} E_{n_1, n_2} &= \left( \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} \right) \frac{\hbar^2}{8m_e} \\ &= \left( \frac{n_1^2}{(L_1/\text{pm})^2} + \frac{n_2^2}{(L_2/\text{pm})^2} \right) \frac{(6.626 \times 10^{-34} \text{ J s})^2}{8 \times 9.11 \times 10^{-31} \text{ kg} \times (10^{-12} \text{ m})^2} \\ &= \left( \frac{n_1^2}{280^2} + \frac{n_2^2}{450^2} \right) \times 6.02 \times 10^{-14} \text{ J}. \end{aligned}$$

The seven lowest energy levels are shown in the table below:

$n_1, n_2$	1,1	1,2	2,1	1,3	2,2	1,4	2,3
$E/10^{-18} \text{ J}$	1.07	1.96	3.37	3.45	4.26	5.53	5.75

- (a) The highest occupied level is (2,2); its energy is  $4.26 \times 10^{-18} \text{ J}$ .

(b) The energy of the photon is equal to the difference in energy levels, in this case between levels (2,2) and (1,4):

$$\Delta E = E_{\text{photon}} = h\nu = (5.53 - 4.26) \times 10^{-18} \text{ J},$$

$$\text{so } \nu = \frac{1.27 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 1.92 \text{ s}^{-1} = \boxed{1.92 \text{ Hz}}.$$

**E9.27**

The angular momentum states are defined by the quantum number  $m_l = 0, \pm 1, \pm 2$ , etc. By rearranging eqn 9.22, we see that the energy of state  $m_l$  is

$$E_{m_l} = \frac{m_l^2 \hbar^2}{2I}$$

and the angular momentum is

$$l_z = m_l \hbar$$

(a) There are 22 electrons, two in each of the lowest 11 states, then the highest occupied state is  $m_l = \pm 5$ ,

$$\text{so } J_z = \pm 5\hbar = \pm 5 \times (1.055 \times 10^{-34} \text{ J s}) = \boxed{5.275 \times 10^{-34} \text{ J s}}$$

$$\text{and } E_{\pm 5} = \frac{25\hbar^2}{2I}.$$

The moment of inertia of an electron on a ring of radius 440 pm is

$$I = mr^2 = (9.11 \times 10^{-31} \text{ kg}) \times (440 \times 10^{-12} \text{ m})^2 = 1.76 \times 10^{-49} \text{ kg m}^{-2}.$$

$$\text{Hence, } E_{\pm 5} = \frac{25 \times (1.055 \times 10^{-34} \text{ J s})^2}{2 \times (1.76 \times 10^{-49} \text{ kg m}^2)} = \boxed{7.89 \times 10^{-19} \text{ J}}$$

(b) The lowest unoccupied energy level is  $m_l = \pm 6$ , which has energy

$$E_{\pm 6} = \frac{36 \times (1.055 \times 10^{-34} \text{ J s})^2}{2 \times (1.76 \times 10^{-49} \text{ kg m}^2)} = 1.14 \times 10^{-18} \text{ J}$$

Radiation that would induce a transition between these levels must have a frequency such that

$$h\nu = \Delta E \quad \text{so} \quad \nu = \frac{\Delta E}{h} = \frac{(11.4 - 7.89) \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = \boxed{5.2 \times 10^{14} \text{ Hz}}$$

This corresponds to a wavelength of about 570 nm, a wave of visible light.

**E9.28**

The wavefunction for a particle in a two-dimensional well is given by eqn 9.13.

$$\psi_{n_x, n_y}(x, y) = X_{n_x}(x) Y_{n_y}(y) = \left( \frac{4}{L_X L_Y} \right)^{1/2} \sin\left(\frac{n_x \pi x}{L_X}\right) \sin\left(\frac{n_y \pi y}{L_Y}\right)$$

$$\text{For a square well with } L_X = L_Y = L \text{ this becomes } \psi_{n_x, n_y} = \left( \frac{2}{L} \right) \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right).$$

The wavefunctions and probability densities are calculated and plotted below using MathCad™ for  
 (1)  $\psi_{1,1}$  (2)  $\psi_{1,2}$  (3)  $\psi_{2,1}$  and (4)  $\psi_{2,2}$ .

$$\frac{v_{\text{DI}}}{v_{\text{HI}}} = \frac{\frac{1}{2\pi} \left( \frac{k_f}{m_D} \right)^{1/2}}{\frac{1}{2\pi} \left( \frac{k_f}{m_H} \right)^{1/2}} = \left( \frac{m_H}{m_D} \right)^{1/2} = \left( \frac{1}{2} \right)^{1/2} = 0.707$$

When hydrogen-1 is replaced by hydrogen-2 (deuterium) in H-I, the vibrational frequency decreases by a factor of 0.707.

**E9.32** (a)  $\psi = Ne^{-ax^2/2} \quad -\infty < x < \infty$

The normalization constant is found as follows:

$$N^2 \int_{-\infty}^{\infty} (e^{-ax^2/2})^2 dx = 1 \quad (\text{See Justification 9.1 for a similar example})$$

$$N^2 \int_{-\infty}^{\infty} e^{-ax^2} dx = 1$$

Using the standard, definite integral  $\int_{-\infty}^{\infty} e^{-ax^2} dx = \left( \frac{\pi}{a} \right)^{1/2}$ , we find that

$$N^2 \left( \frac{\pi}{a} \right)^{1/2} = 1 \quad \text{or} \quad N = \left( \frac{a}{\pi} \right)^{1/4}$$

The normalized wavefunction is  $\psi = \left( \frac{a}{\pi} \right)^{1/4} e^{-ax^2/2}$ .

(b) The function  $\psi = \left( \frac{a}{\pi} \right)^{1/4} e^{-ax^2/2}$  is a “bell” or “Gaussian” function with a maximum at  $x = 0$ .

Consequently,  $\psi^2$  has a maximum value at the displacement  $x = 0$  and the Born interpretation of  $\psi^2$  (see Section 9.2(b)) indicates that the displacement  $x = 0$  is the most probable displacement. It is instructive to use analytic geometry to find the maximum. This requires identification of the displacement for which  $d\psi/dx = 0$  and showing that  $d\psi/dx > 0$  before the maximum and  $d\psi/dx < 0$  after the maximum

$$\frac{d\psi}{dx} = \frac{d}{dx} \left\{ \left( \frac{a}{\pi} \right)^{1/4} e^{-ax^2/2} \right\} = \left( \frac{a}{\pi} \right)^{1/4} \frac{d}{dx} e^{-ax^2/2} = -\left( \frac{a}{\pi} \right)^{1/4} ax e^{-ax^2/2}$$

The factor of  $x$  in the first derivative indicates that the derivative equals zero when  $x = 0$ . Furthermore, the formula for the derivative clearly shows that the derivative is positive when  $x < 0$  and the derivative is negative when  $x > 0$ . The function is a maximum at  $x = 0$ .

**E9.33**  $v = \frac{1}{2\pi} \left( \frac{k_f}{\mu} \right)^{1/2} \quad [9.29], \quad \text{where} \quad \mu = m_A m_B / (m_A + m_B) = M_A M_B / \{N_A (M_A + M_B)\}$

$$(a) \mu_{^{12}\text{C}^{16}\text{O}} = \frac{(12.00) \times (16.00) \times 10^{-3} \text{ kg}}{(6.0221 \times 10^{23}) \times (28.00)} = 1.139 \times 10^{-26} \text{ kg}$$

$$v_{^{12}\text{C}^{16}\text{O}} = \frac{1}{2\pi} \left( \frac{1860 \text{ N m}^{-1}}{1.139 \times 10^{-26} \text{ kg}} \right)^{1/2} = 6.432 \times 10^{13} \text{ s}^{-1}$$

$$(b) \tilde{v}_{^{12}\text{C}^{16}\text{O}} = 1/\lambda_{^{12}\text{C}^{16}\text{O}} = \frac{v_{^{12}\text{C}^{16}\text{O}}}{c}$$

$$= \frac{6.432 \times 10^{13} \text{ s}^{-1}}{2.9979 \times 10^8 \text{ m s}^{-1}} = 2.146 \times 10^5 \text{ m}^{-1} = \boxed{2146 \text{ cm}^{-1}}$$

(c) Computations like those of part (a) and part (b) can be repeated for additional isotopes of carbon monoxide. We will take a short-cut by recognizing that these isotopic CO molecules have identical force constants and differ only in their reduced mass. Consequently, since both the frequency and wavenumber are inversely proportional to  $\mu^{1/2}$ , we write

$$\mu_{^{13}\text{C}^{16}\text{O}} = \frac{(13.00) \times (16.00) \times 10^{-3} \text{ kg}}{(6.0221 \times 10^{23}) \times (29.00)} = 1.191 \times 10^{-26} \text{ kg}$$

$$\begin{aligned} \tilde{v}_{^{13}\text{C}^{16}\text{O}} &= \left( \frac{\mu_{^{12}\text{C}^{16}\text{O}}}{\mu_{^{13}\text{C}^{16}\text{O}}} \right)^{1/2} \tilde{v}_{^{12}\text{C}^{16}\text{O}} \\ &= \left( \frac{1.139}{1.191} \right)^{1/2} \times (2146 \text{ cm}^{-1}) \\ &= \boxed{2099 \text{ cm}^{-1}} \end{aligned}$$

Similarly,

$$\mu_{^{12}\text{C}^{18}\text{O}} = 1.196 \times 10^{-26} \text{ kg} \quad \text{and} \quad \tilde{v}_{^{12}\text{C}^{18}\text{O}} = \boxed{2094 \text{ cm}^{-1}}$$

$$\mu_{^{13}\text{C}^{18}\text{O}} = 1.253 \times 10^{-26} \text{ kg} \quad \text{and} \quad \tilde{v}_{^{13}\text{C}^{18}\text{O}} = \boxed{2046 \text{ cm}^{-1}}$$

**E9.34** The reduced mass is nearly identical for hydrogenic atoms so the Rydberg constant for all of them may be estimated to equal  $R_H$ . Also, the ionization energy is equivalent to the energy of the transition  $n = 1 \rightarrow n = \infty$  so we write

$$I = E_{n=\infty} - E_{n=1} = -hcR_H Z^2 \left( \frac{1}{\infty^2} - \frac{1}{1^2} \right) = hcR_H Z^2$$

Since  $I_{\text{He}^+} = 4hcR_H$ , we may write  $I_{\text{Li}^{2+}} = 9hcR_H = \frac{9}{4}I_{\text{He}^+}$ . With the ionization of  $\text{He}^+$  given as 54.36 eV, the ionization energy of  $\text{Li}^{2+}$  is  $\frac{9}{4} \times (54.36 \text{ eV}) = \boxed{122.31 \text{ eV}}$ .

**E9.35**  $n = 4$  for the N shell

$$n^2 = 4^2 = \boxed{16 \text{ orbitals}}$$

**E9.36** (a) The probability density varies as

$$\psi^2 = \frac{1}{\pi a_0^3} e^{-2r/a_0}$$

The maximum value is at  $r = 0$  and  $\psi^2$  is 25 per cent of the maximum when  $e^{-2r/a_0} = 0.25$ , so that  $r = 1/2 a_0 \ln(0.25)$ , which is at  $\boxed{r = 0.693 a_0}$ , which corresponds to 36.7 pm.

(b) The radial distribution function varies as

$$P = 4\pi r^2 \psi^2 = \frac{4r^2}{a_0^3} e^{-2r/a_0}$$

The maximum value of  $P$  occurs at  $r = a_0$  because

$$\frac{dP}{dr} \propto \left(2r - \frac{2r^2}{a_0}\right) e^{-2r/a_0} = 0 \text{ at } r = a_0 \text{ and } P_{\max} = \frac{4}{a_0} e^{-2}$$

$P$  falls to a fraction  $f$  of its maximum when

$$f = \frac{\frac{4r^2}{a_0^3} e^{-2r/a_0}}{\frac{4}{a_0} e^{-2}} = \frac{r^2}{a_0^2} e^2 e^{-2r/a_0}$$

Therefore, solve

$$\frac{f^{1/2}}{e} = \left(\frac{r}{a_0}\right) e^{-r/a_0}$$

$$f = 0.25$$

solves to  $r = 2.6783 a_0$  or  $0.2320 a_0 = [142 \text{ pm or } 12 \text{ pm}]$

- (c) The most probable distance of a  $1s$  electron from the nucleus occurs when the first derivative of the radial distribution function equals zero.

$$P_{1s} = 4\pi r^2 \psi_{1s}^2 [13.8a] = 4\pi r^2 (Ne^{-r/a_0})^2 [13.7] = 4\pi N^2 (r^2 e^{-2r/a_0})$$

$$\frac{dP_{1s}}{dr} = 4\pi N^2 \frac{d(r^2 e^{-2r/a_0})}{dr} = 4\pi N^2 \left\{ 2re^{-2r/a_0} + r^2 \left(-\frac{2}{a_0} e^{-2r/a_0}\right) \right\} = 8\pi N^2 \left\{ 1 - \frac{r}{a_0} \right\} re^{-2r/a_0}$$

The derivative equals zero when the factor  $1 - r/a_0$  equals zero. Therefore,  $[r_{\max} = a_0]$ .

- E9.37** There are 2 lobes to a p-orbital so the probability that a p-orbital electron will be found in one or the other lobe is  $\left[\frac{1}{2}\right]$ . However, there are 3 degenerate orbitals in a p subshell so the probability of finding a p subshell electron in one or another p-orbital lobe of the subshell is  $\frac{1}{6}$ .

- E9.38** (a) We will make the assumption that  $\psi^2$  is a constant within this very small volume. Then, Probability =  $\int \psi^2(r) \delta V \approx \psi^2 \delta V$  with  $\delta V = 1.0 \text{ pm}^3$

$$\psi^2 = \frac{1}{32\pi a_0^3} \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} = 6.72 \times 10^{-8} \text{ pm}^{-3} \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0}$$

$$(i) \quad \psi^2 = 6.72 \times 10^{-8} \text{ pm}^{-3} \times 2^2 \times 1 = 2.7 \times 10^{-7} \text{ pm}^{-3}$$

$$\psi^2 \delta V = [2.7 \times 10^{-7}]$$

$$(ii) \quad \psi^2 = 6.72 \times 10^{-8} \text{ pm}^{-3} \times 1 \times e^{-1} = 2.47 \times 10^{-8} \text{ pm}^3$$

$$\psi^2 \delta V = [2.5 \times 10^{-8}]$$

$$(iii) \quad \psi^2 = 0, \psi^2 \delta V = [0]. \text{ This is a radial node.}$$