Exc.1 (a) For an electronic transition of known frequency the transition quantum is the corresponding photon energy. Thus,

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

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

and for a mole of photons

$$E_{\text{m}} = N_{\text{A}} h\nu$$

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

(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 ($T = 1/\nu$).

$$\Delta E = h/T$$

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

$$\Delta E_{\text{m}} = N_{\text{A}} E$$

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

(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 $\Delta E = h\nu = h/T$.

$$\Delta E = h/T$$

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

$$\Delta E_{\text{m}} = N_{\text{A}} E$$

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

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.

Exc.2

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

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

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

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

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

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

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

(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 in unclear.

Exc.3

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

$$P = (N_A\ \text{s}^{-1}) \times E_{\text{photon}} = (N_A\ \text{s}^{-1}) \times hc/\lambda$$

$$= (6.022 \times 10^{23}\ \text{s}^{-1}) \times (6.626 \times 10^{-34}\ \text{J s}) \times (2.998 \times 10^{8}\ \text{m s}^{-1})/(650 \times 10^{-9}\ \text{m}) = 184\ \text{kW}$$

(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.

$$F = (N_A\ \text{s}^{-1}) \times p_{\text{photon}}$$

$$= (6.022 \times 10^{23}\ \text{s}^{-1}) \times (1.02 \times 10^{-27}\ \text{kg m s}^{-1}) = \boxed{6.14 \times 10^{-4}\ \text{N}}$$

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

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

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

Exc.4 $\Delta p = 1.00\times10^{-4}\,p$ [i.e. 0.0100% of p] $= 1.00\times10^{-4}\,m_p v$

$$\Delta x = \frac{\hbar}{2\Delta p}\,[9.5] = \frac{\hbar}{2\times(1.00\times10^{-4})\times m_p v}$$

$$= \frac{(1.055\times10^{-34}\ \mathrm{J\,s})}{2\times(1.00\times10^{-4})\times(1.673\times10^{-27}\ \mathrm{kg})\times(3.5\times10^{5}\ \mathrm{m\,s^{-1}})}$$

$$= 9.0\times10^{-10}\ \mathrm{m},\ \text{or}\ \boxed{0.90\ \mathrm{nm}}$$

Exc.5 The minimum uncertainty in position is $\boxed{100\ \mathrm{pm}}$. Therefore, because $\Delta x\Delta p \geq \frac{1}{2}\hbar$[9.5]

$$\Delta p \geq \frac{\hbar}{2\Delta x} = \frac{1.0546\times10^{-34}\ \mathrm{J\,s}}{2(100\times10^{-12}\ \mathrm{m})} = 5.3\times10^{-25}\ \mathrm{kg\,m\,s^{-1}}$$

$$\Delta v = \frac{\Delta p}{m_e} = \frac{5.3\times10^{-25}\ \mathrm{kg\,m\,s^{-1}}}{9.11\times10^{-31}\ \mathrm{kg}} = \boxed{5.8\times10^{5}\ \mathrm{m\,s^{-1}}}$$

Exc.6 $P = \int_{x_1}^{x_2} \psi^2\,\mathrm{d}x$, where $\psi = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{\pi x}{L}\right)$

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

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

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

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

Note that the probabilities sum to 1.

Exc.7 $$\int_{-\infty}^{\infty}\psi^2 dx = \int_0^L \psi^2 dx = \int_0^L A^2 dx = A^2\int_0^L dx = A^2 x\Big|_0^L = A^2 L = 1 \text{ [the normalization condition]}$$

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

Exc.8 (a) The energy levels are given by:

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

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

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

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

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

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

(b) The relationship between energy and frequency is:

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

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

Exc.9 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:

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

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

then $$\frac{T_1}{T_2}\approx\frac{(e^{\kappa L_2}-e^{-\kappa L_2})^2}{(e^{\kappa L_1}-e^{-\kappa L_1})^2}\approx e^{2\kappa(L_2-L_1)}=e^{2(7/\mathrm{nm})(2.0-1.0)\mathrm{nm}}=\boxed{1.2\times10^6}.$$

That is, the tunneling rate increases about a million-fold. Note: if the first approximation does not hold, we need more information, namely $\varepsilon = E/V$. 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.

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

$$E_{n_1,n_2}=\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}\right)\frac{h^2}{8m_e}$$
$$=\left(\frac{n_1^2}{(L_1/\mathrm{pm})^2}+\frac{n_2^2}{(L_2/\mathrm{pm})^2}\right)\frac{(6.626\times10^{-34}\ \mathrm{J\ s})^2}{8\times9.11\times10^{-31}\ \mathrm{kg}\times(10^{-12}\ \mathrm{m})^2}$$
$$=\left(\frac{n_1^2}{280^2}+\frac{n_2^2}{450^2}\right)\times6.02\times10^{-14}\ \mathrm{J}.$$

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
$E/10^{-18}$ 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 $\boxed{4.26\times10^{-18}\ \mathrm{J}}$.

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

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

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

Exc.11 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 $m_l = \pm 5$,

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

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

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

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

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

(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.

Exc.12 (a) $I = m_{\rm H}r^2$ [text Section 9.5(a)]

$$= (1.008\ \text{u}) \times (1.6605 \times 10^{-27}\ \text{kg/u}) \times (161 \times 10^{-12}\ \text{m})^2$$

$$= \boxed{4.34 \times 10^{-47}\ \text{kg m}^2}$$

(b) $E_{m_l} = \dfrac{m_l^2\hbar^2}{2I}$ [9.22], where $m_l = 0, \pm1, \pm2, \ldots$

$$\Delta E = E_1 - E_0 = \frac{h^2}{8\pi^2 I} \quad \text{and} \quad \Delta E = h\nu = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{8\pi^2 cI}{h}$$

$$= \frac{8\pi^2 \times (2.998 \times 10^8\ \text{m s}^{-1}) \times (4.34 \times 10^{-47}\ \text{kg m}^2)}{6.626 \times 10^{-34}\ \text{J s}}$$

$$= 1.55 \times 10^{-3}\ \text{m} = \boxed{1.55\ \text{mm}}$$

This wavelength is in the microwave region of the electromagnetic spectrum.

Exc.13 (a) $\nu = \dfrac{1}{2\pi}\left(\dfrac{k_{\rm f}}{m}\right)^{1/2}$ [9.29]

$$= \frac{1}{2\pi}\left(\frac{314\ \text{N m}^{-1}}{(1.0079\ \text{u}) \times (1.6605 \times 10^{-27}\ \text{kg u}^{-1})}\right)^{1/2} = \boxed{6.89 \times 10^{13}\ \text{s}^{-1}}$$

(b) $\lambda = \dfrac{c}{\nu} = \dfrac{2.998 \times 10^8\ \text{m s}^{-1}}{6.89 \times 10^{13}\ \text{s}^{-1}} = 4.35 \times 10^{-6}\ \text{m} = \boxed{4.35\ \mu\text{m}}$

(c) The D–I bond and the H–I bond are expected to have almost identical bond strengths and identical bonding force constants, k, because bonding is an electronic, not a mass/isotopic, property. However, the vibrational frequency does have a mass dependence.

$$\nu = \frac{1}{2\pi}\left(\frac{k_{\rm f}}{m}\right)^{1/2} \quad [9.29]$$

$$\frac{\nu_{\rm DI}}{\nu_{\rm HI}} = \frac{\dfrac{1}{2\pi}\left(\dfrac{k_{\rm f}}{m_{\rm D}}\right)^{1/2}}{\dfrac{1}{2\pi}\left(\dfrac{k_{\rm f}}{m_{\rm H}}\right)^{1/2}} = \left(\frac{m_{\rm H}}{m_{\rm D}}\right)^{1/2} = \left(\frac{1}{2}\right)^{1/2} = 0.707$$

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

Exc.14 (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 ψ^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 $0.2320\, a_0 =$ $\boxed{142 \text{ pm or } 12 \text{ pm}}$

(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, $\boxed{r_{max} = a_0}$.

Exc.15

Identify l and use angular momentum = $\{l(l+l)\}^{1/2}\hbar$

(a) $l = 0$, so $\boxed{\text{ang. mom.} = 0}$

(b) $l = 0$, so $\boxed{\text{ang. mom.} = 0}$

(c) $l = 2$, so $\boxed{\text{ang. mom.} = \sqrt{6}\,\hbar}$

(d) $l = 1$, so $\boxed{\text{ang. mom.} = \sqrt{2}\,\hbar}$

(e) $l = 1$, so $\boxed{\text{ang. mom.} = \sqrt{2}\,\hbar}$

The total number of nodes is equal to $n - 1$, and the number of angular nodes is equal to l; hence the number of radial nodes is equal to $n - 1 - l$. We can draw up the following table:

	1*s*	3*s*	3*d*	2*p*	3*p*
n, l	1,0	3,0	3,2	2,1	3,1
Ang. nodes	0	0	2	1	1
Rad. nodes	0	2	0	0	1

Exc.16

For a given l there are $2l + 1$ values of m_l and hence $2l + 1$ orbitals. Each orbital may be occupied by two electrons. Therefore, the maximum occupancy is $2(2l + 1)$.

	l	$2(2l+1)$
(a)	0	2
(b)	3	14
(c)	5	22