8B Vibrational motion

Answers to discussion questions

D8B.2 If the quantum number v is large enough, the most probable location shifts to the outside of the well. The probability density will look just like the classical probability. The exponential tails into the classically forbidden region decreases with increasing v, so the quantum oscillator looks more and more like the classical one.

D8B.3 The physical reason is the uncertainty principle (Section 7C.3). If a particle is at least partly localized, its position is not completely uncertain, and therefore its momentum, and hence its kinetic energy, cannot be exactly zero. The potential energy of the harmonic oscillator at least partially localizes the oscillator in the neighbourhood of the equilibrium position, so zero momentum (and therefore zero kinetic energy) is precluded. Furthermore, the confinement is not perfect, which makes the particle's potential energy also differ from zero.

Solutions to exercises

E8B.1(a) $E=\left(v+\frac{1}{2}\right)\hbar\omega, \quad \omega=\left(\frac{k_f}{m}\right)^{1/2}$ [8B.4]

The zero-point energy corresponds to $v=0$; hence

$$E_0 = \frac{1}{2}\hbar\omega = \frac{1}{2}\hbar\left(\frac{k_f}{m}\right)^{1/2} = \left(\frac{1}{2}\right)\times(1.055\times10^{-34}\,\text{Js})\times\left(\frac{155\,\text{N m}^{-1}}{2.33\times10^{-26}\,\text{kg}}\right)^{1/2}$$
$$= \boxed{4.30\times10^{-21}\,\text{J}}$$

E8B.2(a) The difference in adjacent energy levels is

$$\Delta E = E_{v+1} - E_v = \hbar\omega \text{ [8B.5]} = \hbar\left(\frac{k_f}{m}\right)^{1/2} \text{ [8B.4]}$$

Hence

$$k_f = m\left(\frac{\Delta E}{\hbar}\right)^2 = (1.33\times10^{-25}\,\text{kg})\times\left(\frac{4.82\times10^{21}\,\text{J}}{1.055\times10^{-34}\,\text{Js}}\right)^2 = 278\,\text{kg s}^{-2} = \boxed{278\,\text{N m}^{-1}}$$

E8B.3(a) The requirement for a transition to occur is that ΔE(system)=E(photon),

so $\Delta E(\text{system}) = \hbar\omega$ [8B.5]= $E(\text{photon}) = h\nu = \frac{hc}{\lambda}$

Therefore, $\frac{hc}{\lambda} = \frac{h\omega}{2\pi} = \left(\frac{h}{2\pi}\right)\times\left(\frac{k_f}{m}\right)^{1/2}$ [8B.4]

$$\lambda = 2\pi c\left(\frac{m}{k_f}\right)^{1/2} = (2\pi)\times(2.998\times10^8\,\text{m s}^{-1})\times\left(\frac{1.0078\times1.6605\times10^{-27}\,\text{kg}}{855\,\text{N m}^{-1}}\right)^{1/2}$$
$$= 2.64\times10^{-6}\,\text{m} = \boxed{2.64\,\mu\text{m}}$$

E8B.4(a) The frequency of a harmonic oscillator is [8B.4]

$$\omega = \left(\frac{k_f}{m}\right)^{1/2}$$

^{1}H (H) and ^{2}H (D) are isotopes, so we expect that the force constant is the same in H_2 and D_2. They differ in mass. So the frequencies are inversely proportional to the square root of the mass:

$$\omega_D = \omega_H\left(\frac{m_H}{m_D}\right)^{1/2}$$

But the appropriate mass is not the mass of the molecule but its "effective mass" [8B.7]

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m}{2}\ [m_1 = m_2 = m]$$

For H_2: $\mu = \frac{m}{2} = \frac{1.0078\times(1.6605\times10^{-27}\,\text{kg})}{2} = \boxed{8.3673\times10^{-28}\,\text{kg}}$

For D_2: $\mu = \frac{m}{2} = \frac{2.0141\times(1.6605\times10^{-27}\,\text{kg})}{2} = \boxed{1.6722\times10^{-27}\,\text{kg}}$

$$\omega_D = 131.9\text{THz} \times \left(\frac{8.3673\times10^{-28}\,\text{kg}}{1.6722\times10^{-27}\,\text{kg}}\right)^{1/2} = \boxed{93.3\,\text{THz}}$$

E8B.5(a) (a) From introductory physics, we have

$$\omega = \left(\frac{g}{l}\right)^{1/2}$$

$$\Delta E = \hbar\omega \text{ [8B.5]} = (1.055\times10^{-34}\,\text{Js}) \times \left(\frac{9.81\,\text{m s}^{-2}}{1.0\,\text{m}}\right)^{1/2}$$

$$= \boxed{3.3\times10^{-34}\,\text{J}}$$

(b) $\Delta E = h\nu = (6.626\times10^{-34}\,\text{JHz}^{-1}) \times (5\,\text{Hz}) = \boxed{3.3\times10^{-33}\,\text{J}}$

E8B.6(a) The zero-point energy is

$$E_0 = \frac{1}{2}\hbar\omega \text{ [8B.6]} = \frac{\hbar}{2}\left(\frac{k}{\mu}\right)^{1/2} \text{ [8B.4]}$$

$$\mu = 34.9688\times(1.6605\times10^{-27}\,\text{kg})/2 = 2.9033\times10^{-26}\,\text{kg}$$

where we have used eqn 8B.7 for two equal masses, as in Exercise 8B.4(a).

$$\text{so } E_0 = \left(\frac{1.0546\times10^{-34}\,\text{J s}}{2}\right) \times \left(\frac{329\,\text{N m}^{-1}}{2.9033\times10^{-26}\,\text{kg}}\right)^{1/2} = \boxed{5.61\times10^{-21}\,\text{J}}$$

E8B.7(a) The harmonic oscillator wavefunctions have the form [8B.8]

$$\psi_v(x) = N_v H_v(y)\exp\left(-\tfrac{1}{2}y^2\right) \quad \text{with} \quad y = \frac{x}{\alpha} \quad \text{and} \quad \alpha = \left(\frac{\hbar^2}{mk_f}\right)^{1/4}$$

The exponential function approaches zero only as x approaches $\pm\infty$, so the nodes of the wavefunction are the nodes of the Hermite polynomials.

$$H_4(y) = 16y^4 - 48y^2 + 12 = 0 \text{ [Table 8B.1]}$$

Dividing through by 4 and letting $z = y^2$, we have a quadratic equation

$$4z^2 - 12z + 3 = 0$$

$$\text{so } z = \frac{-b\pm\sqrt{b^2-4ac}}{2a} \quad \frac{12\pm\sqrt{12^2-4\times4\times3}}{2\times4} \quad \frac{3\pm\sqrt{6}}{2}$$

Evaluating the result numerically yields $z = 0.275$ or 2.72, so $y = \pm0.525$ or ±1.65. Therefore $x = \boxed{\pm0.525\alpha \text{ or } \pm1.65\alpha}$.

Comment. Numerical values could also be obtained graphically by plotting $H_4(y)$.

E8B.8(a) The most probable displacements are the values of x that maximize ψ^2. As noted in Exercise 8A.8(a), maxima in ψ^2 correspond to maxima *and* minima in ψ itself, so one can solve this exercise by finding all points where $\frac{d\psi}{dx}=0$. The wavefunction is [8B.10]

$$\psi_1 = 2N_1 y \exp\left(-\tfrac{1}{2}y^2\right) \quad \text{with} \quad y=\frac{x}{\alpha} \quad \text{and} \quad \alpha=\left(\frac{\hbar^2}{mk_f}\right)^{1/4}$$

$$\frac{d\psi_1}{dx}=\frac{dy}{dx}\frac{d\psi_1}{dy}=\frac{2N_1}{\alpha}\left\{\exp\left(-\tfrac{1}{2}y^2\right)-y^2\exp\left(-\tfrac{1}{2}y^2\right)\right\}=0$$

Dividing through by constants and the exponential functions yields

$$1-y^2=0 \quad \text{so} \quad y=\pm 1 \quad \text{and} \quad x=\boxed{\pm\alpha}.$$

E8B.9(a) Example 8B.4 analyses the classical turning points of the harmonic oscillator. In terms of the dimensionless variable y, the turning points are $y_{tp}=\pm(2v+1)^{1/2}$. The probability of extension beyond the classical turning point is

$$P=\int_{x_{tp}}^{\infty}\psi_v^2\,dx=\alpha N_v^2\int_{y_{tp}}^{\infty}\{H_v(y)\}^2e^{-y^2}\,dy$$

For $v=1$, $H_1(y)=2y$ and $N_1=\left(\frac{1}{2\alpha\pi^{1/2}}\right)^{1/2}$

$$P=4\alpha N_1^2\int_{3^{1/2}}^{\infty}y^2e^{-y^2}\,dy$$

Use integration by parts:

$$\int u\,dv=uv-\int v\,du$$

where $u=y$, $dv=ye^{-y^2}dy$

so $du=dy$, $v=-\frac{1}{2}e^{-y^2}$

and $P=-2\alpha N_1^2\left(ye^{-y^2}\Big|_{3^{1/2}}^{\infty}-\int_{3^{1/2}}^{\infty}e^{-y^2}\,dy\right)$

$$=\pi^{-1/2}\left(3^{1/2}e^{-3}+\int_{3^{1/2}}^{\infty}e^{-y^2}\,dy\right)$$

The remaining integral can be expressed in terms of the error function.

$$\operatorname{erf} z=1-\frac{2}{\pi^{1/2}}\int_z^{\infty}e^{-y^2}\,dy$$

so $\int_{3^{1/2}}^{\infty}e^{-y^2}\,dy=\dfrac{\pi^{1/2}(1-\operatorname{erf}3^{1/2})}{2}$

Finally, using $\operatorname{erf}3^{1/2}=0.986$,

$$P=\pi^{-1/2}\left(3^{1/2}e^{-3}+\frac{\pi^{1/2}(1-\operatorname{erf}3^{1/2})}{2}\right)=\boxed{0.056}$$

Comment. This is the probability of an extension greater than the positive classical turning point. There is an equal probability of a compression smaller than the negative classical turning point, so the total probability of finding the oscillator in a classically forbidden region is $\boxed{0.112}$.

Comment. Note that molecular parameters such as m and k do not enter into the calculation.

Solutions to problems

P8B.1 $\omega = \left(\frac{k_f}{\mu}\right)^{1/2}$ [8B.4]

Also, $\omega = 2\pi\nu = \frac{2\pi c}{\lambda} = 2\pi c\tilde{\nu}$

Therefore $k_f = \omega\ \mu = 4\pi^2 c^2 \tilde{\nu}^2 \mu = \frac{4\pi^2 c^2 \tilde{\nu}^2 m_1 m_2}{m_1 + m_2}$.

We draw up the following table using isotope masses from the *Resource section*.

	$^1H^{35}Cl$	$^1H^{81}Br$	$^1H^{127}I$	$^{12}C^{16}O$	$^{14}N^{16}O$
$\tilde{\nu}$ / m^{-1}	299000	265 000	231 000	217 000	190400
$10^{27}\, m_1$ / kg	1.6735	1.6735	1.6735	19.926	23.253
$10^{27}\, m_2$ / kg	58.066	134.36	210.72	26.560	26.560
k / (N m^{-1})	516	412	314	1902	1595

Therefore, the order of stiffness, is $[HI < HBr < HCl < NO < CO]$.

P8B.3 Assuming that one can identify the CO peak in the infrared spectrum of the CO–myoglobin complex, taking infrared spectra of each of the isotopic variants of CO–myoglobin complexes can show which atom binds to the haem group and determine the C≡O force constant. Compare isotopic variants to $^{12}C^{16}O$ as the standard; when an isotope changes but the vibrational frequency does not, then the atom whose isotope was varied is the atom that binds to the haem. See table below, which includes predictions of the wavenumber of all isotopic variants compared to that of $\tilde{\nu}$ ($^{12}C^{16}O$). (As usual, the better the experimental results agree with the whole set of predictions, the more confidence one would have with the conclusion.)

Wavenumber for isotopic variant	If O binds	If C binds
$\tilde{\nu}(^{12}C^{18}O) =$	$\tilde{\nu}(^{12}C^{16}O)^*$	$(16/18)^{1/2}\tilde{\nu}(^{12}C^{16}O)$
$\tilde{\nu}(^{13}C^{16}O) =$	$(12/13)^{1/2}\tilde{\nu}(^{12}C^{16}O)$	$\tilde{\nu}(^{12}C^{16}O)^*$
$\tilde{\nu}(^{13}C^{18}O) =$	$(12/13)^{1/2}\tilde{\nu}(^{12}C^{16}O)$	$(16/18)^{1/2}\tilde{\nu}(^{12}C^{16}O)$

*That is, no change compared to the standard.

The wavenumber is related to the force constant as follows [8B.4]:

$$\omega = 2\pi c\tilde{\nu} = \left(\frac{k_f}{m}\right)^{1/2} \quad \text{so} \quad k_f = m(2\pi c\tilde{\nu})^2$$

Hence $k_f = (m/m_u)(1.66\times10^{-27}\,\text{kg})[(2\pi)(2.998\times10^{10}\,\text{cm s}^{-1})\tilde{\nu}(^{12}\text{C}^{16}\text{O})]^2$,

and $k_f/(\text{kg s}^{-2}) = (5.89\times10^{-5})(m/m_u)[\tilde{\nu}(^{12}\text{C}^{16}\text{O})/\text{cm}^{-1}]^2$

Here m is the mass of the atom that is not bound in atomic mass units, i.e. $12m_u$ if O is bound and $16m_u$ if C is bound. (Of course, one can compute k_f from any of the

P8B.8

$$\begin{aligned}\int_{-\infty}^{+\infty}\psi_{\nu'}x\psi_\nu \mathrm{d}x &= \alpha^2 N_\nu^2 \int_{-\infty}^{+\infty} H_{\nu'} y H_\nu \exp\left(-y^2\right)\mathrm{d}y \\ &= \alpha^2 N_\nu^2 \int_{-\infty}^{+\infty} H_{\nu'}\left(\nu H_{\nu-1} + \frac{1}{2}H_{\nu+1}\right)\exp\left(-y^2\right)\mathrm{d}y \\ &= \pi^{1/2}2^{\nu'}\nu'!\alpha^2 N_\nu^2\left(\nu\delta_{\nu',\nu-1} + \frac{1}{2}\delta_{\nu',\nu+1}\right)\end{aligned}$$

Only when ν'=ν±1 the above integral is non-zero. The final result is obvious.

P8B.11 As expressed in the problem, the potential energy function assumes that ϕ is defined as we would expect; that is, $\phi=0$ corresponds to an eclipsed conformation. Thus, $\phi=0$ i s **not** a stable equilibrium point, and small displacements from this point are **not** harmonic; in fact, $\phi=0$ is a position of unstable equilibrium, and small displacements from it would grow larger. We must express the potential energy in terms of displacements from a stable equilibrium position. One such equilibrium position is the staggered conformation directly opposite $\phi=0$, namely $\phi=\pi$. So let the displacement $x=\phi-\pi$. So, in terms of x, the potential energy function is $V=-V_0\cos 3x$. Conventionally, the potential energy in harmonic motion is measured with respect to that stable equilibrium position. Note that the potential energy at the stable equilibrium position is $V=-V_0$. We can redefine the potential energy function to measure energy relative to the stable equilibrium by letting

$$V' = V_0 + V = V_0 - V_0\cos 3x = V_0(1-\cos 3x).$$

Use the first two terms of the Taylor series expansion of cosine:

$$V'=V_0(1-\cos 3x)\approx V_0\left(1-1+\frac{(3x)^2}{2}\right)=\frac{9V_0}{2}x^2$$

The Schrödinger equation becomes

$$-\frac{\hbar^2}{2I}\frac{\partial^2\psi}{\partial x^2}+\frac{9V_0}{2}x^2\psi = E\psi \quad \text{[8C.9b with a non zero potential]}$$

This has the form of the Schrödinger equation for the harmonic oscillator wavefunction (eqn 8B.3). The difference in adjacent energy levels is:

$$E_1 - E_0 = \hbar\omega \text{ [8B.5]} \qquad \text{where} \quad \omega=\left(\frac{9V_0}{I}\right)^{1/2} \text{ [adapting 8B.4]}$$

If the displacements are sufficiently large, the potential energy does not rise as rapidly with the angle as would a harmonic potential (i.e. the cosine potential energy is not well approximated by the first few terms of its expansion). Each successive energy level would become lower than that of a harmonic oscillator, so the energy levels would become progressively closer together.

Question. The next term in the Taylor series for the potential energy is $-\frac{27V_0}{8}x$. Treat this as a perturbation to the harmonic oscillator wavefunction and compute the first-order correction to the energy.

8C Rotational motion

Answers to discussion questions

D8C.1 In quantum mechanics, particles are said to have wave characteristics. The fact of the existence of the particle then requires that the wavelengths of the waves representing it be such that the wave does not experience destructive interference in

its motion around a closed loop. This means that a whole number of wavelengths must fit on the circumference of the ring [8C.3]:

$$n\lambda = 2\pi r$$

making the wavelength quantized. This in turn requires the angular momentum and energy to be quantized (eqns 8C.4 and 8C.5 respectively). Mathematically, this comes out in the cyclic boundary condition discussed in Section 8C.1(b), which restricts the constant m_l in the wavefunction $\psi(\phi) = e^{im_l\phi}$ to be an integer. That way, the wavefunction has the same value at ϕ and at $\phi + 2\pi$—as it must since these two 'different' angles represent the same angular position. The constant m_l must be an integer because that ensures $e^{2\pi i m_l} = 1$.

D8C.3 A vector can be used to represent angular momentum. The vector's length represents the magnitude of the angular momentum, and its direction is along the axis of rotation. In classical mechanics, both the length and direction are well defined and continuously variable. In quantum mechanics, however, the length is quantized. The orientation of the vector is both restricted and indefinite in that one component of the vector (call it the z component) is quantized, while the other two components are indefinite. The result is that the classical mechanical vector is replaced by a set of cones that represent vectors allowed by quantum constraints. (See Section 8C.2(e).) Each cone is the set of vectors of a given (quantized) length and definite z component; the cone is generated by taking one such vector and 'sweeping' it through all possible directions in the xy plane. (The 'sweeping' does not correspond to any sort of motion. At this stage, the model describes time-independent rotational states.)

Solutions to exercises

E8C.1(a) The magnitude of angular momentum is [8C.21a]

$$\langle l^2 \rangle^{1/2} = \{l(l+1)\}^{1/2}\hbar = (1\times 2)^{1/2}\hbar = \boxed{2^{1/2}\hbar}$$

Possible projections on to an arbitrary axis are [8C.21b]

$$\langle l_z \rangle = m_l\hbar$$

where $m_l = 0$ or ± 1. So possible projections include $\boxed{0, \pm\hbar}$

E8C.2(a) Normalization requires [7B.4a]

$$\int \psi^* \psi \, d\tau = 1$$

That is, using the unnormalized wavefunction [8C.11]

$$\int_0^{2\pi} N^2 e^{-im_l\phi} e^{im_l\phi} \, d\phi = N \int_0^{2\pi} d\phi = 2\pi N^2 = 1$$

Thus $N^2 = \dfrac{1}{2\pi}$ $\qquad N = \boxed{\left(\dfrac{1}{2\pi}\right)^{1/2}}$

E8C.3(a) The energy levels of a particle on a ring are given by [8C.6b]

$$E = \frac{m_l^2\hbar^2}{2I} = \frac{m_l^2\hbar^2}{2mr^2}, \quad m_l = 0, \pm 1, \pm 2, \ldots$$

The minimum excitation energy is the energy difference between the ground state ($m = 0$) and the first excited level ($m = +1$). So the minimum excitation energy is

$$\frac{(1^2 - 0^2)\hbar^2}{2mr^2} \qquad \frac{(1.0546 \times 10^{-34}\ \text{J s})^2}{2 \times (1\ 6726 \times 10^{-27}\ \text{k}\sigma) \times (100 \times 10^{-12}\ \text{m})^2} = \boxed{3.32 \times 10^{-22}\ \text{J}}.$$

E8C.4(a) The energy levels are [8C.20]

$$E = \frac{l(l+1)\hbar^2}{2I}, \quad l = 0, 1, 2, \ldots$$

The minimum energy to start it rotating is the minimum excitation energy, the energy to take it from the motionless $l = 0$ to the rotating $l = 1$ state:

$$\Delta E = E_1 = \frac{1 \times 2 \times (1.0546 \times 10^{-34}\ \text{Js})^2}{2 \times (5.27 \times 10^{-47}\ \text{kgm}^2)} = \boxed{2.11 \times 10^{\ 22}\ \text{J}}$$

E8C.5(a) The energy levels are [8C.20]

$$E = \frac{l(l+1)\hbar^2}{2I}, \quad l = 0, 1, 2, \ldots$$

So the excitation energy is

$$\Delta E = E_2 - E_1 = \frac{(2 \times 3 - 1 \times 2) \times (1.0546 \times 10^{-34}\ \text{Js})^2}{2 \times (5.27 \times 10^{-47}\ \text{kgm}^2)} = \boxed{4.22 \times 10^{-22}\ \text{J}}$$

E8C.6(a) The energy levels are [8C.20]

$$E = \frac{l(l+1)\hbar^2}{2I} \quad l = 0, 1, 2, \ldots$$

So the minimum energy ***allowed*** for this system is zero—but that corresponds to rest, not rotation. So the minimum energy of rotation occurs for the state that has $l = 1$. The angular momentum in that state is [8C.21a]

$$\{l(l+1)\}^{1/2}\hbar = \boxed{2^{1/2}\hbar} = 2^{1/2} \times (1.0546 \times 10^{-34}\ \text{Js}) = \boxed{1.49 \times 10^{-34}\ \text{Js}}.$$

Comment. Note that the moment of inertia does not enter into the result. Thus the minimum angular momentum is the same for a molecule of CH_4 as for a molecule of C_{60} as for a football.

E8C.7(a) The diagrams are drawn by forming a vector of length $\{l(l+1)\}^{1/2}$ and with a projection m_j on the z-axis. (See Fig. 8C.1). Each vector represents the edge of a cone around the z-axis (that for $m_j = 0$ represents the side view of a disc perpendicular to z).

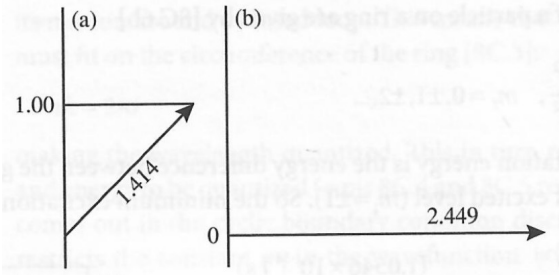

Figure 8C.1

E8C.8(a) The rotational energy depends only on the quantum number l [8C.20], but there are distinct states for every allowed value of m_l, which can range from $-l$ to l in integer steps. For $l=3$, possible values of $m_l=-3, -2, -1, 0, 1, 2, 3$. There are 7 such values, so the degeneracy is $\boxed{7}$.

Solutions to problems

P8C.1 The angular momentum states are defined by the quantum number $m_l=0, \pm1, \pm2$, etc. The energy of state m_l is [8C.6b]

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

and the angular momentum is [8C.4]

$$J_z = m_l\hbar$$

(a) If there are 22 electrons, two in each of the lowest 11 states, then the highest occupied states are $m_l=\pm5$, so,

$$J_z = \pm5\hbar = \pm5\times(1.0546\times10^{-34}\,\text{Js}) = \pm5.275\times10^{-34}\,\text{Js}.$$

and $E_{\pm5} = \dfrac{25\hbar^2}{2I}$.

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

$$I = mr^2 = (9.11\times10^{-31}\,\text{kg})\times(440\times10^{-12}\,\text{m})^2 = 1.76\times10^{-49}\,\text{kg m}^2.$$

Hence $E_{\pm5} = \dfrac{25\times(1.055\times10^{-34}\,\text{Js})^2}{2\times(1.76\times10^{-49}\,\text{kg m}^2)} = \boxed{7.89\times10^{-19}\,\text{J}}$.

(b) The lowest unoccupied energy level is $m_l=\pm6$, which has energy

$$E_{\pm6} = \frac{36\times(1.055\times10^{-34}\,\text{Js})^2}{2\times(1.76\times10^{-49}\,\text{kg m}^2)} = 1.14\times10^{-18}\,\text{J}.$$

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

$$h\nu = \Delta E \quad \text{so} \quad \nu = \frac{\Delta E}{h} = \frac{(11.4-7.89)\times10^{-19}\,\text{J}}{6.626\times10^{-34}\,\text{J}} = \boxed{5.2\times10^{14}\,\text{Hz}}.$$

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

P8C.3 In each case, if the function is an eigenfunction of the operator, the eigenvalue is also the expectation value; if it is not an eigenfunction we form [7C.11]

$$\langle\Omega\rangle = \int \psi^* \hat{\Omega} \psi \, d\tau$$

(a) $\hat{l}_z e^{i\phi} = \frac{\hbar}{i}\frac{d}{d\phi} e^{i\phi}$ [8C.13b] $= \hbar e^{i\phi}$; hence $l_z = \boxed{+\hbar}$

(b) $\hat{l}_z e^{-2i\phi} = \frac{\hbar}{i}\frac{d}{d\phi} e^{-2i\phi} = -2\hbar e^{-2i\phi}$; hence $l_z = \boxed{-2\hbar}$

(c) $\langle l_z \rangle \propto \int_0^{2\pi} \cos\phi \left(\frac{\hbar}{i}\frac{d}{d\phi}\cos\phi \right) d\phi \propto -\frac{\hbar}{i}\int_0^{2\pi} \cos\phi \sin\phi \, d\phi = \boxed{0}$

(d) $\langle l_z \rangle = N^2 \int_0^{2\pi} (\cos\chi e^{i\phi} + \sin\chi e^{-i\phi})^* \left(\frac{\hbar}{i}\frac{d}{d\phi} \right) \times (\cos\chi e^{i\phi} + \sin\chi e^{-i\phi}) d\phi$

$$= \frac{\hbar}{i} N^2 \int_0^{2\pi} (\cos\chi e^{-i\phi} + \sin\chi e^{i\phi}) \times (i\cos\chi e^{i\phi} - i\sin\chi e^{-i\phi}) d\phi$$

$$= \hbar N^2 \int_0^{2\pi} (\cos^2\chi - \sin^2\chi + \cos\chi \sin\chi [e^{2i\phi} - e^{-2i\phi}]) d\phi$$

$$= \hbar N^2 (\cos^2\chi - \sin^2\chi) \times (2\pi) = 2\pi\hbar N^2 \cos 2\chi$$

We must evaluate the normalization constant:

$$N^2 \int_0^{2\pi} (\cos\chi e^{i\phi} + \sin\chi e^{-i\phi})^* (\cos\chi e^{i\phi} + \sin\chi e^{-i\phi}) d\phi = 1$$

$$1 = N^2 \int_0^{2\pi} (\cos^2\chi + \sin^2\chi + \cos\chi \sin\chi [e^{2i\phi} + e^{-2i\phi}]) d\phi$$

$$= 2\pi N^2 (\cos^2\chi + \sin^2\chi) = 2\pi N^2 \quad \text{so } N^2 \quad \frac{1}{2\pi}$$

Therefore

$$\langle l_z \rangle = \boxed{\hbar \cos 2\chi} \; [\chi \text{ is a parameter}]$$

For the kinetic energy we use $\hat{E}_k = \frac{\hat{J}_z^2}{2I}$ [8C.1] $= -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$ [8C.1b]

(a) $\hat{E}_k e^{i\phi} = -\frac{\hbar^2}{2I}(i^2 e^{i\phi}) = \frac{\hbar^2}{2I} e^{i\phi}$; hence $\langle E_k \rangle = \boxed{\frac{\hbar^2}{2I}}$

(b) $\hat{E}_k e^{-2i\phi} = -\frac{\hbar^2}{2I}(2i)^2 e^{-2i\phi} = \frac{4\hbar^2}{2I} e^{2i\phi}$; hence $\langle E_k \rangle = \boxed{\frac{2\hbar^2}{I}}$

(c) $\hat{E}_k \cos\phi = -\frac{\hbar^2}{2I}(-\cos\phi) = \frac{\hbar^2}{2I}\cos\phi$; hence $\langle E_k \rangle = \boxed{\frac{\hbar^2}{2I}}$

(d) $\hat{E}_k (\cos\chi e^{i\phi} + \sin\chi e^{-i\phi}) = -\frac{\hbar^2}{2I}(-\cos\chi e^{i\phi} - \sin\chi e^{-i\phi}) = \frac{\hbar^2}{2I}(\cos\chi e^{i\phi} + \sin\chi e^{-i\phi})$

and hence $\langle E_k \rangle = \boxed{\frac{\hbar^2}{2I}}$

Comment. All of these functions are eigenfunctions of the kinetic energy operator, which is also the total energy or hamiltonian operator, since the potential energy is zero for this system.

P8C.5

$$E=\frac{l(l+1)\hbar^2}{2I}\ [8C.20]=\frac{l(l+1)\hbar^2}{2\mu R^2}\quad [I=\mu R^2]$$

$$=\left(\frac{l(l+1)\times(1.055\times10^{-34}\,\mathrm{Js})^2}{(2)\times(1.6605\times10^{-27}\,\mathrm{kg})\times(160\times10^{-12}\,\mathrm{m})^2}\right)\times\left(\frac{1}{1.008}+\frac{1}{126.90}\right)$$

Therefore,

$$E=l(l+1)\times(1.31\times10^{-22}\,\mathrm{J})$$

The energies may be expressed in terms of equivalent frequencies with

$$\nu=\frac{E}{h}=(1.509\times10^{33}\,\mathrm{J^{-1}\,s^{-1}})E.$$

Hence, the energies and equivalent frequencies are

	0		2	3
$10^{22}\,E/\mathrm{J}$	0	2.62	7.86	15.72
ν/GHz	0	396	1188	2376

P8C.7 Call the integral I:

$$I=\int_0^{\pi}\int_0^{2\pi}Y_{3,3}^{*}Y_{3,3}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi=\left(\frac{1}{64}\right)\times\left(\frac{35}{\pi}\right)\int_0^{\pi}\sin^6\theta\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi\ \ [\text{Table 8C.1}]$$

Integration over $\mathrm{d}\phi$ yields a factor of 2π. Noting that $\sin\theta\,\mathrm{d}\theta=\mathrm{d}\cos\theta$, and that $\sin^2\theta=1-\cos^2\theta$, the integral becomes

$$I=\left(\frac{1}{64}\right)\times\left(\frac{35}{\pi}\right)\times(2\pi)\int_{-1}^{1}(1-\cos^2\theta)^3\,\mathrm{d}\cos\theta$$

Letting $x=\cos\theta$ and expanding the integrand, we have

$$I=\frac{35}{32}\int_{-1}^{1}(1-3x^2+3x^4-x^6)\mathrm{d}x=\frac{35}{32}\left(x-x^3+\tfrac{3}{5}x^5-\tfrac{1}{7}x^7\right)\Big|_{-1}^{1}=\frac{35}{32}\times\frac{32}{35}=\boxed{1}$$

P8C.9

$$\mathbf{l}=\hat{\mathbf{r}}\times\hat{\mathbf{p}}=\begin{vmatrix}\mathbf{i}&\mathbf{j}&\mathbf{k}\\ x&y&z\\ p_x&p_y&p_z\end{vmatrix}\quad[\text{see any book treating the vector product of vectors}]$$

$$=\mathbf{i}(\hat{y}\hat{p}_x-\hat{z}\hat{p}_y)+\mathbf{j}(\hat{z}\hat{p}_x-\hat{x}\hat{p}_z)+\mathbf{k}(\hat{x}\hat{p}_y-\hat{y}\hat{p}_x)$$

Therefore,

$$\hat{l}_x = (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y) = \boxed{\frac{\hbar}{\mathrm{i}}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)}$$

$$\hat{l}_y = (\hat{z}\hat{p}_x - \hat{x}\hat{p}_z) = \frac{\hbar}{\mathrm{i}}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{l}_z = (\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) = \boxed{\frac{\hbar}{\mathrm{i}}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)}$$

We have used $\hat{p}_x = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}$, etc. The commutator of l_x and l_y is $(l_x l_y - l_y l_x)$. We note that the operations always imply operation on a function. We form

$$\hat{l}_x\hat{l}_y f = -\hbar^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)f$$

$$= -\hbar^2\left(yz\frac{\partial^2 f}{\partial z\partial x} + y\frac{\partial f}{\partial x} - yx\frac{\partial^2 f}{\partial z^2} - z^2\frac{\partial^2 f}{\partial y\partial x} + zx\frac{\partial^2 f}{\partial z\partial y}\right)$$

and $\hat{l}_y\hat{l}_x f = -\hbar^2\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)f$

$$= -\hbar^2\left(zy\frac{\partial^2 f}{\partial x\partial z} - z^2\frac{\partial^2 f}{\partial x\partial y} - xy\frac{\partial^2 f}{\partial z^2} + xz\frac{\partial^2 f}{\partial z\partial y} + x\frac{\partial f}{\partial y}\right)$$

Since multiplication and differentiation are each commutative, the results of the operation $l_x l_y$ and $l_y l_x$ differ only in one term. For $\hat{l}_y\hat{l}_x f, x\frac{\partial f}{\partial y}$ replaces $y\frac{\partial f}{\partial x}$. Hence, the commutator of the operations, $(\hat{l}_x\hat{l}_y - \hat{l}_y\hat{l}_x)$ is $-\hbar^2\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)$ or $\boxed{-\frac{\hbar}{\mathrm{i}}\hat{l}_z}$.

Similarly $(\hat{l}_y\hat{l}_z - \hat{l}_z\hat{l}_y) = -\frac{\hbar}{\mathrm{i}}\hat{l}_x$ and $(\hat{l}_z\hat{l}_x - \hat{l}_x\hat{l}_z) = -\frac{\hbar}{\mathrm{i}}\hat{l}_y$.

P8C.11 We are to show that $[l^2, l_z] = [l_x^2 + l_y^2 + l_z^2, l_z] = [l_x^2, l_z] + [l_y^2, l_z] + [l_z^2, l_z] = 0$

The three commutators are:

$$[\hat{l}_z^2, \hat{l}_z] = \hat{l}_z^2\hat{l}_z - \hat{l}_z\hat{l}_z^2 = \hat{l}_z^3 - \hat{l}_z^3 = 0$$

$$[\hat{l}_x^2, \hat{l}_z] = = \hat{l}_x^2\hat{l}_z - \hat{l}_z\hat{l}_x^2 = \hat{l}_x^2\hat{l}_z - \hat{l}_x\hat{l}_z\hat{l}_x + \hat{l}_x\hat{l}_z\hat{l}_x - \hat{l}_z\hat{l}_x^2$$

$$= \hat{l}_x(\hat{l}_x\hat{l}_z - \hat{l}_z\hat{l}_x) + (\hat{l}_x\hat{l}_z - \hat{l}_z\hat{l}_x)\hat{l}_x = \hat{l}_x[\hat{l}_x, \hat{l}_z] + [\hat{l}_x, \hat{l}_z]\hat{l}_x$$

$$= l_x(-\mathrm{i}\hbar l_y) + (-\mathrm{i}\hbar\hat{l}_y)\hat{l}_x = -\mathrm{i}\hbar(\hat{l}_x\hat{l}_y + \hat{l}_y\hat{l}_x) \quad [8C.27]$$

$$[\hat{l}_y^2, \hat{l}_z] = \hat{l}_y^2\hat{l}_z - \hat{l}_z\hat{l}_y^2 = \hat{l}_y^2\hat{l}_z - \hat{l}_y\hat{l}_z\hat{l}_y + \hat{l}_y\hat{l}_z\hat{l}_y - \hat{l}_z\hat{l}_y^2$$

$$= \hat{l}_y(\hat{l}_y\hat{l}_z - \hat{l}_z\hat{l}_y) + (\hat{l}_y\hat{l}_z - \hat{l}_z\hat{l}_y)\hat{l}_y = \hat{l}_y[\hat{l}_y, \hat{l}_z] + [\hat{l}_y, \hat{l}_z]\hat{l}_y$$

$$= l_y(\mathrm{i}\hbar l_x) + (\mathrm{i}\hbar l_x)l_y = \mathrm{i}\hbar(\hat{l}_y\hat{l}_x + \hat{l}_x\hat{l}_y) \quad [8C.27]$$

Therefore, $[\hat{l}^2, \hat{l}_z] = -\mathrm{i}\hbar(\hat{l}_x\hat{l}_y + \hat{l}_y\hat{l}_x) + \mathrm{i}\hbar(\hat{l}_x\hat{l}_y + \hat{l}_y\hat{l}_x) + 0 = 0$

We may also conclude that $[\hat{l}^2, \hat{l}_x] = 0$ and $[\hat{l}^2, \hat{l}_y] = 0$ because l_x, l_y, and l_z occur symmetrically in l^2.

I8.5 (a) Expectation values for $\langle x\rangle$, $\langle x^2\rangle$, $\langle p\rangle$, and $\langle p^2\rangle$ were evaluated in Exercises 8A.5 and 8A.6.

$$\langle x\rangle = \frac{L}{2} \text{ for all } n$$

$$\langle x^2\rangle = L^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right)$$

$$\Delta x = \left[L^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right) - \frac{L^2}{4}\right]^{1/2} = \boxed{L\left(\frac{1}{12} - \frac{1}{2\pi^2 n^2}\right)^{1/2}}$$

$$\langle p\rangle = 0 \text{ for all } n$$

$$\langle p^2\rangle = \frac{n^2h^2}{4L^2}$$

$$\Delta p = \left(\frac{n^2h^2}{4L^2}\right)^{1/2} = \boxed{\frac{nh}{2L}}$$

$$\Delta p\Delta x = \frac{nh}{2L} \times L\left(\frac{1}{12} - \frac{1}{2\pi^2 n^2}\right)^{1/2} = \frac{nh}{2\sqrt{3}}\left(1 - \frac{1}{24\pi^2 n^2}\right)^{1/2} > \frac{\hbar}{2}$$

(b) $\langle x\rangle = 0$ for all v [8B.12a, or by symmetry]

and $\langle x^2\rangle = \left(v+\frac{1}{2}\right)\times\left(\frac{\hbar^2}{mk_f}\right)^{1/2}$ [8B.12] $= \left(v+\frac{1}{2}\right)\times\frac{\hbar}{\omega m}$ [8B.4]

so $\Delta x = \left|\left\{\left(v+\frac{1}{2}\right)\frac{\hbar}{\omega m}\right\}^{1/2}\right|$

$\langle p\rangle = 0$ [by symmetry, or by noting that the integrand is an odd function of x]

and $\langle p^2\rangle = 2m\langle E_k\rangle = 2m\int_{-\infty}^{+\infty}\psi^*\hat{E}_k\psi\,dx$

$$\hat{E}_k = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\ [7C.5] = -\frac{\hbar^2}{2m\alpha^2}\frac{d^2}{dy^2} = -\frac{\hbar\omega}{2}\frac{d^2}{dy^2},\quad \left[x=\alpha y,\ \alpha^2=\frac{\hbar}{m\omega}\right]$$

which implies that

$$\hat{E}_k\psi = -\frac{\hbar\omega}{2}\left(\frac{d^2\psi}{dy^2}\right)$$

We then use $\psi = NHe^{-y^2/2}$, and obtain

$$\frac{d^2\psi}{dy^2} = N\frac{d^2}{dy^2}(He^{-y^2/2}) = N\{H'' - 2yH' - H + y^2H\}e^{-y^2/2}$$

From Table 8B.1

$$H_v'' - 2yH_v' = -2vH_v$$

$$y^2H_v = y\left(\tfrac{1}{2}H_{v+1} + vH_{v-1}\right) = \tfrac{1}{2}\left(\tfrac{1}{2}H_{v+2} + (v+1)H_v\right) + v\left(\tfrac{1}{2}H_v + (v-1)H_{v-2}\right)$$
$$= \tfrac{1}{4}H_{v+2} + v(v-1)H_{v-2} + \left(v+\tfrac{1}{2}\right)H_v$$

Hence, $\frac{d^2\psi}{dy^2} = N\left[\tfrac{1}{4}H_{v+2} + v(v-1)H_{v-2} - \left(v+\frac{1}{2}\right)H_v\right]e^{-y^2/2}$

Therefore,

$$\langle E_k\rangle = N_v^2\left(-\frac{\hbar\omega}{2}\right)\int_{-\infty}^{+\infty}H_v\left\{\frac{1}{4}H_{v+2} + v(v-1)H_{v-2} - \left(v+\frac{1}{2}\right)H_v\right\}e^{-y^2}\,dx\,[dx=\alpha dy]$$

$$= \alpha N_v^2\left(-\frac{1}{2}\hbar\omega\right)\left\{0+0-\left(v+\frac{1}{2}\right)\pi^{1/2}2^v v!\right\}\ [\text{Hermite polynomials orthogonal}]$$

$$= \frac{1}{2}\left(v+\frac{1}{2}\right)\hbar\omega\quad\left[N_v^2 = \frac{1}{\alpha\pi^{1/2}2^v v!},\ \text{Example 8B.2}\right]$$

and $\langle p^2\rangle = \left(v+\frac{1}{2}\right)m\hbar\omega$

$$\Delta p = \left|\left\{\left(v+\frac{1}{2}\right)\hbar\omega m\right\}^{1/2}\right|$$

$$\Delta p\Delta x = \left(v+\frac{1}{2}\right)\hbar \geq \frac{\hbar}{2}$$

Comment. Both results show a consistency with the uncertainty principle in the form $\Delta p\Delta q \geq \frac{\hbar}{2}$ as given in eqn 7C.13.