12 Quantum theory: techniques and applications

Solutions to exercises

Discussion questions

E12.1(b) The correspondence principle states that in the limit of very large quantum numbers quantum mechanics merges with classical mechanics. An example is a molecule of a gas in a box. At room temperature, the particle-in-a-box quantum numbers corresponding to the average energy of the gas molecules ($\frac{1}{2}$ kT per degree of freedom) are extremely large; consequently the separation between the levels is relatively so small (n is always small compared to n^2, compare eqn 12.10 to eqn 12.4) that the energy of the particle is effectively continuous, just as in classical mechanics. We may also look at these equations from the point of view of the mass of the particle. As the mass of the particle increases to macroscopic values, the separation between the energy levels approaches zero. The quantization disappears as we know it must. Tennis balls do not show quantum mechanical effects. (Except those served by Pete Sampras.) We can also see the correspondence principle operating when we examine the wavefunctions for large values of the quantum numbers. The probability density becomes uniform over the path of motion, which is again the classical result. This aspect is discussed in more detail in Section 12.1(c).

The harmonic oscillator provides another example of the correspondence principle. The same effects mentioned above are observed. We see from Fig. 12.22 of the text that probability distribution for large values on n approaches the classical picture of the motion. (Look at the graph for $n = 20$.)

E12.2(b) The physical origin of tunnelling is related to the probability density of the particle which according to the Born interpretation is the square of the wavefunction that represents the particle. This interpretation requires that the wavefunction of the system be everywhere continuous, event at barriers. Therefore, if the wavefunction is non-zero on one side of a barrier it must be non-zero on the other side of the barrier and this implies that the particle has tunnelled through the barrier. The transmission probability depends upon the mass of the particle (specifically $m^{1/2}$, through eqns 12.24 and 12.28): the greater the mass the smaller the probability of tunnelling. Electrons and protons have small masses, molecular groups large masses; therefore, tunnelling effects are more observable in process involving electrons and protons.

E12.3(b) The essential features of the derivation are:

(1) The separation of the hamiltonian into large (unperturbed) and small (perturbed) parts which are independent of each other.

(2) The expansion of the wavefunctions and energies as a power series in an unspecified parameters, λ, which in the end effectively cancels or is set equal to 1.

(3) The calculation of the first-order correction to the energies by an integration of the perturbation over the zero-order wavefunctions.

(4) The expansion of the first-order correction to the wavefunction in terms of the complete set of functions which are a solution of the unperturbed Schrodinger equation.

(5) The calculation of the second-order correction to the energies with use of the corrected first order wavefunctions.

See *Justification* 12.7 and *Further reading* for a more complete discussion of the method.

Numerical exercises

E12.4(b) $$E = \frac{n^2h^2}{8m_eL^2}$$

$$\frac{h^2}{8m_eL^2} = \frac{(6.626\times10^{-34}\,\text{J s})^2}{8(9.109\times10^{-31}\,\text{kg})\times(1.50\times10^{-9}\,\text{m})^2} = 2.67\overline{8}\times10^{-20}\,\text{J}$$

Conversion factors

$$\frac{E}{\text{kJ mol}^{-1}} = \frac{N_A}{10^3}E/\text{J}$$

$$1\,\text{eV} = 1.602\times10^{-19}\,\text{J}$$

$$1\,\text{cm}^{-1} = 1.986\times10^{-23}\,\text{J}$$

(a) $$E_3 - E_1 = (9-1)\frac{h^2}{8m_eL^2} = 8(2.678\times10^{-20}\,\text{J})$$

$$= \boxed{2.14\times10^{-19}\,\text{J}} = \boxed{129\,\text{kJ mol}^{-1}} = \boxed{1.34\,\text{eV}} = \boxed{1.08\times10^4\,\text{cm}^{-1}}$$

(b) $$E_7 - E_6 = (49-36)\frac{h^2}{8m_eL^2}$$

$$= 13(2.678\times10^{-20}\,\text{J})$$

$$= \boxed{3.48\times10^{-19}\,\text{J}} = \boxed{210\,\text{kJ mol}^{-1}} = \boxed{2.17\,\text{eV}} = \boxed{1.75\times10^4\,\text{cm}^{-1}}$$

E12.5(b) The probability is

$$P = \int \psi^*\psi\,\text{d}x = \frac{2}{L}\int \sin^2\left(\frac{n\pi x}{L}\right)\text{d}x = \frac{2\Delta x}{L}\sin^2\left(\frac{n\pi x}{L}\right)$$

where $\Delta x = 0.02L$ and the function is evaluated at $x = 0.66L$.

(a) For $n = 1$

$$P = \frac{2(0.02L)}{L}\sin^2(0.66\pi) = \boxed{0.03\overline{1}}$$

(b) For $n = 2$

$$P = \frac{2(0.02L)}{L}\sin^2[2(0.66\pi)] = \boxed{0.02\overline{9}}$$

E12.6(b) The expectation value is

$$\langle\hat{p}\rangle = \int \psi^*\hat{p}\psi\,\text{d}x$$

but first we need $\hat{p}\psi$

$$\hat{p}\psi = -\text{i}\hbar\frac{\text{d}}{\text{d}x}\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right) = -\text{i}\hbar\left(\frac{2}{L}\right)^{1/2}\frac{n\pi}{L}\cos\left(\frac{n\pi x}{L}\right)$$

so $\langle \hat{p} \rangle = \dfrac{-2\mathrm{i}\hbar n\pi}{L^2} \displaystyle\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x = \boxed{0}$ for all n

$$\langle \hat{p}^2 \rangle = 2m\langle \hat{H} \rangle = 2mE_n = \frac{h^2n^2}{4L^2}$$

for all n. So for $n = 2$

$$\langle \hat{p}^2 \rangle = \boxed{\frac{h^2}{L^2}}$$

E12.7(b) $n = 5$

$$\psi_5 = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{5\pi x}{L}\right)$$

$$P(x) \propto \psi_5^2 \propto \sin^2\left(\frac{5\pi x}{L}\right)$$

Maxima and minima in $P(x)$ correspond to $\dfrac{\mathrm{d}P(x)}{\mathrm{d}x} = 0$

$$\frac{\mathrm{d}}{\mathrm{d}x}P(x) \propto \frac{\mathrm{d}\psi^2}{\mathrm{d}x} \propto \sin\left(\frac{5\pi x}{L}\right)\cos\left(\frac{5\pi x}{L}\right) \propto \sin\left(\frac{10\pi x}{L}\right) \quad (2\sin\alpha\cos\alpha = \sin 2\alpha)$$

$$\sin\theta = 0 \quad \text{when } \theta = 0, \pi, 2\pi, \ldots = n'\pi \quad (n' = 0, 1, 2, \ldots)$$

$$\frac{10\pi x}{L} = n'\pi \quad n' \le 10$$

$$x = \frac{n'L}{10}$$

Minima at $x = 0,\ x = L$

Maxima and minima alternate: maxima correspond to

$$n' = 1, 3, 5, 7, 9 \qquad x = \boxed{\frac{L}{10}}, \boxed{\frac{3L}{10}}, \boxed{\frac{L}{2}}, \boxed{\frac{7L}{10}}, \boxed{\frac{9L}{10}}$$

E12.8(b) The energy levels are

$$E_{n_1,n_2,n_3} = \frac{(n_1^2 + n_2^2 + n_3^2)h^2}{8mL^2} = E_1(n_1^2 + n_2^2 + n_3^2)$$

where E_1 combines all constants besides quantum numbers. The minimum value for all the quantum numbers is 1, so the lowest energy is

$$E_{1,1,1} = 3E_1$$

The question asks about an energy 14/3 times this amount, namely $14E_1$. This energy level can be obtained by any combination of allowed quantum numbers such that

$$n_1^2 + n_2^2 + n_3^2 = 14 = 3^2 + 2^2 + 1^2$$

The degeneracy, then, is $\boxed{6}$, corresponding to $(n_1, n_2, n_3) = (1, 2, 3), (2, 1, 3), (1, 3, 2), (2, 3, 1), (3, 1, 2)$, or $(3, 2, 1)$.

E12.9(b) $E = \frac{3}{2}kT$ is the average translational energy of a gaseous molecule (see Chapter 20).

$$E = \tfrac{3}{2}kT = \frac{(n_1^2 + n_2^2 + n_3^2)h^2}{8mL^2} = \frac{n^2h^2}{8mL^2}$$

$$E = \left(\tfrac{3}{2}\right) \times (1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (300\,\mathrm{K}) = 6.21\overline{4} \times 10^{-21}\,\mathrm{J}$$

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

If $L^3 = 1.00\,\mathrm{m^3}$, $L^2 = 1.00\,\mathrm{m^2}$

$$\frac{h^2}{8mL^2} = \frac{(6.626 \times 10^{-34}\,\mathrm{J\,s})^2}{(8) \times \left(\frac{0.02802\,\mathrm{kg\,mol^{-1}}}{6.022\times 10^{23}\,\mathrm{mol^{-1}}}\right) \times (1.00\,\mathrm{m^2})} = 1.18\overline{0} \times 10^{-42}\,\mathrm{J}$$

$$n^2 = \frac{6.21\overline{4} \times 10^{-21}\,\mathrm{J}}{1.180 \times 10^{-42}\,\mathrm{J}} = 5.26\overline{5} \times 10^{21}; \qquad n = \boxed{7.26 \times 10^{10}}$$

$$\Delta E = E_{n+1} - E_n = E_{7.26\times 10^{10}+1} - E_{7.26\times 10^{10}}$$

$$\Delta E = (2n+1) \times \left(\frac{h^2}{8mL^2}\right) = [(2) \times (7.26 \times 10^{10} + 1)] \times \left(\frac{h^2}{8mL^2}\right) = \frac{14.5\overline{2} \times 10^{10}h^2}{8mL^2}$$

$$= (14.5\overline{2} \times 10^{10}) \times (1.18\overline{0} \times 10^{-42}\,\mathrm{J}) = \boxed{1.71 \times 10^{-31}\,\mathrm{J}}$$

The de Broglie wavelength is obtained from

$$\lambda = \frac{h}{p} = \frac{h}{mv}\ \text{[Section 11.2]}$$

The velocity is obtained from

$$E_\mathrm{K} = \tfrac{1}{2}mv^2 = \tfrac{3}{2}kT = 6.21\overline{4} \times 10^{-21}\,\mathrm{J}$$

$$v^2 = \frac{6.21\overline{4} \times 10^{-21}\,\mathrm{J}}{\left(\frac{1}{2}\right) \times \left(\frac{0.02802\,\mathrm{kg\,mol^{-1}}}{6.022\times 10^{23}\,\mathrm{mol^{-1}}}\right)} = 2.67\overline{1} \times 10^5; \qquad v = 517\,\mathrm{m\,s^{-1}}$$

$$\lambda = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{(4.65 \times 10^{-26}\,\mathrm{kg}) \times (517\,\mathrm{m\,s^{-1}})} = 2.75 \times 10^{-11}\,\mathrm{m} = \boxed{27.5\,\mathrm{pm}}$$

The conclusion to be drawn from all of these calculations is that the translational motion of the nitrogen molecule can be described classically. The energy of the molecule is essentially continuous, $\frac{\Delta E}{E} \lll 1$.

E12.10(b) The zero-point energy is

$$E_0 = \tfrac{1}{2}\hbar\omega = \tfrac{1}{2}\hbar\left(\frac{k}{m}\right)^{1/2} = \tfrac{1}{2}(1.0546 \times 10^{-34}\,\mathrm{J\,s}) \times \left(\frac{285\,\mathrm{N\,m^{-1}}}{5.16 \times 10^{-26}\,\mathrm{kg}}\right)^{1/2}$$

$$= \boxed{3.92 \times 10^{-21}\,\mathrm{J}}$$

E12.11(b) The difference in adjacent energy levels is

$$\Delta E = \hbar\omega = \hbar\left(\frac{k}{m}\right)^{1/2} \quad \text{so} \quad k = \frac{m(\Delta E)^2}{\hbar^2} = \frac{(2.88\times10^{-25}\,\text{kg})\times(3.17\times10^{-21}\,\text{J})^2}{(1.0546\times10^{-34}\,\text{J s})^2}$$

$$k = \boxed{260\,\text{N m}^{-1}}$$

E12.12(b) The difference in adjacent energy levels, which is equal to the energy of the photon, is

$$\Delta E = \hbar\omega = h\nu \quad \text{so} \quad \hbar\left(\frac{k}{m}\right)^{1/2} = \frac{hc}{\lambda}$$

$$\text{and } \lambda = \frac{hc}{\hbar}\left(\frac{k}{m}\right)^{1/2} = 2\pi c\left(\frac{m}{k}\right)^{1/2}$$

$$= 2\pi(2.998\times10^{8}\,\text{m s}^{-1})\times\left(\frac{(15.9949\,\text{u})\times(1.66\times10^{-27}\,\text{kg u}^{-1})}{544\,\text{N m}^{-1}}\right)^{1/2}$$

$$\lambda = 1.32\times10^{-5}\,\text{m} = \boxed{13.2\,\mu\text{m}}$$

E12.13(b) The difference in adjacent energy levels, which is equal to the energy of the photon, is

$$\Delta E = \hbar\omega = h\nu \quad \text{so} \quad \hbar\left(\frac{k}{m}\right)^{1/2} = \frac{hc}{\lambda}$$

$$\text{and } \lambda = \frac{hc}{\hbar}\left(\frac{k}{m}\right)^{1/2} = 2\pi c\left(\frac{m}{k}\right)^{1/2}$$

Doubling the mass, then, increases the wavelength by $2^{1/2}$. So taking the result from Ex. 12.12(b), the new wavelength is

$$\lambda = 2^{1/2}(13.2\,\mu\text{m}) = \boxed{18.7\,\mu\text{m}}$$

E12.14(b) $\omega = \left(\frac{g}{l}\right)^{1/2}$ [elementary physics]

$$\Delta E = \hbar\omega = h\nu$$

(a) $\Delta E = h\nu = (6.626\times10^{-34}\,\text{J Hz}^{-1})\times(33\times10^{3}\,\text{Hz}) = \boxed{2.2\times10^{-29}\,\text{J}}$

(b) $\Delta E = \hbar\omega = \hbar\left(\frac{k}{m_{\text{eff}}}\right)^{1/2} \quad \left[\frac{1}{m_{\text{eff}}} = \frac{1}{m_1} + \frac{1}{m_2} \text{ with } m_1 = m_2\right]$

For a two-particle oscillator m_{eff}, replaces m in the expression for ω. (See Chapter 16 for a more complete discussion of the vibration of a diatomic molecule.)

$$\Delta E = \hbar\left(\frac{2k}{m}\right)^{1/2} = (1.055\times10^{-34}\,\text{J s})\times\left(\frac{(2)\times(1177\,\text{N m}^{-1})}{(16.00)\times(1.6605\times10^{-27}\,\text{kg})}\right)^{1/2}$$

$$= \boxed{3.14\times10^{-20}\,\text{J}}$$

E12.15(b) The first excited-state wavefunction has the form

$$\psi = 2N_1 y \exp\left(-\tfrac{1}{2}y^2\right)$$

where N_1 is a collection of constants and $y \equiv x\left(\frac{m\omega}{\hbar}\right)^{1/2}$. To see if it satisfies Schrödinger's equation, we see what happens when we apply the energy operator to this function

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \tfrac{1}{2}m\omega^2x^2\psi$$

We need derivatives of ψ

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = \frac{\mathrm{d}\psi}{\mathrm{d}y}\frac{\mathrm{d}y}{\mathrm{d}x} = \left(\frac{m\omega}{\hbar}\right)^{1/2}(2N_1)\times(1-y^2)\times\exp\left(-\tfrac{1}{2}y^2\right)$$

and $\dfrac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \dfrac{\mathrm{d}^2\psi}{\mathrm{d}y^2}\left(\dfrac{\mathrm{d}y}{\mathrm{d}x}\right)^2 = \left(\dfrac{m\omega}{\hbar}\right)\times(2N_1)\times(-3y+y^3)\times\exp\left(-\tfrac{1}{2}y^2\right) = \left(\dfrac{m\omega}{\hbar}\right)\times(y^2-3)\psi$

So $\hat{H}\psi = -\dfrac{\hbar^2}{2m}\times\left(\dfrac{m\omega}{\hbar}\right)\times(y^2-3)\psi + \tfrac{1}{2}m\omega^2x^2\psi$

$$= -\tfrac{1}{2}\hbar\omega\times(y^2-3)\times\psi + \tfrac{1}{2}\hbar\omega y^2\psi = \tfrac{3}{2}\hbar\omega\psi$$

Thus, ψ is an eigenfunction of $\hat{H}$ (i.e. it obeys the Schrödinger equation) with eigenvalue

$$E = \boxed{\tfrac{3}{2}\hbar\omega}$$

E12.16(b) The zero-point energy is

$$E_0 = \tfrac{1}{2}\hbar\omega = \tfrac{1}{2}\hbar\left(\frac{k}{m_{\mathrm{eff}}}\right)^{1/2}$$

For a homonuclear diatomic molecule, the effective mass is half the mass of an atom, so

$$E_0 = \tfrac{1}{2}(1.0546\times10^{-34}\,\mathrm{J\,s})\times\left(\frac{2293.8\,\mathrm{N\,m^{-1}}}{\tfrac{1}{2}(14.0031\,\mathrm{u})\times(1.66054\times10^{-27}\,\mathrm{kg\,u^{-1}})}\right)^{1/2}$$

$$E_0 = \boxed{2.3421\times10^{-20}\,\mathrm{J}}$$

E12.17(b) Orthogonality requires that

$$\int\psi_m^*\psi_n\,\mathrm{d}\tau = 0$$

if $m \neq n$.

Performing the integration

$$\int\psi_m^*\psi_n\,\mathrm{d}\tau = \int_0^{2\pi}N\mathrm{e}^{-\mathrm{i}m\phi}N\mathrm{e}^{\mathrm{i}n\phi}\,\mathrm{d}\phi = N^2\int_0^{2\pi}\mathrm{e}^{\mathrm{i}(n-m)\phi}\,\mathrm{d}\phi$$

If $m \neq n$, then

$$\int \psi_m^* \psi_n \, \mathrm{d}\tau = \frac{N^2}{\mathrm{i}(n-m)} \mathrm{e}^{\mathrm{i}(n-m)\phi} \Big|_0^{2\pi} = \frac{N^2}{\mathrm{i}(n-m)}(1-1) = 0$$

Therefore, they are orthogonal.

E12.18(b) The magnitude of angular momentum is

$$\langle \hat{L}^2 \rangle^{1/2} = (l(l+1))^{1/2}\hbar = (2(3))^{1/2}(1.0546 \times 10^{-34}\,\mathrm{J\,s}) = \boxed{2.58 \times 10^{-34}\,\mathrm{J\,s}}$$

Possible projections on to an arbitrary axis are

$$\langle \hat{L}_z \rangle = m_l \hbar$$

where $m_l = 0$ or ± 1 or ± 2. So possible projections include

$$\boxed{0,\ \pm 1.0546 \times 10^{-34}\,\mathrm{J\,s}\ \text{and}\ 2.1109 \times 10^{-34}\,\mathrm{J\,s}}$$

E12.19(b) The cones are constructed as described in Section 12.7(c) and Fig. 12.36 of the text; their edges are of length $\{6(6+1)\}^{1/2} = 6.48$ and their projections are $m_j = +6, +5, \ldots, -6$. See Fig. 12.1(a).

The vectors follow, in units of $\hbar$. From the highest-pointing to the lowest-pointing vectors (Fig. 12.1(b)), the values of m_l are 6, 5, 4, 3, 2, 1, 0, −1, −2, −3, −4, −5, and −6.

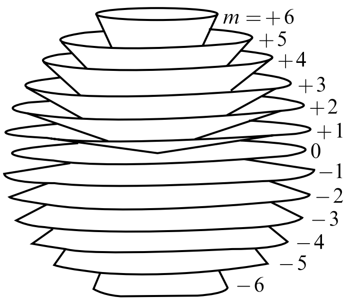

Figure 12.1(a)

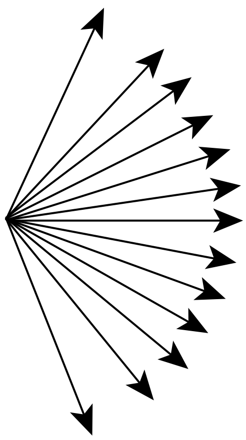

Figure 12.1(b)

Solutions to problems

Solutions to numerical problems

P12.4

$$E = \frac{l(l+1)\hbar^2}{2I}[12.65] = \frac{l(l+1)\hbar^2}{2m_{\text{eff}}R^2} \quad [I = m_{\text{eff}}R^2,\ m_{\text{eff}} \text{ in place of } m]$$

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

$$\left[\frac{1}{m_{\text{eff}}} = \frac{1}{m_1}+\frac{1}{m_2}\right]$$

The energies may be expressed in terms of equivalent frequencies with $\nu = \frac{E}{h} = 1.509\times10^{33}\,E$.

Therefore,

$$E = l(l+1)\times(1.31\times10^{-22}\,\text{J}) = l(l+1)\times(198\,\text{GHz})$$

Hence, the energies and equivalent frequencies are

l	0	1	2	3
$10^{22}\,E/\text{J}$	$\boxed{0}$	$\boxed{2.62}$	$\boxed{7.86}$	$\boxed{15.72}$
ν/GHz	0	396	1188	2376

P12.6 Treat the gravitational potential energy as a perturbation in the energy operator:

$$H^{(1)} = mgx.$$

The first-order correction to the ground-state energy, E_1, is:

$$E_1{}^{(1)} = \int_0^L \Psi_1^{(0)*}H^{(1)}\Psi_1^{(0)}\text{d}x = \int_0^L \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{\pi x}{L}\right)mgx\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{\pi x}{L}\right)dx,$$

$$E_1{}^{(1)} = \frac{2mg}{L}\int_0^L x\sin^2\left(\frac{\pi x}{L}\right)dx,$$

$$E_1{}^{(1)} = \frac{2mg}{L}\left(\frac{x^2}{4}-\frac{xL}{2\pi}\cos\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi x}{L}\right)-\frac{L^2}{4\pi^2}\cos^2\left(\frac{\pi x}{L}\right)\right)\Bigg|_0^L,$$

$$E_1{}^{(1)} = \boxed{\tfrac{1}{2}mgL}$$

Not surprisingly, this amounts to the energy perturbation evaluated at the midpoint of the box. For $m = m_e$, $E_1{}^{(1)}/\text{L} = 4.47\times10^{-30}\,\text{J m}^{-1}$.

Solutions to theoretical problems

P12.8 $$-\left(\frac{\hbar^2}{2m}\right)\times\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi = E\psi \quad [V=0]$$

We try the solution $\psi = X(x)Y(y)Z(z)$

$$-\frac{\hbar^2}{2m}(X''YZ + XY''Z + XYZ'') = EXYZ$$

$$-\frac{\hbar^2}{2m}\left(\frac{X''}{X}+\frac{Y''}{Y}+\frac{Z''}{Z}\right) = E$$

$\frac{X''}{X}$ depends only on x; therefore, when x changes only this term changes, but the sum of the three terms is constant. Therefore, $\frac{X''}{X}$ must also be constant. We write

$$-\frac{\hbar^2}{2m}\frac{X''}{X} = E^X, \quad \text{with analogous terms for } y,\ z$$

Hence we solve

$$\left.\begin{aligned} -\frac{\hbar^2}{2m}X'' &= E^X X \\ -\frac{\hbar^2}{2m}Y'' &= E^Y Y \\ -\frac{\hbar^2}{2m}Z'' &= E^Z Z \end{aligned}\right\} E = E^X + E^Y + E^Z, \quad \psi = XYZ$$

The three-dimensional equation has therefore separated into three one-dimensional equations, and we can write

$$\boxed{E = \frac{h^2}{8m}\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}+\frac{n_3^2}{L_3^2}\right)} \quad n_1, n_2, n_3 = 1, 2, 3, \ldots$$

$$\psi = \left(\frac{8}{L_1L_2L_3}\right)^{1/2}\sin\left(\frac{n_1\pi x}{L_1}\right)\sin\left(\frac{n_2\pi y}{L_2}\right)\sin\left(\frac{n_3\pi z}{L_3}\right)$$

For a cubic box

$$\boxed{E = (n_1^2+n_2^2+n_3^2)\frac{h^2}{8mL^2}}$$

P12.10 The wavefunctions in each region (see Fig. 12.2(a)) are (eqns 12.22–12.25):

$$\psi_1(x) = e^{ik_1x} + B_1e^{-ik_2x}$$
$$\psi_2(x) = A_2e^{k_2x} + B_2e^{-k_2x}$$
$$\psi_3(x) = A_3e^{ik_3x}$$

with the above choice of $A_1 = 1$ the transmission probability is simply $T = |A_3|^2$. The wavefunction coefficients are determined by the criteria that both the wavefunctions and their first derivatives w/r/t

x be continuous at potential boundaries

$$\psi_1(0) = \psi_2(0); \quad \psi_2(L) = \psi_3(L)$$
$$\frac{d\psi_1(0)}{dx} = \frac{d\psi_2(0)}{dx}; \quad \frac{d\psi_2(L)}{dx} = \frac{d\psi_3(L)}{dx}$$

These criteria establish the algebraic relationships:

$$1 + B_1 - A_2 - B_2 = 0$$
$$(-ik_1 - k_2)A_2 + (-ik_1 + k_2)B_2 + 2ik_1 = 0$$
$$A_2 e^{k_2 L} + B_2 e^{-k_2 L} - A_3 e^{ik_3 L} = 0$$
$$A_2 k_2 e^{k_2 L} - B_2 k_2 e^{-k_2 L} - iA_3 k_3 e^{ik_3 L} = 0$$

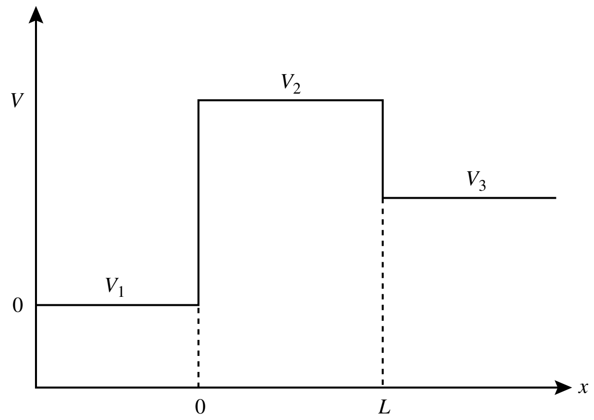

Figure 12.2(a)

Solving the simultaneous equations for A_3 gives

$$A_3 = \frac{4k_1 k_2\, e^{ik_3 L}}{(ia + b)\, e^{k_2 L} - (ia - b)\, e^{-k_2 L}}$$

where $a = k_2^2 - k_1 k_3$ and $b = k_1 k_2 + k_2 k_3$.

since $\sinh(z) = (e^z - e^{-z})/2$ or $e^z = 2\sinh(z) + e^{-z}$, substitute $e^{k_2 L} = 2\sinh(k_2 L) + e^{-k_2 L}$ giving:

$$A_3 = \frac{2k_1 k_2 e^{ik_3 L}}{(ia + b)\sinh(k_2 L) + b\, e^{-k_2 L}}$$

$$T = |A_3|^2 = A_3 \bar{A}_3 = \frac{4k_1^2 k_2^2}{(a^2 + b^2)\sinh^2(k_2 L) + b^2}$$

where $a^2 + b^2 = (k_1^2 + k_2^2)(k_2^2 + k_3^2)$ and $b^2 = k_2^2(k_1 + k_3)^2$

(b) In the special case for which $V_1 = V_3 = 0$, eqns 12.22 and 12.25 require that $k_1 = k_3$. Additionally,

$$\left(\frac{k_1}{k_2}\right)^2 = \frac{E}{V_2 - E} = \frac{\varepsilon}{1 - \varepsilon} \text{ where } \varepsilon = E/V_2.$$

$$a^2 + b^2 = (k_1^2 + k_2^2)^2 = k_2^4 \left\{1 + \left(\frac{k_1}{k_2}\right)^2\right\}^2$$

$$b^2 = 4k_1^2\, k_2^2$$

$$\frac{a^2+b^2}{b^2} = \frac{k_2^2\left\{1+\left(\frac{k_1}{k_2}\right)^2\right\}^2}{4k_1^2} = \frac{1}{4\varepsilon(1-\varepsilon)}$$

$$T = \frac{b^2}{b^2+(a^2+b^2)\sinh^2(k_2L)} = \frac{1}{1+\left(\frac{a^2+b^2}{b^2}\right)\sinh^2(k_2L)}$$

$$T = \left\{1+\frac{\sinh^2(k_2L)}{4\varepsilon(1-\varepsilon)}\right\}^{-1} = \left\{1+\frac{(e^{k_2L}-e^{-k_2L})^2}{16\varepsilon(1-\varepsilon)}\right\}^{-1}$$

This proves eqn 12.28a where $V_1 = V_3 = 0$

In the high wide barrier limit $k_2L \gg 1$. This implies both that e^{-k_2L} is negligibly small compared to e^{k_2L} and that 1 is negligibly small compared to $e^{2\,k_2L}/\{16\varepsilon(1-\varepsilon)\}$. The previous equation simplifies to

$$T = 16\,\varepsilon(1-\varepsilon)e^{-2\,k_2L} \quad \text{[eqn12.28b]}$$

(c)

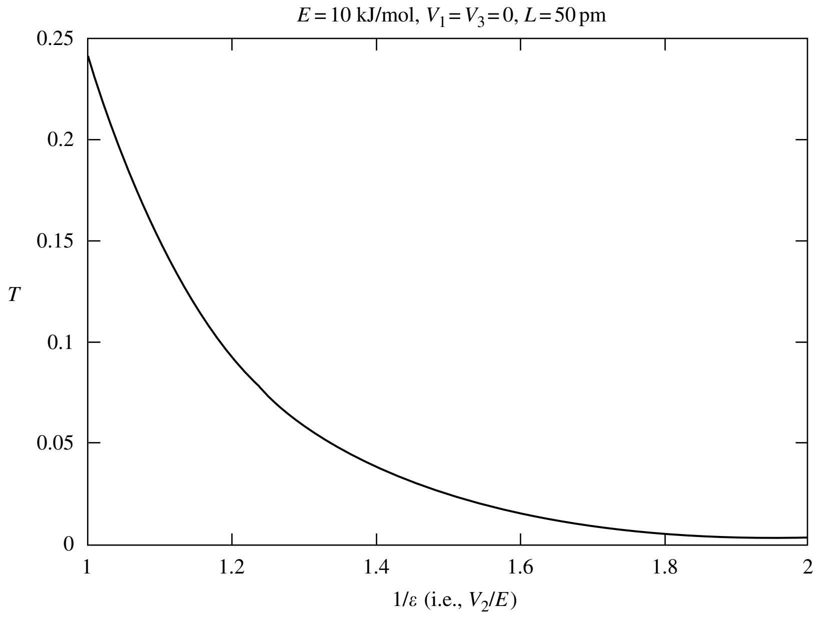

Figure 12.2(b)

P12.12 The Schrödinger equation is $-\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi$

and we write $\psi = e^{-gx^2}$, so $\dfrac{d\psi}{dx} = -2gxe^{-gx^2}$

$$\frac{d^2\psi}{dx^2} = -2ge^{-gx^2} + 4g^2x^2e^{-gx^2} = -2g\psi + 4g^2x^2\psi$$

$$\left(\frac{\hbar^2 g}{m}\right)\psi - \left(\frac{2\hbar^2 g^2}{m}\right)x^2\psi + \tfrac{1}{2}kx^2\psi = E\psi$$

$$\left[\left(\frac{\hbar^2 g}{m}\right) - E\right]\psi + \left(\tfrac{1}{2}k - \frac{2\hbar^2 g^2}{m}\right)x^2\psi = 0$$

This equation is satisfied if

$$E = \frac{\hbar^2 g}{m} \quad \text{and} \quad 2\hbar^2 g^2 = \tfrac{1}{2}mk, \quad \text{or} \quad \boxed{g = \tfrac{1}{2}\left(\frac{mk}{\hbar^2}\right)^{1/2}}$$

Therefore,

$$E = \tfrac{1}{2}\hbar\left(\frac{k}{m}\right)^{1/2} = \tfrac{1}{2}\hbar\omega \quad \text{if } \omega = \left(\frac{k}{m}\right)^{1/2}$$

P12.14

$$\langle x^n\rangle = \alpha^n\langle y^n\rangle = \alpha^n\int_{-\infty}^{+\infty}\psi y^n\psi\,\mathrm{d}x = \alpha^{n+1}\int_{-\infty}^{+\infty}\psi^2 y^n\,\mathrm{d}y \quad [x = \alpha y]$$

$$\langle x^3\rangle \propto \int_{-\infty}^{+\infty}\psi^2 y^3\,\mathrm{d}y = \boxed{0} \text{ by symmetry} \quad [y^3 \text{ is an odd function of } y]$$

$$\langle x^4\rangle = \alpha^5\int_{-\infty}^{+\infty}\psi y^4\psi\,\mathrm{d}y$$

$$y^4\psi = y^4 N H_v \mathrm{e}^{-y^2/2}$$

$$\begin{aligned}
y^4 H_v &= y^3\left(\tfrac{1}{2}H_{v+1} + vH_{v-1}\right) = y^2\left[\tfrac{1}{2}\left(\tfrac{1}{2}H_{v+2} + (v+1)H_v\right) + v\left(\tfrac{1}{2}H_v + (v-1)H_{v-2}\right)\right] \\
&= y^2\left[\tfrac{1}{4}H_{v+2} + \left(v + \tfrac{1}{2}\right)H_v + v(v-1)H_{v-2}\right] \\
&= y\left[\tfrac{1}{4}\left(\tfrac{1}{2}H_{v+3} + (v+2)H_{v+1}\right) + \left(v + \tfrac{1}{2}\right) \times \left(\tfrac{1}{2}H_{v+1} + vH_{v-1}\right)\right. \\
&\quad \left. + v(v-1) \times \left(\tfrac{1}{2}H_{v-1} + (v-2)H_{v-3}\right)\right] \\
&= y\left(\tfrac{1}{8}H_{v+3} + \tfrac{3}{4}(v+1)H_{v+1} + \tfrac{3}{2}v^2H_{v-1} + v(v-1) \times (v-2)H_{v-3}\right)
\end{aligned}$$

Only yH_{v+1} and yH_{v-1} lead to H_v and contribute to the expectation value (since H_v is orthogonal to all except H_v) [Table 12.1]; hence

$$\begin{aligned}
y^4 H_v &= \tfrac{3}{4}y\{(v+1)H_{v+1} + 2v^2 H_{v-1}\} + \cdots \\
&= \tfrac{3}{4}\left[(v+1)\left(\tfrac{1}{2}H_{v+2} + (v+1)H_v\right) + 2v^2\left(\tfrac{1}{2}H_v + (v-1)H_{v-2}\right)\right] + \cdots \\
&= \tfrac{3}{4}\{(v+1)^2 H_v + v^2 H_v\} + \cdots \\
&= \tfrac{3}{4}(2v^2 + 2v + 1)H_v + \cdots
\end{aligned}$$

Therefore

$$\int_{-\infty}^{+\infty}\psi y^4\psi\,\mathrm{d}y = \tfrac{3}{4}(2v^2 + 2v + 1)N^2\int_{-\infty}^{+\infty}H_v^2\mathrm{e}^{-y^2}\,\mathrm{d}y = \frac{3}{4\alpha}(2v^2 + 2v + 1)$$

and so

$$\langle x^4\rangle = (\alpha^5) \times \left(\frac{3}{4\alpha}\right) \times (2v^2 + 2v + 1) = \boxed{\tfrac{3}{4}(2v^2 + 2v + 1)\alpha^4}$$

P12.17 $V = -\dfrac{e^2}{4\pi\varepsilon_0}\cdot\dfrac{1}{r}$ [13.5 with $Z = 1$] $= \alpha x^b$ with $b = -1$ $[x \to r]$

Since $2\langle T\rangle = b\langle V\rangle$ [12.45, $\langle T\rangle \equiv E_K$]

$$2\langle T\rangle = -\langle V\rangle$$

Therefore, $\boxed{\langle T\rangle = -\tfrac{1}{2}\langle V\rangle}$

P12.18 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

$$\langle\Omega\rangle = \int \psi^*\hat{\Omega}\psi\,\mathrm{d}\tau \text{ [11.39]}$$

(a) $\hat{l}_z e^{i\phi} = \dfrac{\hbar}{i}\dfrac{d}{d\phi}e^{i\phi} = \hbar e^{i\phi}$; hence $J_z = \boxed{+\hbar}$

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

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

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

$$\begin{aligned}N^2&\int_0^{2\pi}(\cos\chi e^{i\phi} + \sin\chi e^{-i\phi})^*(\cos\chi e^{i\phi} + \sin\chi e^{-i\phi})\,d\phi\\
&= N^2\int_0^{2\pi}(\cos^2\chi + \sin^2\chi + \cos\chi\sin\chi[e^{2i\phi} + e^{-2i\phi}])\,d\phi\\
&= 2\pi N^2(\cos^2\chi + \sin^2\chi) = 2\pi N^2 = 1 \quad \text{if } N^2 = \frac{1}{2\pi}\end{aligned}$$

Therefore

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

For the kinetic energy we use $\hat{T} \equiv \hat{E}_K = \dfrac{\hat{J}_z^2}{2I}$[12.47] $= -\dfrac{\hbar^2}{2I}\dfrac{d^2}{d\phi^2}$ [12.52]

(a) $\hat{T}e^{i\phi} = -\dfrac{\hbar^2}{2I}(i^2e^{i\phi}) = \dfrac{\hbar^2}{2I}e^{i\phi}$; hence $\langle T\rangle = \boxed{\dfrac{\hbar^2}{2I}}$

(b) $\hat{T}e^{-2i\phi} = -\dfrac{\hbar^2}{2I}(2i)^2e^{-2i\phi} = \dfrac{4\hbar^2}{2I}e^{-2i\phi}$; hence $\langle T\rangle = \boxed{\dfrac{2\hbar^2}{I}}$

(c) $\hat{T}\cos\phi = -\dfrac{\hbar^2}{2I}(-\cos\phi) = \dfrac{\hbar^2}{2I}\cos\phi$; hence $\langle T\rangle = \boxed{\dfrac{\hbar^2}{2I}}$

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

and hence $\langle T\rangle = \boxed{\dfrac{\hbar^2}{2I}}$

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.

P12.20

$$\int_0^{\pi}\int_0^{2\pi} Y_{3,3}^{*}Y_{3,3}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = \int_0^{\pi}\left(\tfrac{1}{64}\right)\times\left(\frac{35}{\pi}\right)\sin^6\theta\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi \text{ [Table 12.3]}$$

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

$$[\sin\theta\,\mathrm{d}\theta = \mathrm{d}\cos\theta,\ \sin^2\theta = 1-\cos^2\theta]$$

$$= \tfrac{35}{32}\int_{-1}^{1}(1-3x^2+3x^4-x^6)\,\mathrm{d}x \quad [x=\cos\theta]$$

$$= \tfrac{35}{32}\left(x - x^3 + \tfrac{3}{5}x^5 - \tfrac{1}{7}x^7\right)\Big|_{-1}^{1} = \frac{35}{32}\times\frac{32}{35} = \boxed{1}$$

P12.22

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\frac{\partial^2}{\partial x^2}f = -a^2 f \qquad \frac{\partial^2}{\partial y^2}f = -b^2 f \qquad \frac{\partial^2}{\partial y^2}f = -c^2 f$$

and f is an eigenfunction with eigenvalue $\boxed{-(a^2+b^2+c^2)}$

P12.25 **(a)** Suppose that a particle moves classically at the constant speed v. It starts at $x = 0$ at $t = 0$ and at $t = \tau$ is at position $x = L$. $v = \dfrac{L}{\tau}$ and $x = vt$.

$$\langle x\rangle = \frac{1}{\tau}\int_{t=0}^{\tau} x\,\mathrm{d}t = \frac{1}{\tau}\int_{t=0}^{\tau} vt\,\mathrm{d}t$$

$$= \frac{v}{\tau}\int_{t=0}^{\tau} t\,\mathrm{d}t = \frac{v}{2\tau}t^2\Big|_{t=0}^{\tau}$$

$$= \frac{v\tau^2}{2\tau} = \frac{v\tau}{2} = \boxed{\frac{L}{2} = \langle x\rangle}$$

$$\langle x^2\rangle = \frac{1}{\tau}\int_{t=0}^{\tau} x^2\,\mathrm{d}t = \frac{v^2}{\tau}\int_{t=0}^{\tau} t^2\,\mathrm{d}t$$

$$= \frac{v^2}{3\tau}t^3\Big|_{t=0}^{\tau} = \frac{(v\tau)^2}{3} = \frac{L^2}{3}$$

$$\boxed{\langle x^2\rangle^{1/2} = \frac{L}{3^{1/2}}}$$

(b) $$\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \quad \text{for } 0 \le x \le L \text{ [12.7]}$$

$$\langle x \rangle_n = \int_{x=0}^{L} \psi_n^* x \psi_n \, \mathrm{d}x = \frac{2}{L}\int_0^L x \sin^2\left(\frac{n\pi x}{L}\right) \mathrm{d}x$$

$$= \frac{2}{L}\left[\frac{x^2}{4} - \frac{x\sin\left(\frac{2n\pi x}{L}\right)}{4(n\pi/L)} - \frac{\cos\left(\frac{2n\pi x}{L}\right)}{8(n\pi/L)^2}\right]_{x=0}^{x=L}$$

$$= \frac{2}{L}\left[\frac{L^2}{4}\right] = \boxed{\frac{L}{2} = \langle x \rangle_n}$$

This agrees with the classical result.

$$\langle x^2 \rangle_n = \int_{x=0}^{L} \psi_n^* x^2 \psi_n \, \mathrm{d}x = \frac{2}{L}\int_{x=0}^{L} x^2 \sin^2\left(\frac{n\pi x}{L}\right) \mathrm{d}x$$

$$= \frac{2}{L}\left[\frac{x^3}{6} - \left(\frac{x^2}{4(n\pi/L)} - \frac{1}{8(n\pi/L)^3}\right)\sin\left(\frac{2n\pi x}{L}\right) - \frac{x\cos\left(\frac{2n\pi x}{L}\right)}{8(n\pi/L)^2}\right]_{x=0}^{x=L}$$

$$= \frac{2}{L}\left[\frac{L^3}{6} - \frac{L}{8(n\pi/L)^2}\right]$$

$$= \frac{L^2}{3} - \frac{1}{4(n\pi/L)^2}$$

$$\boxed{\langle x^2 \rangle_n^{1/2} = \left(\frac{L^2}{3} - \frac{1}{4(n\pi/L)^2}\right)^{1/2}}$$

$$\lim_{n\to\infty} \langle x^2 \rangle_n^{1/2} = \frac{L}{3^{1/2}}$$

This agrees with the classical result.

P12.27 **(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:

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

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

(b) The relationship between energy and frequency is:

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

(c) The frequency computed in this problem is about twice that computed in problem 12.26b, suggesting that *the absorption spectrum of a linear polyene shifts to* $\boxed{\textit{lower}}$ *frequency as the number of conjugated atoms* $\boxed{\textit{increases}}$. The reason for this is apparent if we look at the terms in the energy expression (which is proportional to the frequency) that change with the number of conjugated atoms, N. The energy and frequency are inversely proportional to L^2 and directly proportional to $(n+1)^2 - n^2 = 2n + 1$, where n is the quantum number of the highest occupied state. Since n is proportional to N (equal to $N/2$) and L is approximately proportional to N (strictly to $N - 1$), the energy and frequency are approximately proportional to N^{-1}.

P12.29 In effect, we are looking for the vibrational frequency of an O atom bound, with a force constant equal to that of free CO, to an infinitely massive and immobile protein complex. The angular frequency is

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

where m is the mass of the O atom.

$$m = (16.0\,\text{u})(1.66 \times 10^{-27}\,\text{kg}\,\text{u}^{-1}) = 2.66 \times 10^{-26}\,\text{kg},$$

and k is the same force constant as in problem 12.2, namely $1902\,\text{N}\,\text{m}^{-1}$:

$$\omega = \left(\frac{1902\,\text{N}\,\text{m}^{-1}}{2.66 \times 10^{-26}\,\text{kg}}\right)^{1/2} = \boxed{2.68 \times 10^{14}\,\text{s}^{-1}}.$$