Discussion questions

8B.2 In what ways does the quantum mechanical description of a harmonic oscillator merge with its classical description at high quantum numbers?

8B.3 What is the physical reason for the existence of a zero-point vibrational energy?

8C.1 Discuss the physical origin of quantization of energy for a particle confined to motion around a ring.

8C.3 Describe the vector model of angular momentum in quantum mechanics. What features does it capture? What is its status as a model?

Exercises

8B.2(a) For a certain harmonic oscillator of effective mass 1.33×10^{-25} kg, the difference in adjacent energy levels is 4.82 zJ. Calculate the force constant of the oscillator.

8B.3(a) Calculate the wavelength of a photon needed to excite a transition between neighbouring energy levels of a harmonic oscillator of effective mass equal to that of a proton ($1.0078m_u$) and force constant $855\,\mathrm{N\,m^{-1}}$.

8B.5(a) Calculate the minimum excitation energies of (i) a pendulum of length 1.0 m on the surface of the Earth, (ii) the balance-wheel of a clockwork watch ($\nu = 5$ Hz).

8B.6(a) Assuming that the vibrations of a $^{35}Cl_2$ molecule are equivalent to those of a harmonic oscillator with a force constant $k_f = 329\,\mathrm{N\,m^{-1}}$, what is the zero-point energy of vibration of this molecule? The effective mass of a homonuclear diatomic molecule is half its total mass, and $m(^{35}Cl) = 34.9688m_u$.

8B.8(a) What are the most probable displacements of a harmonic oscillator with $v = 1$?

8C.1(a) The rotation of a molecule can be represented by the motion of a point mass moving over the surface of a sphere. Calculate the magnitude of its angular momentum when $l = 1$ and the possible components of the angular momentum on an arbitrary axis. Express your results as multiples of $\hbar$.

8C.3(a) Calculate the minimum excitation energy of a proton constrained to rotate in a circle of radius 100 pm around a fixed point.

8C.4(a) The moment of inertia of a CH_4 molecule is $5.27 \times 10^{-47}\,\mathrm{kg\,m^2}$. What is the minimum energy needed to start it rotating?

8C.6(a) What is the magnitude of the angular momentum of a CH_4 molecule when it is rotating with its minimum energy?

8C.8(a) The number of states corresponding to a given energy plays a crucial role in atomic structure and thermodynamic properties. Determine the degeneracy of a body rotating with $l = 3$.

Problems

8B.1 The mass to use in the expression for the vibrational frequency of a diatomic molecule is the effective mass $\mu = m_A m_B/(m_A + m_B)$, where m_A and m_B are the masses of the individual atoms. The following data on the infrared absorption wavenumbers (wavenumbers in $\mathrm{cm^{-1}}$) of molecules are taken from *Spectra of diatomic molecules*, G. Herzberg, van Nostrand (1950):

$H^{35}Cl$	$H^{81}Br$	HI	CO	NO
2990	2650	2310	2170	1904

Calculate the force constants of the bonds and arrange them in order of increasing stiffness.

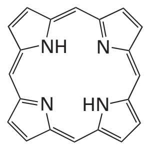
8B.5 Calculate the mean kinetic energy of a harmonic oscillator by using the relations in Table 8B.1.

Table 8B.1 The Hermite polynomials, $H_v(y)$

v	$H_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$

8B.11 The potential energy of the rotation of one CH_3 group relative to its neighbour in ethane can be expressed as $V(\phi) = V_0 \cos 3\phi$. Show that for small displacements the motion of the group is quantized and calculate the energy of excitation from $v = 0$ to $v = 1$. What do you expect to happen to the energy levels and wavefunctions as the excitation increases to high quantum numbers?

8C.1 The particle on a ring is a useful model for the motion of electrons around the porphine ring (**2**), the conjugated macrocycle that forms the structural basis of the haem group and the chlorophylls.



2 Porphine (porphin) ring

We may treat the group as a circular ring of radius 440 pm, with 22 electrons in the conjugated system moving along the perimeter of the ring. In the ground state of the molecule each state is occupied by two electrons. (a) Calculate the energy and angular momentum of an electron in the highest occupied level. (b) Calculate the frequency of radiation that can induce a transition between the highest occupied and lowest unoccupied levels.

8C.3 Evaluate the z-component of the angular momentum and the kinetic energy of a particle on a ring that is described by the (unnormalized) wavefunctions (a) $e^{i\phi}$, (b) $e^{-2i\phi}$, (c) $\cos\phi$, and (d) $(\cos\chi)e^{i\phi} + (\sin\chi)e^{-i\phi}$.

8C.5 Calculate the energies of the first four rotational levels of $^1H^{127}I$ free to rotate in three dimensions, using for its moment of inertia $I = \mu R^2$, with $\mu = m_H m_I/(m_H + m_I)$ and $R = 160$ pm.

8C.7 Confirm that $Y_{3,+3}$ is normalized to 1. (The integration required is over the surface of a sphere.)

8C.8 Show that the function $f = \cos ax \cos by \cos cz$ is an eigenfunction of ∇^2, and determine its eigenvalue.

8C.9 Develop an expression (in Cartesian coordinates) for the quantum mechanical operators for the three components of angular momentum starting from the classical definition of angular momentum, $\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}$. Show that any two of the components do not mutually commute, and find their commutator.