

TOPIC 7B Dynamics of microscopic systems

Discussion questions

7B.1 Describe how a wavefunction summarizes the dynamical properties of a system and how those properties may be predicted.

7B.2 Discuss the relation between probability amplitude, probability density, and probability.

7B.3 Describe the constraints that the Born interpretation puts on acceptable wavefunctions.

7B.4 What are the advantages of working with normalized wavefunctions?

Exercises

7B.1(a) Consider a time-independent wavefunction of a particle moving in three-dimensional space. Identify the variables upon which the wavefunction depends.

7B.1(b) Consider a time-dependent wavefunction of a particle moving in two-dimensional space. Identify the variables upon which the wavefunction depends.

7B.2(a) Consider a time-independent wavefunction of a hydrogen atom. Identify the variables upon which the wavefunction depends. Use spherical polar coordinates.

7B.2(b) Consider a time-dependent wavefunction of a helium atom. Identify the variables upon which the wavefunction depends. Use spherical polar coordinates.

7B.3(a) An unnormalized wavefunction for a light atom rotating around a heavy atom to which it is bonded is $\psi(\phi) = e^{i\phi}$ with $0 \leq \phi \leq 2\pi$. Normalize this wavefunction.

7B.3(b) An unnormalized wavefunction for an electron in a carbon nanotube of length L is $\sin(2\pi x/L)$. Normalize this wavefunction.

7B.4(a) For the system described in Exercise 7B.3(a), what is the probability of finding the light atom in the volume element $d\phi$ at $\phi = \pi$?

7B.4(b) For the system described in Exercise 7B.3(b), what is the probability of finding the electron in the range dx at $x = L/2$?

7B.5(a) For the system described in Exercise 7B.3(a), what is the probability of finding the light atom between $\phi = \pi/2$ and $\phi = 3\pi/2$?

7B.5(b) For the system described in Exercise 7B.3(b), what is the probability of finding the electron between $x = L/4$ and $x = L/2$?

Problems

7B.1 Normalize the following wavefunctions: (i) $\sin(n\pi x/L)$ in the range $0 \leq x \leq L$, where $n = 1, 2, 3, \dots$ (this wavefunction can be used to describe delocalized electrons in a linear polyene), (ii) a constant in the range $-L \leq x \leq L$, (iii) $e^{-r/a}$ in three-dimensional space (this wavefunction can be used to describe the electron in the ion He^+), (iv) $x e^{-r/2a}$ in three-dimensional space. *Hint:* The volume element in three dimensions is $d\tau = r^2 dr \sin \theta d\theta d\phi$, with $0 \leq r < \infty$, $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$.

7B.2 Two (unnormalized) excited state wavefunctions of the H atom are

$$(i) \psi(r) = \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \quad (ii) \psi(r, \theta, \phi) = r \sin \theta \cos \phi e^{-r/2a_0}$$

(a) Normalize both functions to 1. (b) Confirm that these two functions are mutually orthogonal.

7B.3 A particle free to move along one dimension x (with $0 \leq x < \infty$) is described by the unnormalized wavefunction $\psi(x) = e^{-ax}$ with $a = 2 \text{ m}^{-1}$. What is the probability of finding the particle at a distance $x \geq 1 \text{ m}$?

7B.4 The ground-state wavefunction for a particle confined to a one-dimensional box of length L is $\psi = (2/L)^{1/2} \sin(\pi x/L)$. Suppose the box is

* These problems were supplied by Charles Trapp and Carmen Giunta.

10.0 nm long. Calculate the probability that the particle is (a) between $x=4.95$ nm and 5.05 nm, (b) between $x=1.95$ nm and 2.05 nm, (c) between $x=9.90$ nm and 10.00 nm, (d) in the right half of the box, (e) in the central third of the box.

7B.5 The ground-state wavefunction of a hydrogen atom is $\psi = (1/\pi a_0^3)^{1/2} e^{-r/a_0}$ where $a_0 = 53$ pm (the Bohr radius). (a) Calculate the probability that the electron will be found somewhere within a small sphere of radius 1.0 pm centred on the nucleus. (b) Now suppose that the same sphere is located at $r = a_0$. What is the probability that the electron is inside it?

7B.6 Atoms in a chemical bond vibrate around the equilibrium bond length. An atom undergoing vibrational motion is described by the wavefunction $\psi(x) = Ne^{-x^2/2a^2}$, where a is a constant and $-\infty < x < \infty$. (a) Normalize this function. (b) Calculate the probability of finding the particle in the range $-a \leq x \leq a$. *Hint:* The integral encountered in part (ii) is the error function. It is provided in most mathematical software packages.

7B.7 Suppose that the state of the vibrating atom in Problem 7B.6 is described by the wavefunction $\psi(x) = Nxe^{-x^2/2a^2}$. Where is the most probable location of the particle?

TOPIC 7C The principles of quantum theory

Discussion questions

7C.1 Suggest how the general shape of a wavefunction can be predicted without solving the Schrödinger equation explicitly.

7C.2 Describe the relationship between operators and observables in quantum mechanics.

7C.3 Account for the uncertainty relation between position and linear momentum in terms of the shape of the wavefunction.

7C.4 Describe the properties of wavepackets in terms of the Heisenberg uncertainty principle.

Exercises

7C.1(a) Construct the potential energy operator of a particle subjected to a harmonic oscillator potential (see Topic 8B).

7C.1(b) Construct the potential energy operator of a particle subjected to a Coulomb potential.

7C.2(a) Confirm that the kinetic energy operator, $-(\hbar^2/2m)d^2/dx^2$, is hermitian.

7C.2(b) The operator corresponding to the angular momentum of a particle is $(\hbar/i)d/d\phi$, where ϕ is an angle. Is this operator hermitian?

7C.3(a) Functions of the form $\sin(n\pi x/L)$ can be used to model the wavefunctions of electrons in a carbon nanotube of length L . Show that the wavefunctions $\sin(n\pi x/L)$ and $\sin(m\pi x/L)$, where $n \neq m$, are orthogonal for a particle confined to the region $0 \leq x \leq L$.

7C.3(b) Functions of the form $\cos(n\pi x/L)$ can be used to model the wavefunctions of electrons in metals. Show that the wavefunctions $\cos(n\pi x/L)$ and $\cos(m\pi x/L)$, where $n \neq m$, are orthogonal for a particle confined to the region $0 \leq x \leq L$.

7C.4(a) A light atom rotating around a heavy atom to which it is bonded is described by a wavefunction of the form $\psi(\phi) = e^{im\phi}$ with $0 \leq \phi \leq 2\pi$ and m an integer. Show that the $m=+1$ and $m=+2$ wavefunctions are orthogonal.

7C.4(b) Repeat Exercise 7C.4(a) for the $m=+1$ and $m=-1$ wavefunctions.

7C.5(a) An electron in a carbon nanotube of length L is described by the wavefunction $\psi(x) = \sin(2\pi x/L)$. Compute the expectation value of the position of the electron.

7C.5(b) An electron in a carbon nanotube of length L is described by the wavefunction $\psi(x) = (2/L)^{1/2} \sin(\pi x/L)$. Compute the expectation value of the kinetic energy of the electron.

7C.6(a) An electron in a one-dimensional metal of length L is described by the wavefunction $\psi(x) = \sin(\pi x/L)$. Compute the expectation value of the momentum of the electron.

7C.6(b) A light atom rotating around a heavy atom to which it is bonded is described by a wavefunction of the form $\psi(\phi) = e^{i\phi}$ with $0 \leq \phi \leq 2\pi$. If the operator corresponding to angular momentum is given by $(\hbar/i)d/d\phi$, compute the expectation value of the angular momentum of the light atom.

7C.7(a) Calculate the minimum uncertainty in the speed of a ball of mass 500 g that is known to be within 1.0 μm of a certain point on a bat. What is the minimum uncertainty in the position of a bullet of mass 5.0 g that is known to have a speed somewhere between 350.000 01 m s^{-1} and 350.000 00 m s^{-1} ?

7C.7(b) An electron is confined to a linear region with a length of the same order as the diameter of an atom (about 100 pm). Calculate the minimum uncertainties in its position and speed.

7C.8(a) The speed of a certain proton is 0.45 Mm s^{-1} . If the uncertainty in its momentum is to be reduced to 0.0100 per cent, what uncertainty in its location must be tolerated?

7C.8(b) The speed of a certain electron is 995 km s^{-1} . If the uncertainty in its momentum is to be reduced to 0.0010 per cent, what uncertainty in its location must be tolerated?

7C.9(a) Determine the commutators of the operators (i) d/dx and $1/x$, (ii) d/dx and x^2 .

7C.9(b) Determine the commutators of the operators a and a^\dagger , where $a = (x+ip)/2^{1/2}$ and $a^\dagger = (x-ip)/2^{1/2}$.

Problems

7C.1 Write the time-independent Schrödinger equations for (a) an electron moving in one dimension about a stationary proton and subjected to a Coulomb potential, (b) a free particle, (c) a particle subjected to a constant, uniform force.

7C.2 Construct quantum mechanical operators for the following observables: (a) kinetic energy in one and in three dimensions, (b) the inverse separation,

$1/x$, (c) electric dipole moment in one dimension, (d) the mean square deviations of the position and momentum of a particle (in one dimension) from the mean values.

7C.3 Identify which of the following functions are eigenfunctions of the operator d/dx : (a) e^{ikx} , (b) k , (c) kx , (d) e^{-ax^2} . Give the corresponding eigenvalue where appropriate.

7C.4 Determine which of the following functions are eigenfunctions of the inversion operator \hat{i} which has the effect of making the replacement $x \rightarrow -x$: (a) $x^3 - kx$, (b) $\cos kx$, (c) $x^2 + 3x - 1$. State the eigenvalue of \hat{i} when relevant.

7C.5 Which of the functions in Problem 7C.3 are (a) also eigenfunctions of d^2/dx^2 and (b) only eigenfunctions of d^2/dx^2 ? Give the eigenvalues where appropriate.

7C.6 Show that the product of a hermitian operator with itself is also a hermitian operator.

7C.7 Calculate the average linear momentum of a particle described by the following wavefunctions: (a) e^{ikx} , (b) $\cos kx$, (c) e^{-ax^2} , where in each one x ranges from $-\infty$ to $+\infty$.

7C.8 The normalized wavefunctions for a particle confined to move on a circle are $\psi(\phi) = (1/2\pi)^{1/2} e^{-im\phi}$, where $m = 0, \pm 1, \pm 2, \pm 3, \dots$ and $0 \leq \phi < 2\pi$. Determine $\langle \phi \rangle$.

7C.9 A particle freely moving in one dimension x with $0 \leq x < \infty$ is in a state described by the wavefunction $\psi(x) = a^{1/2} e^{-ax/2}$, where a is a constant. Determine the expectation value of the position operator.

7C.10 The wavefunction of an electron in a linear accelerator is $\psi = (\cos \chi)e^{ikx} + (\sin \chi)e^{-ikx}$, where χ (chi) is a parameter. (i) What is the probability that the electron will be found with a linear momentum (a) $+k\hbar$, (b) $-k\hbar$? (c) What form would the wavefunction have if it were 90 per cent certain that the electron had linear momentum $+k\hbar$? (c) Evaluate the kinetic energy of the electron.

7C.11 Two (unnormalized) excited state wavefunctions of the H atom are (i) $\psi = (2-r/a_0)e^{-r/2a_0}$ and (ii) $\psi = r \sin \theta \cos \phi e^{-r/2a_0}$. (a) Normalize both

functions to 1. (b) Confirm that these two functions are mutually orthogonal. (c) Evaluate the expectation values of r and r^2 for the atom.

7C.12 The ground-state wavefunction of a hydrogen atom is $\psi = (1/\pi a_0^3)^{1/2} e^{-r/a_0}$. Calculate (a) the mean potential energy and (b) the mean kinetic energy of an electron in the ground state of a hydrogenic atom.

7C.13 Show that the expectation value of an operator that can be written as the square of a hermitian operator is positive.

7C.14 A particle is in a state described by the wavefunction $\psi(x) = (2a/\pi)^{1/4} e^{-ax^2}$, where a is a constant and $-\infty \leq x \leq \infty$. Verify that the value of the product $\Delta p \Delta x$ is consistent with the predictions from the uncertainty principle.

7C.15 A particle is in a state described by the wavefunction $\psi(x) = (2a)^{1/2} e^{-ax}$, where a is a constant and $0 \leq x \leq \infty$. Determine the expectation value of the commutator of the position and momentum operators.

7C.16 Evaluate the commutators (a) $[\hat{H}, \hat{p}_x]$ and (b) $[\hat{H}, \hat{x}]$ where $\hat{H} = \hat{p}_x^2/2m + \hat{V}(x)$. Choose (i) $V(x) = V$, a constant, (ii) $V(x) = \frac{1}{2} k_f x^2$.

7C.17 (a) Given that any operators used to represent observables must satisfy the commutation relation in eqn 7C.16, what would be the operator for position if the choice had been made to represent linear momentum parallel to the x -axis by multiplication by the linear momentum. These different choices are all valid 'representations' of quantum mechanics. (b) With the identification of \hat{x} in this representation, what would be the operator for $1/x$? *Hint:* Think of $1/x$ as x^{-1} .

Integrated activities

7.2 Suppose that the wavefunction of an electron in a carbon nanotube is a linear combination of $\cos(nx)$ functions. (a) Use mathematical software, a

spreadsheet, or the *Living graphs* on the web site of this book to construct superpositions of cosine functions as

$$\psi(x) = \frac{1}{N} \sum_{k=1}^N \cos(k\pi x)$$

where the constant $1/N$ is introduced to keep the superpositions with the same overall magnitude. Set $x=0$ at the centre of the screen and build the superposition there. (b) Explore how the probability density $\psi^2(x)$ changes with the value of N . (c) Evaluate the root mean square location of the packet, $\langle x^2 \rangle^{1/2}$. (d) Determine the probability that a given momentum will be observed.

CHAPTER 8 The quantum theory of motion

TOPIC 8A Translation

Discussion questions

8A.1 Discuss the physical origin of quantization energy for a particle confined to moving inside a one-dimensional box.

8A.2 Describe the features of the solution of the particle in a one-dimensional box that appear in the solutions of the particle in two- and three-dimensional boxes. What concept applies to the latter but not to a one-dimensional box?

8A.3 Discuss the physical origins of quantum mechanical tunnelling. Why is tunnelling more likely to contribute to the mechanisms of electron transfer and proton transfer processes than to mechanisms of group transfer reactions, such as $AB + C \rightarrow A + BC$ (where A, B, and C are large molecular groups)?

Exercises

8A.1(a) Determine the linear momentum and kinetic energy of a free electron described by the wavefunction e^{ikx} with $k = 3 \text{ nm}^{-1}$.

8A.1(b) Determine the linear momentum and kinetic energy of a free proton described by the wavefunction e^{-ikx} with $k = 5 \text{ nm}^{-1}$.

8A.2(a) Write the wavefunction for a particle of mass 2.0 g travelling to the left with a kinetic energy of 20 J.

8A.2(b) Write the wavefunction for a particle of mass 1.0 g travelling to the right at 10 m s^{-1} .

8A.3(a) Calculate the energy separations in joules, kilojoules per mole, electronvolts, and reciprocal centimetres between the levels (i) $n=2$ and $n=1$, (ii) $n=6$ and $n=5$ of an electron in a box of length 1.0 nm.

8A.3(b) Calculate the energy separations in joules, kilojoules per mole, electronvolts, and reciprocal centimetres between the levels (i) $n=3$ and $n=1$, (ii) $n=7$ and $n=6$ of an electron in a box of length 1.50 nm.

8A.4(a) Calculate the probability that a particle will be found between $0.49L$ and $0.51L$ in a box of length L when it has (i) $n=1$, (ii) $n=2$. Take the wavefunction to be a constant in this range.

8A.4(b) Calculate the probability that a particle will be found between $0.65L$ and $0.67L$ in a box of length L when it has (i) $n=1$, (ii) $n=2$. Take the wavefunction to be a constant in this range.

8A.5(a) Calculate the expectation values of \hat{p} and \hat{p}^2 for a particle in the state $n=1$ in a one-dimensional square-well potential.

8A.5(b) Calculate the expectation values of \hat{p} and \hat{p}^2 for a particle in the state $n=2$ in a one-dimensional square-well potential.

8A.6(a) Calculate the expectation values of \hat{x} and \hat{x}^2 for a particle in the state $n=1$ in a one-dimensional square-well potential.

8A.6(b) Calculate the expectation values of \hat{x} and \hat{x}^2 for a particle in the state $n=2$ in a one-dimensional square-well potential.

8A.7(a) An electron is confined to a square well of length L . What would be the length of the box such that the zero-point energy of the electron is equal to its rest mass energy, $m_e c^2$? Express your answer in terms of the parameter $\lambda_c = h/m_e c$, the 'Compton wavelength' of the electron.

8A.7(b) Repeat Exercise 8A.7(a) for a general particle of mass m in a cubic box.

8A.8(a) What are the most likely locations of a particle in a box of length L in the state $n=3$?

8A.8(b) What are the most likely locations of a particle in a box of length L in the state $n=5$?

8A.9(a) Calculate the percentage change in a given energy level of a particle in a one-dimensional box when the length of the box is increased by 10 per cent.

8A.9(b) Calculate the percentage change in a given energy level of a particle in a cubic box when the length of the edge of the cube is decreased by 10 per cent in each direction.

8A.10(a) What is the value of n of a particle in a one-dimensional box such that the separation between neighbouring levels is equal to the mean energy of thermal motion ($\frac{1}{2}kT$).

8A.10(b) A nitrogen molecule is confined in a cubic box of volume 1.00 m^3 . (i) Assuming that the molecule has an energy equal to $\frac{3}{2}kT$ at $T=300 \text{ K}$, what is the value of $n=(n_x^2+n_y^2+n_z^2)^{1/2}$ for this molecule? (ii) What is the energy separation between the levels n and $n+1$? (iii) What is its de Broglie wavelength?

8A.11(a) For a particle in a rectangular box with sides of length $L_1=L$ and $L_2=2L$, find a state that is degenerate with the state $n_1=n_2=2$. Degeneracy is normally associated with symmetry; why, then, are these two states degenerate?

8A.11(b) For a particle in a rectangular box with sides of length $L_1=L$ and $L_2=2L$, find a state that is degenerate with the state $n_1=2, n_2=8$. Degeneracy is normally associated with symmetry; why, then, are these two states degenerate?

8A.12(a) Consider a particle in a cubic box. What is the degeneracy of the level that has an energy three times that of the lowest level?

8A.12(b) Consider a particle in a cubic box. What is the degeneracy of the level that has an energy $\frac{14}{3}$ times that of the lowest level?

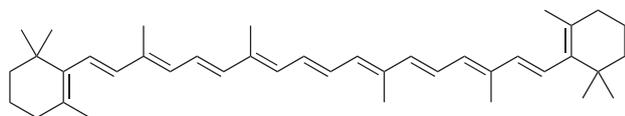
8A.13(a) Suppose that the junction between two semiconductors can be represented by a barrier of height 2.0 eV and length 100 pm. Calculate the transmission probability of an electron with energy 1.5 eV.

8A.13(b) Suppose that a proton of an acidic hydrogen atom is confined to an acid that can be represented by a barrier of height 2.0 eV and length 100 pm. Calculate the probability that a proton with energy 1.5 eV can escape from the acid.

Problems

8A.1 Calculate the separation between the two lowest levels for an O_2 molecule in a one-dimensional container of length 5.0 cm. At what value of n does the energy of the molecule reach $\frac{1}{2}kT$ at 300 K, and what is the separation of this level from the one immediately below?

8A.2 When β -carotene (1) is oxidized *in vivo*, it breaks in half and forms two molecules of retinal (vitamin A), which is a precursor to the pigment in the retina responsible for vision.

1 β -Carotene

The conjugated system of retinal consists of 11 C atoms and one O atom. In the ground state of retinal, each level up to $n=6$ is occupied by two electrons. Assuming an average internuclear distance of 140 pm, calculate (a) the separation in energy between the ground state and the first excited state in which one electron occupies the state with $n=7$, and (b) the frequency of the radiation required to produce a transition between these two states. (c) Using your results, choose among the words in parentheses to generate a rule for the prediction of frequency shifts in the absorption spectra of linear polyenes:

The absorption spectrum of a linear polyene shifts to (higher/lower) frequency as the number of conjugated atoms (increases/decreases).

8A.3* A particle is confined to move in a one-dimensional box of length L . (a) If the particle is classical, show that the average value of x is $\frac{1}{2}L$ and that the root-mean square value is $L/3^{1/2}$. (b) Show that for large values of n , a quantum particle approaches the classical values. This result is an example of the correspondence principle, which states that, for very large values of the quantum numbers, the predictions of quantum mechanics approach those of classical mechanics.

8A.4 Here we explore further the idea introduced in *Impact* I8.1 that quantum mechanical effects need to be invoked in the description of the electronic properties of metallic nanocrystals, here modelled as three-dimensional boxes. (a) Set up the Schrödinger equation for a particle of mass m in a three-dimensional rectangular box with sides L_1 , L_2 , and L_3 . Show that the Schrödinger equation is separable. (b) Show that the wavefunction and the energy are defined by three quantum numbers. (c) Specialize the result from part (b) to an electron moving in a cubic box of side $L=5$ nm and draw an energy diagram resembling Fig. 8A.2 and showing the first 15 energy levels. Note that each energy level may consist of degenerate energy states. (d) Compare the energy level diagram from part (c) with the energy level

diagram for an electron in a one-dimensional box of length $L=5$ nm. Are the energy levels more or less sparsely distributed in the cubic box than in the one-dimensional box?

8A.5 Many biological electron transfer reactions, such as those associated with biological energy conversion, may be visualized as arising from electron tunnelling between protein-bound cofactors, such as cytochromes, quinones, flavins, and chlorophylls. This tunnelling occurs over distances that are often greater than 1.0 nm, with sections of protein separating electron donor from acceptor. For a specific combination of donor and acceptor, the rate of electron tunnelling is proportional to the transmission probability, with $\kappa \approx 7 \text{ nm}^{-1}$ (eqn 8A.23). By what factor does the rate of electron tunnelling between two cofactors increase as the distance between them changes from 2.0 nm to 1.0 nm?

8A.6 Derive eqn 8A.23a, the expression for the transmission probability and show that then $\kappa L \gg 1$ it reduces to eqn 8A.23b.

8A.7† Consider the one-dimensional space in which a particle has one of three potential energies depending upon its position. They are: $V=0$ for $-\infty < x \leq 0$, $V=V_2$ for $0 \leq x \leq L$, and $V=V_3$ for $L \leq x < \infty$. The particle wavefunction has both a component e^{ik_1x} that is incident upon the barrier V_2 and a reflected component e^{-ik_1x} in Zone 1 ($-\infty < x \leq 0$). In Zone 2 ($0 \leq x \leq L$) the wavefunction has components e^{k_2x} and e^{-k_2x} . In Zone 3 the wavefunction has only a forward component, e^{ik_3x} , which represents a particle that has traversed the barrier. The energy of the particle, E , is somewhere in the range $V_2 > E > V_3$. The transmission probability, T , is the ratio of the square modulus of Zone 3 amplitude to the square modulus of the incident amplitude. (a) Base your calculation on the continuity of the amplitude and slope of the wavefunction at the locations of the zone boundaries and derive a general equation for T . (b) Show that the general equation for T reduces to eqn 8A.23b in the high, wide barrier limit when $V_1=V_3=0$. (c) Draw a graph of the probability of proton tunnelling when $V_3=0$, $L=50$ pm, and $E=10 \text{ kJ mol}^{-1}$ in the barrier range $E < V_2 < 2E$.

8A.8 The wavefunction inside a long barrier of height V is $\psi = Ne^{-\kappa x}$. Calculate (a) the probability that the particle is inside the barrier and (b) the average penetration depth of the particle into the barrier.

TOPIC 8B Vibrational motion

Discussion questions

8B.1 Describe the variation of the separation of the vibrational energy levels with the mass and force constant of the harmonic oscillator.

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?

Exercises

8B.1(a) Calculate the zero-point energy of a harmonic oscillator consisting of a particle of mass $2.33 \times 10^{-26} \text{ kg}$ and force constant 155 N m^{-1} .

8B.1(b) Calculate the zero-point energy of a harmonic oscillator consisting of a particle of mass $5.16 \times 10^{-26} \text{ kg}$ and force constant 285 N m^{-1} .

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

8B.2(b) For a certain harmonic oscillator of effective mass $2.88 \times 10^{-25} \text{ kg}$, the difference in adjacent energy levels is 3.17 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 ($1.0078m_p$) and force constant 855 N m^{-1} .

8B.3(b) 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 an oxygen atom ($15.9949m_p$) and force constant 544 N m^{-1} .

* These problems were supplied by Charles Trapp and Carmen Giunta.

8B.4(a) The vibrational frequency of H_2 is 131.9 THz. What is the vibrational frequency of D_2 ($\text{D} = {}^2\text{H}$)?

8B.4(b) The vibrational frequency of H_2 is 131.9 THz. What is the vibrational frequency of T_2 ($\text{T} = {}^3\text{H}$)?

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.5(b) Calculate the minimum excitation energies of (i) the 33 kHz quartz crystal of a watch, (ii) the bond between two O atoms in O_2 , for which $k_f = 1177 \text{ N m}^{-1}$.

8B.6(a) Assuming that the vibrations of a ${}^{35}\text{Cl}_2$ molecule are equivalent to those of a harmonic oscillator with a force constant $k_f = 329 \text{ N m}^{-1}$, 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 $m({}^{35}\text{Cl}) = 34.9688 m_u$.

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 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.2 Carbon monoxide binds strongly to the Fe^{2+} ion of the haem group of the protein myoglobin. Estimate the vibrational frequency of CO bound to myoglobin by using the data in Problem 8B.1 and by making the following assumptions: the atom that binds to the haem group is immobilized, the protein is infinitely more massive than either the C or O atom, the C atom binds to the Fe^{2+} ion, and binding of CO to the protein does not alter the force constant of the C=O bond.

8B.3 Of the four assumptions made in Problem 8B.2, the last two are questionable. Suppose that the first two assumptions are still reasonable and that you have at your disposal a supply of myoglobin, a suitable buffer in which to suspend the protein, ${}^{12}\text{C}^{16}\text{O}$, ${}^{13}\text{C}^{16}\text{O}$, ${}^{12}\text{C}^{18}\text{O}$, ${}^{13}\text{C}^{18}\text{O}$, and an infrared spectrometer. Assuming that isotopic substitution does not affect the force constant of the C=O bond, describe a set of experiments that: (a) proves which atom, C or O, binds to the haem group of myoglobin, and (b) allows for the determination of the force constant of the C=O bond for myoglobin-bound carbon monoxide.

8B.4 Confirm that a function of the form e^{-gx^2} is a solution of the Schrödinger equation for the ground state of a harmonic oscillator and find an expression for g in terms of the mass and force constant of the oscillator.

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

8B.6(b) Assuming that the vibrations of a ${}^{14}\text{N}_2$ molecule are equivalent to those of a harmonic oscillator with a force constant $k_f = 2293.8 \text{ N m}^{-1}$, 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 $m({}^{14}\text{N}) = 14.0031 m_u$.

8B.7(a) Locate the nodes of the harmonic oscillator wavefunction with $\nu = 4$.

8B.7(b) Locate the nodes of the harmonic oscillator wavefunction with $\nu = 5$.

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

8B.8(b) What are the most probable displacements of a harmonic oscillator with $\nu = 3$?

8B.9(a) Calculate the probability that an O—H bond treated as a harmonic oscillator will be found at a classically forbidden extension when $\nu = 1$.

8B.9(b) Calculate the probability that an O—H bond treated as a harmonic oscillator will be found at a classically forbidden extension when $\nu = 2$.

8B.6 Calculate the values of $\langle x^3 \rangle$ and $\langle x^4 \rangle$ for a harmonic oscillator by using the relations in Table 8B.1.

8B.7 Extend the calculation in *Example 8B.4* by using mathematical software to calculate the probability that a harmonic oscillator will be found outside the classically allowed displacements for general ν and plot the probability as a function of ν .

8B.8 The intensities of spectroscopic transitions between the vibrational states of a molecule are proportional to the square of the integral $\int \psi_{\nu'} x \psi_{\nu} dx$ over all space. Use the relations between Hermite polynomials given in Table 8B.1 to show that the only permitted transitions are those for which $\nu' = \nu \pm 1$ and evaluate the integral in these cases.

8B.9 Use mathematical software to construct a harmonic oscillator wavepacket of the form

$$\Psi(x, t) = \sum_{\nu=0}^N c_{\nu} \psi_{\nu}(x) e^{-iE_{\nu} t / \hbar}$$

where the wavefunctions and energies are those of a harmonic oscillator and with coefficients of your choice (for example, all equal). Explore how the wavepacket oscillates to and fro with time.

8B.10 Show that, whatever superposition of harmonic oscillator states is used to construct a wavepacket (as in Problem 8B.9), it is localized at the same place at the times $0, T, 2T, \dots$, where T is the classical period of the oscillator.

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 $\nu = 0$ to $\nu = 1$. What do you expect to happen to the energy levels and wavefunctions as the excitation increases to high quantum numbers?

8B.12 Use the virial theorem to obtain an expression for the relation between the mean kinetic and potential energies of an electron in a hydrogen atom.

TOPIC 8C Rotational motion

Discussion questions

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

8C.2 Describe the features of the solution of the particle on a ring that appear in the solution of the particle on a sphere. What concept applies to the latter but not to the former?

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

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.1(b) The rotation of a molecule can be represented by the motion of a point mass moving over the surface of a sphere with angular momentum quantum number $l=2$. Calculate the magnitude of its angular momentum and the possible components of the angular momentum on an arbitrary axis. Express your results as multiples of \hbar .

8C.2(a) The wavefunction, $\psi(\phi)$, for the motion of a particle in a ring is of the form $\psi = Ne^{im\phi}$. Determine the normalization constant, N .

8C.2(b) Confirm that wavefunctions for a particle in a ring with different values of the quantum number m_l are mutually orthogonal.

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.3(b) Calculate the value of $|m_l|$ for the system described in the preceding exercise corresponding to a rotational energy equal to the classical average energy at 25 °C (which is equal to $\frac{1}{2}kT$).

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

8C.4(b) The moment of inertia of an SF_6 molecule is $3.07 \times 10^{-45} \text{ kg m}^2$. What is the minimum energy needed to start it rotating?

8C.5(a) Use the data in Exercise 8C.4(a) to calculate the energy needed to excite a CH_4 molecule from a state with $l=1$ to a state with $l=2$.

8C.5(b) Use the data in Exercise 8C.4(b) to calculate the energy needed to excite an SF_6 molecule from a state with $l=2$ to a state with $l=3$.

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.6(b) What is the magnitude of the angular momentum of an SF_6 molecule when it is rotating with its minimum energy?

8C.7(a) Draw scale vector diagrams to represent the states (i) $l=1, m_l=+1$, (ii) $l=2, m_l=0$.

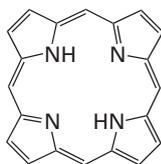
8C.7(b) Draw the vector diagram for all the permitted states of a particle with $l=6$.

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 $l=3$.

8C.8(b) 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 $l=4$.

Problems

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.2 Use mathematical software to construct a wavepacket for a particle moving on a circular ring of the form

$$\Psi(\phi, t) = \sum_{m_l=0}^{m_{l,\max}} c_{m_l} e^{i(m_l\phi - E_{m_l}t/\hbar)} \quad E_{m_l} = m_l^2 \hbar^2 / 2I$$

with coefficients c of your choice (for example, all equal). Explore how the wavepacket migrates on the ring but spreads with time.

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.4 Is the Schrödinger equation for a particle on an elliptical ring of semi-major axes a and b separable? *Hint:* Although r varies with angle ϕ , the two are related by $r^2 = a^2 \sin^2 \phi + b^2 \cos^2 \phi$.

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

8C.6 Confirm that the spherical harmonics (a) $Y_{0,0}$, (b) $Y_{2,-1}$, and (c) $Y_{3,+3}$ satisfy the Schrödinger equation for a particle free to rotate in three dimensions, and find its energy and angular momentum in each case.

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, $l = r \times p$. Show that any two of the components do not mutually commute, and find their commutator.

8C.10 Starting from the operator $\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$, prove that in spherical polar coordinates $\hat{L}_z = -i\hbar \partial/\partial \phi$.

8C.11 Show that $[L^2, L_z] = 0$, and then, without further calculation, justify the remark that $\hat{L}^2, \hat{L}_q = 0$ for all $q = x, y, \text{ and } z$.

8C.12 A particle confined to within a spherical cavity is a reasonable starting point for the discussion of the electronic properties of spherical metal nanoparticles (*Impact* I8.1). Here, you are invited to show in a series of steps that the $l=0$ energy levels of an electron in a spherical cavity of radius R are quantized and given by

$$E_n = \frac{n^2 \hbar^2}{8m_e R^2}$$

(a) The hamiltonian for a particle free to move inside a sphere of radius a is

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2$$

Show that the Schrödinger equation is separable into radial and angular components. That is, begin by writing $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$, where $R(r)$ depends only on the distance of the particle from the centre of the sphere, and $Y(\theta, \phi)$ is a spherical harmonic. Then show that the Schrödinger equation can be separated into two equations, one for $R(r)$, the radial equation, and the other for $Y(\theta, \phi)$, the angular equation. (b) Consider the case $l=0$. Show by differentiation that the solution of the radial equation has the form

$$R(r) = (2\pi a)^{-1/2} \frac{\sin(n\pi r/a)}{r}$$

(c) Now go on to show (by acknowledging the appropriate boundary conditions) that the allowed energies are given by $E_n = n^2 h^2 / 8ma^2$. With substitution of m_e for m and of R for a , this is the equation given above for the energy.

Integrated activities

8.1 Describe the features that stem from nanometre-scale dimensions that are not found in macroscopic objects.

8.2 Explain why the particle in a box and the harmonic oscillator are useful models for quantum mechanical systems: what chemically significant systems can they be used to represent?

8.4 Determine the values of $\Delta x = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2}$ and $\Delta p = (\langle p^2 \rangle - \langle p \rangle^2)^{1/2}$ for the ground state of (a) a particle in a box of length L and (b) an harmonic oscillator. Discuss these quantities with reference to the uncertainty principle.

8.5 Repeat Problem 8.4 for (a) a particle in a box and (b) a harmonic oscillator in a general quantum state (n and ν , respectively).

8.6 Use mathematical software, a spreadsheet, or the *Living graphs* on the web site of this book for the following exercises:

(a) Plot the probability density for a particle in a box with $n=1, 2, \dots, 5$ and $n=50$. How do your plots illustrate the correspondence principle?

(b) Plot the transmission probability T against E/V for passage by (i) a hydrogen molecule, (ii) a proton, and (iii) an electron through a barrier of height V .

(c) To gain some insight into the origins of the nodes in the harmonic oscillator wavefunctions, plot the Hermite polynomials $H_\nu(y)$ for $\nu=0$ through 5.

(d) Use mathematical software to generate three-dimensional plots of the wavefunctions for a particle confined to a rectangular surface with (i) $n_1=1, n_2=1$, the state of lowest energy, (ii) $n_1=1, n_2=2$, (iii) $n_1=2, n_2=1$, and (iv) $n_1=2, n_2=2$. Deduce a rule for the number of nodal lines in a wavefunction as a function of the values of n_1 and n_2 .