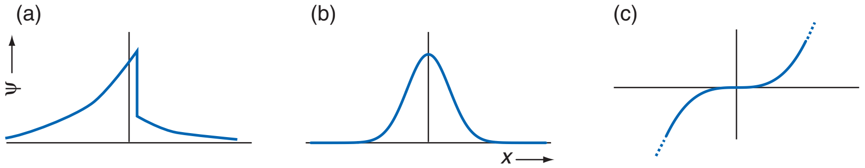
18 Quantum mechanics and spectroscopy

Physical constants: $h = 6.626 \times 10^{-34}$ J s, $k_B = 1.381 \times 10^{-23}$ J K^{-1}, $N_A = 6.022 \times 10^{23}$ mol^{-1}, $c = 2.998 \times 10^{8}$ m s^{-1}, mass unit (u) = 1.6605×10^{-27} kg.

18.1 Show that $\phi_1(x) = A\sin(Bx)$ and $\phi_2(x) = C\cos(Bx)$ are both eigenfunctions of the operator $\mathrm{d}^2/\mathrm{d}x^2$, and find the corresponding eigenvalue in each case. Do different values of A and C give different eigenfunctions? Are these two eigenfunctions degenerate?

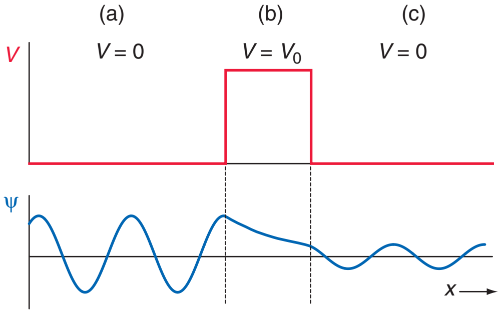
18.2 State the *Born interpretation* of the wavefunction and use is to explain whether or not the following (one-dimensional) functions are likely to be acceptable wavefunctions. (The dashed lines in (c) imply that the sine function continues indefinitely to positive and negative x.)



18.3 Imagine a free particle, moving in one dimension, which has total energy E and experiences a fixed potential energy V_0. Explain why it is that in classical mechanics the potential energy cannot exceed the total energy.

Without going into mathematical details, describe the behaviour of a typical eigenfunction of the hamiltonian (the operator for energy) for the classical case where $E > V_0$, and for the non-classical case where $E < V_0$. What happens to the eigenfunction when the potential V_0 becomes very large?

18.4 Consider a particle which experiences the potential shown below in red. The potential is zero in the region (a), equal to V_0 in the region (b), and zero again in the region (c). Also shown in blue is a typical eigenfunction ψ of the hamiltonian; rationalize the behaviour of this eigenfunction. What will happen to ψ as V_0 is increased, and as V_0 is decreased?



18.5 (a) Write down the hamiltonian for a particle of mass m experiencing a potential $V_0 = 0$ and moving in one dimension. Show that $\psi(x) = A\cos(kx)$ is an eigenfunction of this hamiltonian, and give an expression for the energy (the eigenvalue) in terms of k.

(b) Explain the boundary conditions which are imposed on the wavefunction by a potential which is zero between $x = 0$ and $x = L$, and infinite elsewhere.

(c) Discuss whether or not $\psi(x) = A\cos(kx)$ satisfies these boundary conditions.

18.6 With reference to the wavefunctions and energy levels for the particle in a (one-dimensional) box, explain what you understand by the terms (a) quantum number, (b) normalized, (c) orthogonal, and (d) zero-point energy.

18.7 Why do the number of nodes in a wavefunction increase as its energy increases?

18.8 (a) With reference to the case of a particle in a two-dimensional square well (described in section 18.4 on page 681), explain what you understand by a *degenerate* energy level.

(b) Calculate the energies (expressed as multiples of $(\hbar^2\pi^2)/(2mL^2)$), for all of the levels with n_x in the range 1 to 4, and for n_y in the range 1 to 4. Arrange these in order of increasing total energy. Why are some of the levels degenerate, while others are not?

18.9 In the case of an harmonic oscillator with potential $V(x) = \frac{1}{2}k_f x^2$, what do you understand by the 'classical' and 'non-classical' regions of the oscillation? How does the behaviour of the wavefunction differ between the two regions?

18.10 In the IR spectrum of $^1H^{35}Cl$ there is a strong absorption centred at 2885 cm^{-1}. Assuming that the vibrational energy levels can be approximated by those of the harmonic oscillator, use this observation to (a) determine the frequency of the oscillation (in Hz and in rad s^{-1}), (b) determine the force constant of the bond. (^1H = 1.0078 mass units and ^{35}Cl = 34.9689 mass units).

18.11 The 'energy in wavenumbers' of the energy levels of a Morse oscillator are given by Eq. 18.29 on page 699

$$\tilde{E}_\upsilon = \left(\upsilon + \tfrac{1}{2}\right)\tilde{\omega}_e - \left(\upsilon + \tfrac{1}{2}\right)^2 \tilde{\omega}_e x_e,$$

(a) Using these energies, show that the wavenumber of the $0 \rightarrow 1$ and $0 \rightarrow 2$ transitions are given by $\tilde{\omega}_e - 2\tilde{\omega}_e x_e$ and $2\tilde{\omega}_e - 6\tilde{\omega}_e x_e$, respectively.

(b) In the spectrum of $^1H^{35}Cl$ there is a strong absorption centred at 2885 cm^{-1}, and a weaker absorption centred at 5665 cm^{-1}. Use these data to find values for $\tilde{\omega}_e$ and $\tilde{\omega}_e x_e$ (in cm^{-1}), explaining your method.

(c) Convert the values of $\tilde{\omega}_e$ and $\tilde{\omega}_e x_e$ from cm^{-1} to rad s^{-1}. Hence determine the values of the Morse parameters a and D_e.

18.12 Using the expression for the energy levels of the Morse oscillator (in cm^{-1}) given in the previous question, show that the value of the vibrational quantum number at which dissociation occurs, υ_{max}, is given by

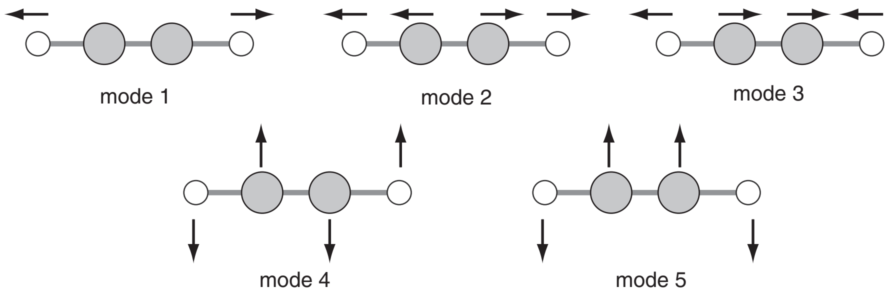
$$\upsilon_{max} = \frac{1}{2x_e} - \frac{1}{2}.$$

Hence show that the dissociation energy, expressed in wavenumbers, is

$$\tilde{D}_e = \frac{(\tilde{\omega}_e)^2}{4\tilde{\omega}_e x_e}.$$

Using the values of $\tilde{\omega}_e$ and $\tilde{\omega}_e x_e$ from the previous question, determine $\tilde{D}_e$ (in wavenumbers). Convert your answer to joules and confirm that it is the same as you obtained in the previous question.

18.13 Illustrated below are five of the normal modes of ethyne (acetylene, HCCH). At its equilibrium geometry this molecule has no dipole moment, but for some of the normal modes the distortion during the vibration induces a dipole. Determine which of the normal modes are IR active and explain why modes 4 and 5 are each doubly degenerate.



18.14 In a Raman scattering experiment on $^1H_2$ using a green argon ion laser (which emits at a frequency of 20492 cm^{-1}) very strong scattering of light at 20492 cm^{-1} was seen, along with much weaker scattering at 16333 cm^{-1}. Explain the origin of the scattered light at these two different frequencies. Hence determine the vibrational frequency of $^1H_2$ and the corresponding force constant (use the harmonic oscillator energy levels; ^1H = 1.0078 mass units).

18.15 The microwave (rotational) spectrum of $^{12}C^{16}O$ consists of a series of lines spaced by 115.3 GHz (1 GHz ≡ 10^9 Hz). Assuming that the rotational energy levels of this molecule can be approximated by those of the rigid rotor, use these data to determine a value for the rotational constant B, the moment of inertia I, and hence the bond length R. Be careful to work in SI units throughout. (^{12}C = 12.000 mass units and ^{16}O = 15.995 mass units.)

18.16 Using the same approach as is described in section 18.13 on page 713, show that the frequencies of the lines in the P branch of the vibration–rotation spectrum of a diatomic are given by

$$\tilde{\nu}_P(J'') = \tilde{\omega} - 2\tilde{B}J''.$$

What range of values can the quantum number J'' take in this expression?

18.17 In the IR spectrum of $^{12}C^{16}O$ there is a strong band at around 2157 cm^{-1} which, on closer inspection, shows P/R branch structure. The spacing between successive lines in the two branches is roughly constant at 3.85 cm^{-1}. Use these data to estimate the bond length in $^{12}C^{16}O$, explaining any approximations you find it necessary to make. (^{12}C = 12.000 mass units and ^{16}O = 15.995 mass units.)

18.18 Why is it that although the rotational level with $J = 0$ has the lowest energy, the first line in the R branch (R_0) is not the most intense?

18.19 Verify that the wavelengths quoted in Table 18.2 on page 718 are correct.

18.20 A very simple model for the electronic structure of a conjugated polyene

is to assume that the π electrons move in a one-dimensional box of length Na, where N is the number of conjugated double bonds and a is the typical length of such a bond. Given that the energy levels of a particle in a box are

$$E_n = \frac{n^2h^2}{8mL^2} \qquad n = 1, 2, \ldots,$$

the energy levels available to the π electrons are therefore

$$E_n = \frac{n^2h^2}{8m_eN^2a^2} \qquad n = 1, 2, \ldots,$$

where m_e is the mass of the electron (9.11×10^{-31} kg).

(a) Given that N conjugated π bonds contribute $2N$ π electrons, and that two electrons occupy each energy level, explain why the highest occupied level has $n = N$, and the lowest unoccupied level has $n = N + 1$.

(b) Show that the energy of the photon needed to cause a transition between the highest occupied and lowest unoccupied levels is given by

$$E_{\text{photon}} = \frac{(2N+1)h^2}{8m_eN^2a^2},$$

and hence that the corresponding wavelength of the light that will cause this transition is

$$\lambda = \frac{8m_ecN^2a^2}{(2N+1)h}.$$

(c) Explain why this expression for λ predicts that as the number of conjugated double bonds increases the wavelength of the absorption also increases. Taking the value of the length a to be 220 pm, find the value of λ for $N = 6$. What region of the spectrum does this correspond to?