

QUANTUM MECHANICS II

QUESTION 1

- a) Sketch the energy level (Grotrian) diagram for a hydrogen atom. Use it to explain the atomic spectrum that is observed for hydrogen.
- b) What is meant by the term radial distribution function when discussing atomic orbitals? Sketch the radial distribution functions of the 2s and 2p orbitals of lithium.
- c) The principal series of lines in the emission spectrum of atomic lithium arise from the $np \rightarrow 2s$ transitions, where n is the principal quantum number. The first five lines in the series are observed at wavenumbers of 14 908, 30 935, 36 479, 39 024, and 40 399 cm^{-1} . Use a graphical method to estimate the ionization energy (expressed as a wavenumber, in cm^{-1}) of the 2s electron in lithium.
- d) In fact, under higher resolution, the $2p \rightarrow 2s$ transition in b) is split into a doublet separated by 0.3 cm^{-1} . Explain this observation.

QUESTION 2

- a) Write down the Rydberg equation and explain briefly its value in analysis of atomic spectra of hydrogenic atoms. The lowest energy electronic transition in ground state hydrogen atoms occurs at a wavelength of 121.8nm, and the lowest energy transition in ground state helium occurs at a wavelength of 58.43 nm. Calculate the ratio of the Rydberg constants for hydrogen and helium.
- b) What is meant by a *radial probability distribution function* for an electron in an atom? In what way is it different from the *radial wavefunction*? Outline how a knowledge of the radial wavefunction can help explain the energy ordering of the s, p, and d orbitals in an atom.
- c) If helium gas is excited in an electrical discharge, an emission spectrum showing a large number of spectral lines is observed. Many of these lines are absent from the absorption spectrum of helium. Explain this observation as fully as possible.
- d) What is the Uncertainty Principle? Describe one experiment that provides evidence for the Uncertainty Principle.

QUESTION 3

- a) Write notes on the following topics:
- Principal quantum number, n .
 - Orbital angular momentum quantum number, l .
 - Spin quantum number, s .
 - Magnetic quantum number, m_l .
- b) The wavefunction for a $2p_z$ electron in a hydrogenic atom of atomic number Z is

$$\psi = Nr \cos\theta e^{-Zr/2a_0},$$

where a_0 is the Bohr radius and N is a normalisation constant.

i) Normalise this wavefunction. For this step, you will need the integrals

$$\int_0^{\infty} r^n e^{-\alpha r} dr = \frac{n!}{\alpha^{n+1}}, \quad \int_0^{\pi} \cos^2 \theta \sin \theta d\theta = \frac{2}{3}, \quad \int_0^{2\pi} d\phi = 2\pi$$

ii) Evaluate the most probable distance of the electron from the nucleus.

iii) Identify the most probable location of the electron in terms of r and θ .

QUESTION 4

a) Explain what is meant by the terms *eigenfunction*, *eigenvalue* and *normalization constant*.

b) Show that: i) e^{ibt} ; and ii) $a \cos(bt+c)$; in which a , b and c are constants, are eigenfunctions of the operator $\frac{d^2}{dt^2}$ and in each case determine the associated eigenvalue.

c) A simple model for the molecule β -carotene (whose structure is shown below) treats the π electrons as though they were confined to a one-dimensional box with infinitely high potential walls. The electrons can then be described according to the "particle-in-a-box" model, with each energy level able to accommodate a maximum of two electrons.

i) What value must the wavefunction for the electrons in the box have at each end of the box? Why?

ii) β -carotene is orange; in what region of the visible spectrum does it absorb light?

iii) It is possible to synthesize molecules of structure similar to β -carotene, in which the length of the conjugated π system is greater than that in β -carotene. The energy of electrons confined to a one-dimensional box is given by

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

in which n is a quantum number and L the length of the box. How would the wavelength of the light absorbed by the π electrons be affected if the length of the conjugated system were increased? Justify your answer.

