Quantum II

Physical Chemistry Tutorials

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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 → 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 → 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:

   i. Principal quantum number, n

   ii. Orbital angular momentum quantum number, l

   iii. Spin quantum number, s

   iv. Magnetic quantum number, m_l

b) The wavefunction for a $2p_z$ electron in a hydrogenic atom of atomic number Z is

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

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

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

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

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 $a\cos(bt+c)$; 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 what equation? 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.