ATOMIC SPECTRA

1 When light of sufficiently short wavelength falls on a metal, electrons having a range of energies are emitted. This is the photoelectric effect.

(a) Summarise the main characteristics of the photoelectric effect and explain their significance for understanding the nature of light. [5]

(b) Sketch an apparatus that could be used to measure the maximum energy of the emitted photoelectrons. Explain why the *maximum energy* is important. [6]

(c) Give an equation relating the maximum electron kinetic energy to the wavelength of the light. Explain the meaning of the terms you introduce in the equation. [5]

(d) The following maximum electron kinetic energies were obtained from experiments on a single metal at two different wavelengths. Use the data to estimate a value of the Planck constant *h*. [9]

λ/nm	Maximum kinetic energy / J
120	8.55×10^{-19}
58	26.3×10^{-19}

TT2000

2 In a sample of hydrogen atoms the 1s electrons are excited to the n = 6 level by the absorption of light. Ignoring any splitting of the levels caused by spin-orbit coupling, answer the following:

(a) Which energy levels can the excited electrons reach *directly* by emitting a photon? [3]

(b) Sketch and label clearly the emission spectrum due to transitions from the n = 6 level. [6]

(c) The ionization energy of a ground state hydrogen atom is 13.6 eV. Calculate the energy in electron volts required to ionize an electron from the n = 6 energy level. [5]

(d) Determine whether the energy provided by a UV laser operating at 280 nm is sufficient to excite the 1s electron in a ground state hydrogen atom to the n = 6 level. [6]

(e) It is found that some transitions of the 1s electron in hydrogen have almost exactly the same energy as some transitions of the single electron in the He^+ ion. Which transition **in He^+ has the same energy as the 1s → 2p transition in hydrogen? What is the energy of this transition?** [5] TT2000

3 Write down and explain the atomic term symbols for lithium and boron in their lowest energy electronic states. **[8]**

LV 1999

4 (a) Write notes explaining the meanings of the quantum numbers n, l, m_l and s for the electron of a hydrogen atom. [8]

(b) The emission spectrum of atomic deuterium shows lines at 15238, 20571, 23029 and 24380 cm^{-1}. Determine the ionization energy of the lower state, and the value of the Rydberg constant for deuterium, R_D. [8]

(c) What is meant by the *radial distribution function* of an atomic orbital? [4]

(d) The wavefunction for a hydrogenic 1s orbital is

$$P(r) = 2(Z/a_o)^{\frac{3}{2}} e^{-\rho/2}$$

in which $\rho = 2Zr/na_o$ and Z is the atomic number.

Calculate the most probable radius at which the electron will be found when it occupies the 1s orbital of Li^{2+}. [a_o = 52.9 pm.] [5] TT 1999

5 **Answer any TWO of sections (a) to (d)** (all sections carry equal marks).

(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 121.8 nm, and the lowest energy transition in ground state helium atoms 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 which provides evidence for the Uncertainty Principle.

LV 1998

6 The main assumptions of the Bohr model for *one-electron* atoms may be summarized

i. the electron moves in circular orbits around a nucleus of infinite mass,

ii. its angular momentum is an integer multiple of $\hbar$, and

iii. radiation is emitted only when the electron changes orbit.

(a) Explain the consequences of each assumption, giving equations expressing the assumptions wherever possible. [6]

(b) How can assumption (ii.) be justified (retrospectively) in terms of de Broglie's wave hypothesis? [4]

When the above assumptions are combined, the frequency of light (expressed in Hz) emitted or absorbed is calculated to be

$$\nu = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \qquad R_\infty = \frac{e^4 m_e Z^2}{8\epsilon_0^2 h^3}$$

where Z is the nuclear charge number. The frequencies of the first absorption lines for three known one-electron atoms, and one unidentified one-electron atom (X^{m+}) are:

Species	$\nu/(10^{15}\,\mathrm{Hz})$
^1H	2.466024
^2D	2.466699
$^4He^+$	9.868012
X^{m+}	22.20435

(c) Find the nuclear charge of the unidentified atom. [5]

(d) Comment on the difference in frequency between H and D, and use the data for the identified atoms to obtain a *precise* value of the Rydberg constant R_∞ for $Z = 1$. [10]

[Take the atomic masses of H, D, and He to be 1.0 u, 2.0 u and 4.0 u respectively.]

TT1995

7 (a) With reference to atoms, explain the meanings of the terms *first ionization potential*, *orbital* and *shielding*. [9]

(b) Given that the ionization energy of a ground state hydrogen atom is 13.6 eV, calculate the ionization energy of the electron from the 2*s* orbital in a hydrogen atom. [4]

(c) Using diagrams where appropriate, compare the wavefunction and energy for an electron in the 2*s* orbital of the hydrogen atom, with the wavefunction and energy for an electron in the 2*s* orbital in the helium ion (He^+). [7]

(d) Would you expect the energy of an electron in the 2*p* orbital of an excited hydrogen atom to be equal to the energy of an electron in the 2*s* orbital of an excited hydrogen atom? Justify your answer as fully as possible. [5]

TT1998

8

(a) State the selection rules applicable to the emission spectra of hydrogenic atoms. [3]

(b) The first transition in the Lyman series of the emission spectrum of a hydrogen atom is observed at 82 258 cm^{-1}. Predict the wavenumbers of the next three lines in this series. [4]

(c) Four lines of another series of lines in the emission spectrum of a hydrogen atom are observed at 5331.5, 7799.3, 9139.8, and 9948.0 cm^{1}. Assign these lines, explaining your procedure. [4]

(d) Would the energy required to ionize the $2s$ electron in the ground state of a lithium atom be greater or less than that required to ionize a hydrogen atom with configuration $2s^1$? Give your reasons. [6]

(e) Discuss the differences between the series of lines arising from $np \rightarrow 2s$ transitions in the emission spectra of hydrogen and lithium atoms. [8]

LV1997

9

(a) Sketch the energy level (Grotrian) diagram for a hydrogen atom. Use it to explain the atomic spectrum that is observed for hydrogen. [6]

(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. [6]

(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 the following wavenumbers:

$$14\,908,\ 30\,935,\ 36\,470,\ 39\,024,\ 40\,399\ \mathrm{cm}^{-1}$$

Use a graphical method to estimate the ionisation energy (expressed as a wavenumber, in cm^{-1}) of the $2s$ electron in lithium. [8]

(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. [5]

TT 1997