Second Year

Hilary Term 2002

Physical Chemistry

Tutorial on Atomic Spectra

Dr Frank Schreiber
frank.schreiber@chem.ox.ac.uk
phone (2)-75179
room 30.40 in PTCL

Please hand the work in to my pigeon hole in Wadham by 1:00 p.m. on Thursday (25 April 2002).

You should consider the questions marked *"Supplement"* as those to work on *only* once you have worked on all others.

We will meet for the tutorial in three groups on Friday (26 April 2002) at 2:30, 4:00, and 5:30 p.m. in Library Court 6.

Literature

Softley, Oxford Primer
Richards / Scott, Oxford Primer
Atkins / Friedman, Molecular Quantum Mechanics
Howard, Handouts for lecture on Atomic Spectra (given by Bain in the present term)

Keywords

Hydrogenic atoms, Rydberg constant, Alkali atoms, Helium, Many electron atoms, Spin-orbit coupling, LS coupling, jj coupling, Fine structure, Hyperfine structure, Selection rules and their origin, Ionization energy, Zeeman and Stark effect, Hund's rules, Stern-Gerlach experiment

Revision and Background

Write down *briefly* the definitions / most important facts / equations related to the above keywords.

Problem 1 Hydrogenic Atoms

1. Wavenumbers of some of the transitions in (i) the emission spectrum of atomic hydrogen and (ii) the absorption spectrum of an unknown hydrogenic ion (e.g., He^+, Li^{2+}, etc.) are
   (i) Hydrogen:
   5500.8; 4616.5; 3808.2; 2467.8 cm^{-1}
   (ii) Unknown ion:
   1719865; 1706927; 1685468; 1645965 cm^{-1}
   (a) Identify the principal quantum numbers for the upper and lower states for each of the transitions listed in (i) (without using the literature value for the Rydberg constant, R) and determine a value for R_H of atomic hydrogen.
   (b) Suggest an identification of the unknown ion and assign the transition in (ii). Derive a value of R_x for this ion and varify that the ratio that the ratio R_x/R_H is in agreement with that predicted from the reduced masses on the basis of your identification ($m_e = 5.486 \times 10^{-4}$ amu).
   (Hint: There is a noticeable reduced mass effect on R for hydrogen and if you compare accurate values of R obtained in the two experiments you can extract an approximate mass of the nucleus of the second atom.)

2. *Supplement:*
   For a given n the eigenstates for maximum l (i.e., $l = n - 1$) and maximum m (i.e., $m = n - 1$) have the following form

$$\psi_{n,l=n-1,m=n-1} = \frac{1}{((2n)!)^{1/2}} \left(\frac{2}{nr_0}\right)^{3/2} \left(\frac{2\rho}{n}\right)^{n-1} e^{-\rho/n}\, Y_{n-1,n-1}(\theta,\phi) \qquad (1)$$

   with

$$Y_{n-1,n-1}(\theta,\phi) \sim (\sin\theta)^{n-1}\, e^{i(n-1)\phi} \qquad (2)$$

   Here $\rho = r/r_0$ and $r_0 = \hbar^2/(me^2)$. Calculate the expectation values $< r >$ and $< r^2 >$ and $\Delta r = (< r^2 > - < r >^2)^{1/2}$. The result, together with the behavior of $|Y_{n-1,n-1}|^2$ allows, for large n, a comparison with the orbits of the old Bohr model. Check this!
   (Hint: You may use $\int_0^\infty x^n e^{-ax} dx = n!/a^{n+1}$.)

Problem 2 Alkali Atoms

1. In a simple picture alkali atoms may be viewed as being similar to hydrogenic atoms, but with the valence electron seeing a potential, which is partly screened by the inner (closed) shells. Explain why the l-degeneration is removed for alkalis. Explain why the s-electrons are more strongly bound than the p electrons etc. Why was there l-degeneration for hydrogenic atoms ?

2. The fundamental series of the emission spectrum of sodium shows transitions at the vacuum wavelengths (in nm) 1846.4; 1268.27; 1083.75; and 996.38. Assuming the quantum defects for the nf levels are zero, and using the 3s to 3d separation of 29172.9 cm^{-1} (ignore spin-orbit splitting of the 3d level), estimate the ionization energy of sodium (R_{Na} =109735 cm^{-1}).

3. For the principal series of potassium, four sequential lines occur at the wavelengths (in nm) 321.833; 310.279; 303.573; and 299.311. Use these lines to determine the ionization energy of potassium. To do this, you may devise a suitable graphical method, use some kind of iteration or, probably the easiest, use trial and error.

Problem 3 Helium Atom

The energy levels of Helium-like atoms with one electron in the ground state (n =1) and the other electron in an excited state ($n > 1$) can be described by

$$E = -RhcZ^2 - \frac{Rhc(Z-1)^2}{n^2}. \tag{3}$$

Here it is assumed that the electron in the ground state is screening the equivalent of one elementary charge of the nucleus. Discuss the plausibility of this expression. Calculate the energy levels of He with n = 2, 3, and 4, and compare with experimental results. Does the accuracy of the above formula for E increase if n decreases or if n increases ? Why ?

Problem 4 Many Electron Atoms

1. Show that the spin-orbit coupling interaction, represented by the operator $(A/\hbar^2)\mathbf{L}\cdot\mathbf{S}$ leads to a splitting determined by

$$\Delta = \frac{A}{2}[J(J+1) - L(L+1) - S(S+1)]. \tag{4}$$

   Analysis of the atomic spectrum of a certain atom shows that the ground term is split into three levels with relative energies 0 cm^{-1}, 77 cm^{-1}, and 231 cm^{-1}. Assign J values to the three levels involved and obtain a value for A. What are the possible values for L and S for this term ?

2. Ignoring spin-orbit coupling, determine the number of possible terms of an excited carbon atom with the electron configuration $1s^2\ 2s^2\ 2p\ 3d$.

Problem 5 Zeeman Effect and g Factor

Consider the states $^1D_2$ and $^1P_1$ of an atom in a weak magnetic field.

1. How do these states split in the magnetic field ? What is the splitting energy ?
2. Sketch a scheme of the possible transitions from $^1D_2$ to $^1P_1$. How many different lines are observed ?

Problem 6 Hyperfine Structure

Into how many hyperfine structure components do the following ground states split ?

1. ^{3}H $(^2\mathrm{S}_{1/2};\ I = 1/2)$
2. ^{14}N $(^4\mathrm{S}_{3/2};\ I = 1)$
3. ^{35}Cl $(^2\mathrm{P}_{3/2};\ I = 3/2)$

Problem 7 Photoelectron Spectroscopy

("photon in – electron out")

Consider photoelectrons excited by photons incident along the z direction linearly polarised (i.e., having their electrical field vector) along the x direction. Where would you place your detector to get maximum photoelectron yield ? What is the angular distribution of the intensity of the photoelectrons in the $x-z$ plane as a function of angle relative to the x axis ? Sketch it.

(Hint: Assume the validity of the dipole approximation. Although the excitation of photoelectrons is a quantum mechanical process, for the angular distribution you may use a classical picture with the electron being accelerated in an electrical field.)

Consider the subsequent Auger decay of the ions (some time after a photoelectron has left the atom). What is the angular distribution for Auger electrons ?

Problem 8 Core-level spectrum of Cu and generation of X-rays

("electron in – photon out")

In the "traditional" way to generate X-rays, e.g., for structure determination in the laboratory, electrons are accelerated to an energy of around 40 keV and then strike a (water-cooled) Cu target.

1. List briefly the processes that occur in the Cu target due to electron collision.
2. What are the most important characteristic photon emission lines (in the X-ray regime) ?
3. (i) K_α denotes the photons emitted by an electron making a transition into the K shell from the next higher shell (L). If spin-orbit splitting is taken into account, how many K_α lines are observed ? What are their relative intensities ?

   (ii) K_β denotes a transition from the M shell to the K shell. Answer the corresponding question from (i) for K_β.
4. Sketch qualitatively the photon spectrum emitted by the Cu target as a function of energy. Check your answers on the first two points above. Sketch (in the same diagramme) the photon spectrum after passing through a thin Ni foil. What are the main effects (concentrate on the relative intensities of the K_α lines compared to the K_β lines) ?
5. *Supplement:*
   When you want to use the X-ray source for structure determination, you would usually want to use only one line (i.e., one wavelength). How would you monochromatize your X-ray source ?
6. *Supplement:*
   Could you think of other ways to generate X-rays ? Which ? What would be the features of the radiation of these other X-ray sources ?