## Problem Set 0 *Review of hydrogen and helium*

Some questions require further reading or looking up of facts, but many answers can be found in the lecture notes. They should be written out nevertheless - important derivations and proofs need to be worked through. The questions have been chosen to cover the ground as economically as possible, so there is little repetition. Familiarity with atomic hydrogen and helium is a prerequisite to the understanding of the structure of many-electron atoms. This material should be revised with *problem set 0* prior to starting with any new material.

**1.** (a) Write down an expression for the energy levels in a hydrogen-like atom where the positively charged particle has mass $M$, charge $Ze$ and the negatively charged particle has mass $m$, charge $-e$. Give your results in terms of the reduced mass, and define this quantity. Evaluate the ionization energy of hydrogen to three significant figures in electron volts. Find the difference in the ionization energies of hydrogen and deuterium to three significant figures in GHz.

(b) A muon has mass 206 times the electronic mass, and charge equal to that of an electron. The particle may be captured by an atom and the radiation which is emitted as the muon cascades through the energy levels can be measured. Assuming the muon-nucleus system can be treated as hydrogen-like, find the energy in MeV of the photon emitted as the muon goes from a state with principal quantum number 2 to the ground state in an atom of lead. Neglect the reduced mass correction.

(c) The experimental value is around 5 MeV. This is likely to be significantly different from your theoretical value. What effect(s) might be responsible for the discrepancy? [*Hint* - find the order of magnitude of the size of the region occupied by the muon in its ground state.]

**2.** Certain quantities which appear in the theory of hydrogen have wider application in atomic physics: the Bohr radius $a_0$, the Rydberg constant $R$, the fine structure constant $\alpha$, and the Bohr magneton $\mu_B$. Give a defining expression for each, and write a sentence or two on each explaining their significance.

**3.** Revise the important physical properties of the hydrogenic wave-functions, and make sure you know the significance of the quantum numbers. Learn the spectroscopic nomenclature for referring to $n$ and $l$, so that you will know immediately what is meant by, e.g., a 4d electron.

**4.** [A non-mathematical question, which invites you to think about properties of the hydrogenic wave-functions.] Neglecting relativistic and other small effects, the energies of the s, p, d.... states in hydrogen for a given value of the principal quantum number $n$ are the same. They have the same potential energy, and the same kinetic energy. However, a student argues as follows: "compared with high angular momentum states of the same $n$, the low angular momentum states have a higher probability of being near the nucleus, so their potential energy must be more negative. Their low angular momentum means they have smaller kinetic energy also. So why don't the low angular momentum states lie deeper in energy?"

Explain to the student what is wrong with his argument.

**5.** (a) Explain qualitatively why the energy required to remove one electron from the ground state of the helium atom is much larger than that in hydrogen, while for other states the hydrogenic value is quite a good approximation, e.g. the 1s2s levels in helium have energies very similar to the 2s energy in hydrogen.

(b) The 1s2s configuration in helium is split into two levels. Explain briefly the physical origin of the splitting, and how it comes about that these different energies should be associated with different relative orientations of the intrinsic spins of the two electrons (so that one of the levels is called a "singlet", and the other a "triplet").

**6.** (a) Summarize briefly the evidence that the electron has a spin (intrinsic angular momentum) and a magnetic moment.

(b) Estimate the angular deflection of a beam of atoms after passing through a magnet 0.5 m long which produces a field gradient of 500 T/m in a direction perpendicular to the direction of motion of the atoms. Assume that only one electron in the atom is responsible for its magnetic moment, and that this is an s-electron. The atoms originate in an oven at 1800 K. Point out any approximations you make.

## Problem Set 1 — *Atomic structure and spin-orbit coupling*

**7.** Explain what is meant by the *central field approximation*, and how it leads to the concept of *configurations*. State the Pauli exclusion principle, and show that it follows from the requirement that the wave-function describing a pair of fermions should be antisymmetric with respect to exchange. Account qualitatively for the order of filling of individual electron quantum states in atoms with atomic number up to $Z = 36$.

Explain why the ionization potential of chlorine is less than that of argon, but more than that of potassium. How would you expect the second ionization potentials of these atoms to compare with each other? [The second ionization potential is the energy required to remove a further electron from the singly ionized atom.]

**8.** Explain what is meant by the term *quantum defect*, used in the description of alkali energy levels. Give a brief qualitative account of how you would expect the quantum defect to vary

(i) from lower to higher values of the orbital quantum number $l$ in a given alkali

(ii) from lighter to heavier alkalies for a given value of $l$.

The sodium atom has atomic number $Z = 11$. Write down the complete configuration of the ground (3s) level. Find the quantum defect of this level, given that the first ionization potential of sodium is 5.14 eV.

**9.** [Notes - This question follows on from (8), and is concerned with transitions between energy levels of sodium. You need to know that when an electron undergoes a transition, the value of $n$ can change by any amount, but $l$ has to change by $\pm 1$. As we are concerned here only with gross structure, we neglect spin-orbit interaction; this effect splits most of the energy levels of sodium into closely-spaced doublets, but we treat each doublet as a single level here.]

Sodium has a single series of absorption lines. Make use of the data in question 8 to find the wavelength of the series limit. The longest wavelength absorption line (3s – 3p) is at $\lambda_1 = 589$ nm. Find the quantum defect of the 3p level. Hence estimate the wavelength $\lambda_2$ of the second line in the series (3s – 4p).

Sodium atoms are illuminated with light of wavelength around $\lambda_2$, so that they are excited to the 4p level. Make a rough copy of enough of the energy level diagram to indicate the routes by which the atoms may return to the ground level. You should find that the fluorescence spectrum contains 6 spectral lines, two of which are the transitions at $\lambda_1$ and $\lambda_2$. Two of the others have wavelengths of 1.14 $\mu$m and 2.21 $\mu$m. Again using the properties of the quantum defect, identify these latter two transitions on your energy level diagram.

Use the information given to improve your estimate of $\lambda_2$.

**10.** The Hamiltonian representing spin-orbit interaction of an electron bound in an atom can to a certain approximation be written as

$$\hat{\boldsymbol{H}} = \frac{1}{2m_e^2c^2}\,\frac{1}{r}\,\frac{\partial U(r)}{\partial r}\,\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}}$$

Use any reference you find helpful to derive this expression (including without proof a factor of 1/2 to take account of Thomas precession). From there, show that spin-orbit interaction is

shifting the positions of the energy levels of hydrogen-like atoms by

$$\Delta E(n,l,s,j) = \frac{\mu_0}{4\pi} Z^4 g_s \mu_B^2 \frac{1}{n^3 a_0^3 l(l+1/2)(l+1)} \times \frac{j(j+1) - l(l+1) - s(s+1)}{2}$$

We are concerned with the physics behind this expression and its derivation:

(a) In simple "vector-model" terms, what is the direction of the $\boldsymbol{B}$-field experienced by the electron, relative to its orbital angular momentum? What is the direction of the intrinsic magnetic moment of the electron relative to its spin angular momentum?

(b) In the light of (a), and given that the interaction is of the form $-\boldsymbol{\mu} \cdot \boldsymbol{B}$, should the energy be higher or lower for $j = l+1/2$ as compared with $j = l-1/2$? Check that your conclusion is correct by inspecting the expression given above.

(c) Explain in physical terms where the $Z^4$ dependence comes from.

**11.** Show that the splitting due to spin-orbit interaction between the $J = 3/2$ and $J = 1/2$ levels of the 2p configuration in hydrogen is 11 GHz. Draw a diagram showing the positions of the split levels with reference to the unperturbed level, and label the levels with the appropriate quantum numbers. Using the known $n$-dependence, find the splitting also of the 3p configuration.

Show that spin-orbit interaction displaces the 3/2 level upwards by half the downwards shift of the 1/2 level. Hence show that the mean energy of the states in the 3p configuration is unaffected by the interaction.

The splitting between the $J = 3/2$ and $J = 1/2$ levels in the 3p configuration of sodium is $1.72 \times 10^3\,\mathrm{m}^{-1}$. Why is this so much larger than the splitting in the corresponding configuration in hydrogen?

**12.** A way of studying the small shifts caused by quantum electrodynamic effects is to use high-$Z$ atoms, with all the electrons stripped off except one. One method is to take a tunable laser operating in the visible region (say around 600nm) and excite transitions within the fine structure of the $n = 2$ manifold. Using your expression for the spin-orbit splitting as a function of $Z$, suggest a suitable element for study.

**13.** By considering the successive application of two perturbations, the residual electrostatic interaction and spin-orbit interaction, explain the splitting of a configuration into terms and levels. Hence explain what is meant by $LS$ coupling, making clear the conditions under which it applies.

Three low-lying configurations of the neutral calcium atom ($Z = 20$) are $4s^2$, 4s4p, 4s5s. Write down the terms and levels which arise from these configurations, using conventional spectroscopic nomenclature. Explain the meanings of the various symbols you use. Discuss the specific mechanisms responsible for the relative ordering of these levels. Derive the Interval Rule in $LS$ coupling, and explain whether you would expect it to be obeyed in calcium in any of the terms arising from the 4s5s or 4s4p configurations.

Which of the following levels do not exist in hydrogen, and why?

$$3f\ {}^2F_{3/2}, \quad 3p\ {}^2P_{3/2}, \quad 3s\ {}^2S_{3/2}, \quad 3d\ {}^3D_2, \quad 2p\ {}^2D_{3/2}$$

## Problem Set 2 *Hyperfine structure, Zeeman effect & X-ray spectra*

**14.** State the selection rules for electric dipole radiation between levels for which $LS$ coupling is appropriate. Use simple arguments to justify three of these rules.

Give reasons why the following transitions obey or disobey electric dipole selection rules:

$1s^2 2p\ {}^2P_{1/2} - 1s^2 3d\ {}^2D_{5/2}$
$1s^2 2s2p\ {}^1P_1 - 1s^2 2p3p\ {}^1P_1$
$1s^2 2s^2\ {}^1S_0 - 1s^2 2p^2\ {}^3P_1$

**15.** The emission spectrum of calcium contains strong lines at 422.8, 610.4, 612.4, 616.4 and 1035 nm, all arising from transitions between the levels of the $4s^2$, 4s4p and 4s5s configurations (see question 13). The transition at 422.8 nm is also observed in absorption. Given that the singlet-triplet splitting in the 4s5s configuration is $177\,700\,\mathrm{m}^{-1}$, draw a quantitative energy level diagram (units of $\mathrm{m}^{-1}$, referred to zero at the ground level) showing the transitions giving rise to the spectral lines listed above, and state any selection rules used in its deduction.

**16.** A term of the form $A_J \boldsymbol{I} \cdot \boldsymbol{J}$ is included in the atomic Hamiltonian in order to account for part of the interaction between the nucleus and the atomic electrons. What does the term describe, and why does it have this form?

Hyperfine levels with quantum numbers $F$ and $F-1$ are separated in energy by $\Delta E_{F,F-1}$. Show that the hyperfine levels associated with a given electronic level should obey the Interval Rule

$$\frac{\Delta E_{F,F-1}}{\Delta E_{F-1,F-2}} = \frac{F}{F-1}.$$

It commonly happens that the hyperfine structure in a transition is dominated by the contribution of an s-electron in one of the levels. What property of s-electrons could be responsible for this?

A transition of this kind occurs at 494 nm in singly ionised $^{133}$Cs (cesium) between a level from the $5p^5 6s$ configuration and one from the $5p^5 6p$ configuration. Five hyperfine structure components are observed with wavenumbers relative to that with the lowest wavenumber as follows: 0.0, 8.1, 19.5, 33.7, $51.3\,\mathrm{m}^{-1}$. The experimental uncertainty in the position of each component is of order $0.1\,\mathrm{m}^{-1}$. Find the nuclear spin of $^{133}$Cs, and the value of $J$ for the level arising from the $5p^5 6s$ configuration.

**17.** Distinguish between the *Normal* and *Anomalous* Zeeman effects. Define the Landé splitting factor $g_J$, and, assuming an $LS$ coupling scheme, obtain an expression for $g_J$ in terms of the quantum numbers $L$, $S$ and $J$. Values of $g_J$ are usually positive, but they can be negative; give an example, and use the vector model to explain qualitatively how the situation arises. Show that $g_J = 0$ for a ${}^4D_{1/2}$ level.

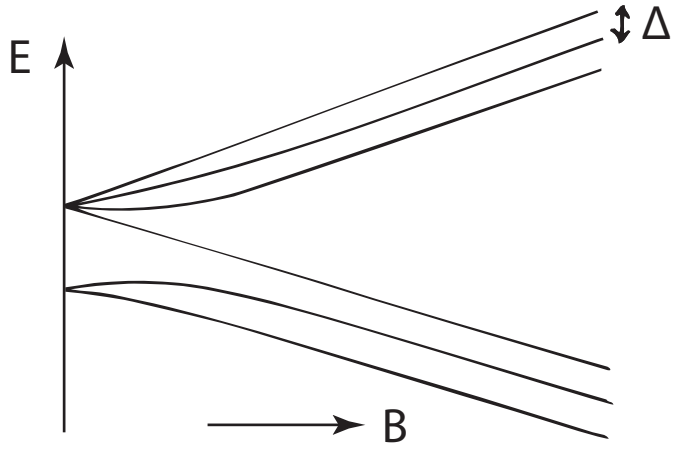
The ground level of atomic nitrogen ($Z = 7$) is found to split into four Zeeman sublevels in a magnetic field of 1 T. The separation between adjacent sublevels is 28 GHz. What are $L$, $S$ and $J$ for this level?

Briefly describe the important features of the Paschen-Back (strong field) effect. In the lowest ${}^4P$ term of nitrogen the ${}^4P_{5/2}$ and ${}^4P_{1/2}$ levels are separated by 0.01 eV. Estimate the

field required to exhibit the Paschen-Back effect in this term, and comment on its realizability.

**18.** Draw out the energy level diagram, together with the transitions, for the 671 nm transition in $^6$Li ($Z = 3$), $1s^2 2s^2 S_{1/2}$ – $1s^2 2p^2 P_{3/2}$ in a weak field of magnitude $B$. Give the splittings of the levels in terms of $\mu_B B$, and the frequency intervals between the components in units of $eB/4\pi m_e$. Indicate which components would not be present if only radiation along the field direction were detected. The levels of the $1s^2 2p\ ^2P$ term are separated by 10 GHz; estimate the range of field strength which could be described as weak in this case.

**19.** The diagram shows the hyperfine structure of the ground level of one of the isotopes of hydrogen, as a function of an applied magnetic field $B$. Make a rough copy of the diagram, and label the states with appropriate quantum numbers in both weak and strong fields. What is meant by a "strong" field in the context of hyperfine structure?




Deduce from the diagram the nuclear spin of this isotope and the sign of its nuclear $g$-factor.

The measured zero-field splitting is 327.4 MHz. Find the separation of adjacent states in strong field ($\Delta$ in the diagram).

**20.** The energies of X-ray transitions are often represented by the expression

$$E_{n,m} = hcR\left(\frac{(Z-\sigma_n)^2}{n^2} - \frac{(Z-\sigma_m)^2}{m^2}\right).$$

Explain the form of this expression, and indicate the physical significance of the quantities $\sigma_m$ and $\sigma_n$.

An X-ray tube operates with a tungsten target (atomic number 74). As the tube voltage is increased from around 2 kV, groups of X-ray lines are found to appear. There are three groups in all. The first appears at a tube voltage of about 2.5 kV, the lines having wavelengths around 0.65 nm. The second appears at 12 kV, the wavelengths being around 0.13 nm. Explain the origin of these groups.

As the tube voltage is put up still further, the third and final group appears. Estimate the tube voltage at which this occurs, and the wavelength of the strongest line of the group.

These lines are accompanied by a continous X-ray spectrum. Explain qualitatively the origin of this spectrum, and why is has a low wavelength cut-off. What is the this cut-off wavelength when the tube voltage is 60 kV?

Explain what is meant by the Auger effect. Under what circumstances can an Auger electron be emitted from the L shell in tungsten? Estimate from the data given the minimum kinetic energy such an electron could have.