64-311/5: Atomic and Molecular Spectra

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SECTION 1: REVISION QUESTIONS FROM 64-310/14

ε₀ = 8.854187817 x 10^{-12} Fm^{-1}, \hbar = 1.05457266 x 10^{-34} Js, e = 1.60217733 x 10^{-19} C, me = 9.1093897 x 10^{-31} kg

1 Using the semi-classical equations of the Bohr model, determine:

(a) How many orbits does an electron in the \( n = 2 \) state of hydrogen make before returning to the ground state, if the average lifetime of an excited state is 1 ns?

(b) Determine size and ground state energy of the highly-charged ion \( \text{U}^{91+} \) (\( Z = 92 \)). What is the velocity of the electron in the ground state? Is it still appropriate to consider this situation as a non-relativistic problem?

(c) A Kaon (\( \text{K}^- \)) resembles a heavy electron (m = 967m_e) and it can be captured by a proton to form a kaonic atom. Calculate for \( (p^+\text{K}^-) \):

(i) the radius of the first Bohr orbit;
(ii) the ionisation energy in electron volts;
(iii) the energy and wavelength corresponding to the Lyman \( \alpha \) transition. In which part of the electromagnetic spectrum does this lie?

If the lifetime of \( \text{K}^- \) is 12 ns is it reasonable to consider the ground state kaonic atom to be stable? Why?

(d) Determine the size of a hydrogen atom with a principal quantum number of 100. What is the electron's binding energy in this state? How does this compare with thermal energies?

2 By considering only the radial variation in the eigenfunctions of one-electron atoms, determine:

(a) The distance from the nucleus (in units of \( a_0 \)) for which the electron probability density is a maximum, and

(b) The expectation value of the radial co-ordinate, for both the \( n = 1, \ell = 0 \) and the \( n = 2, \ell = 1 \) states of hydrogen. Discuss why your answers to (a) and (b) are different. How do they compare with the Bohr model?

[Use eigenfunctions and expectation value equations from lecture notes, handouts or textbooks.]

3 Consider the hydrogen eigenfunction: \( \Psi_{3,1,1} \), determine:

(a) the corresponding energy eigenvalue in eV;
(b) the square of the total orbital angular momentum;
(c) the \( z \) component of angular momentum;
(d) how many other \( L_z \) components will there be for the same \( \ell \)?
(e) how many other \( \ell \) values can have the same total energy?
(f) what is the total number of degenerate states with the same total energy? (exclude spin effects).

SECTION 2: ONE ELECTRON ATOMS

All \( s \) states (\( \ell = 0 \)) are spherically symmetric. However, Unsöld's theorem (1927) states that for any value of the orbital angular momentum quantum number \( \ell \), the probability densities summed overall possible states from \( m = -\ell \) to \( +\ell \) yields a constant independent of \( \theta \) and \( \phi \); ie:

\[
\sum_{m=-\ell}^{\ell} Y^*(\theta,\phi)Y(\theta,\phi) = \text{constant}
\]

This useful theorem means that every closed (fully occupied) "subshell" in an atom (or ion) has spherical symmetry. Verify Unsöld's theorem for the \( \ell = 0, \ell = 1 \) and \( \ell = 2 \) eigenfunctions of hydrogen. [Use equations for \( Y(\theta,\phi) \) from handouts or textbooks.]

In Bohr's one-electron atom, the electron is regarded as moving in a circular orbit of radius \( r \). Use classical electromagnetism and quantised (orbital) angular momentum to show that the magnitude of the magnetic field experienced by the nucleus due to the electronic motion is:

\[
B = \frac{\mu_B \mu_B}{2\pi^3} \sqrt{\ell(\ell+1)}
\]

where \( \mu_B \) is the Bohr magneton \( [= \frac{e}{2m} = 9.27 \times 10^{-24} \text{ Am}^2 \text{ (or JT}^{-1})] \)

[Hint: use as the starting point the classical expression for a B field at the centre of a 'current loop']

Calculate the magnitude of the magnetic field due to an electron in the excited \( 2p \) state of hydrogen. Is result for all the \( s \) states surprising?

Neutral silver atoms (atomic mass = 108) emerge from an oven, maintained at 1000K, into a 20 cm long Stern-Gerlach magnet with a dB/dz = 100Tm\(^{-1}\). On leaving the magnet, the atoms travel a further distance in a field-free region before being detected. The ground state of silver is an S state (\( L = 0 \)) and has a magnetic dipole moment of 1 Bohr magneton, like hydrogen.

(a) What distribution of Ag atoms would one observe at the detector?
(b) How is this different from classical expectations?
(c) How is this different from non-relativistic quantum predictions?
(d) What is the angular deflection of the atomic beam at the exit of the magnet?
(e) How does this provide evidence for a 'spin g factor' of 2?

When Goudsmit and Uhlenbeck (1925) proposed that the electron had intrinsic angular momentum - "spin" - they were fully aware of its inconsistency with classical physics. In the classical picture, an electron could be regarded as a charged sphere with a size given by its Coulomb self-energy:

\[
\frac{3e^2}{5 \times 4\pi\epsilon_0 R} = \left( \frac{3}{5} \right) \frac{e^2}{4\pi\epsilon_0 R}.
\]
Determine the surface velocity of a spinning classical electron and show that it is much greater than the speed of light. [Moment of inertia = $(2MR^2/5)$]

The Schrödinger model for hydrogen agreed with the Bohr model in that they both resulted in the energies of the excited states being only a function of principal quantum number $n$. This 'accidental degeneracy' for the different $\ell$ states is not strictly true as closer scrutiny of the spectral lines revealed 'fine-structure'. One factor which contributes to this is the spin-orbit coupling, which results from the electron spin interacting with the magnetic field experienced by the electron due to its motion.

The energy splitting due to this interaction is given by

$$\Delta E_{so} = \frac{1}{2m^2c^2} \left( \frac{1}{r} \frac{dV}{dr} \right) \mathbf{S} \cdot \mathbf{L} \quad \text{where} \quad V = \frac{-Ze^2}{4\pi\epsilon_0 r}$$

(a) The spin-orbit interaction splits all the states of group I atoms, except s states, into two substates, or 'doublets'. Why are s states exceptions to this rule? Why are there no more than 2 substates?

(b) After manipulating the $\mathbf{S} \cdot \mathbf{L}$ product into a form containing "good" quantum numbers, evaluate the energy difference between the J levels of the $2p$ state of hydrogen due to the spin-orbit interaction. What are the spectroscopic labels for these states? The $2p$ fine structure splitting is $4.52 \times 10^{-5}$ eV. How does this compare with your spin-orbit splitting? What other factors contribute to the fine structure in hydrogen?

Note: \(1/r^3 = (a_o n^3 \ell (\ell + 1)/2(\ell + 1))^{-1}\)

9 (a) Explain what is meant by "degeneracy", making specific reference to orbital angular momentum as an example. A hydrogenic electron has a principal quantum number $n = 3$. Give a list of all the values of the quantum numbers $\ell$, $\ell_z$, $s$ and $s_z$ for all the possible states of this electron. How many states in total are possible?

(b) By combining $\mathbf{L}$ and $\mathbf{S}$ to form $\mathbf{J}$, express the levels of the $n = 3$ electron in terms of spectroscopic notation. By considering the possible values of $J_z$, deduce the total number of states for the $n = 3$ electron. How does this compare with the result of (a)?

(c) The energy degeneracy is removed by spin-orbit and relativistic effects, resulting in an energy splitting given by:

$$\Delta E = \frac{E_n Z^2 \alpha^2}{n} \left[ \frac{1}{J + \frac{1}{2}} - \frac{3}{4n} \right]$$

according to the Dirac theory (ie. ignoring the Lamb shift), where $E_n$ is the energy of the $n$th level and the other symbols have their usual meanings.

Into how many different energy levels will the $n = 3$ split? Label the different levels and determine their relative spacing in electron-volts.

10 (a) By combining spin and orbital angular momentum, determine the different possible $J$ values for a $d$ electron within the LS coupling scheme. What are the magnitudes (in units of $\hbar$) of the total
angular momenta? Determine the angle between $L$ and $S$ for the different $J$ values within the vector model.
(b) “Translate” the state labels listed below, in spectroscopic notation, into three quantum numbers, \( L, S \) and \( J \). Which of these states correspond to possible values of \( L, S \) and \( J \) for a one-electron atom? For each rejected set \((L, S, J)\) give at least one reason why it cannot be realised.

\[
2S_{1/2}; \ 2D_{1/2}; \ 2P_0; \ 3P_1; \ 2P_{1/2}; \ 2F_{7/2}; \ 1S_0; \ 2S_{3/2}; \ 2D_{5/2}; \ 2P_{3/2}; \ 2P_{5/2}; \ 2D_{3/2}
\]

11 What is meant by a 'forbidden' transition? What are the electric dipole selection rules for an atom in the absence of any external fields? Explain qualitatively their origin by considering (a) the angular momentum of photons, and (b) parity and its application to the evaluation of the electric dipole moment for the atom.

Which of the following electric dipole transitions are forbidden for a one-electron atom and why?

\[
\begin{align*}
3S_{1/2} & \rightarrow 2S_{1/2}; \quad 2P_{1/2} \rightarrow 2S_{1/2}; \quad 3P_{3/2} \rightarrow 1S_{1/2} \\
3D_{5/2} & \rightarrow 2P_{3/2}; \quad 3D_{5/2} \rightarrow 2P_{1/2}; \quad 3D_{3/2} \rightarrow 1S_{1/2}
\end{align*}
\]

SECTION 3: MULTI-ELECTRON ATOMS

12 Explain the following in terms of the Hartree theory:

(a) why does the electronic field structure of noble gases cause them to be chemically inert?

(b) why can the noble gases be considered to be spherically symmetric? What other atoms have this property?

(c) why are all atoms approximately the same size?

(d) why are 2s states more tightly bound than 2p states?

13 Explain the following for the case of the helium atom:

(a) why does the 1^3S state not exist, when the 2^3S state does exist?

(b) why do singlets and triplets have different energies?

(c) why is the 2^3S state described as "metastable"?

(d) why did early spectroscopists think there were two forms (ortho- and para-) of helium?

14 (a) Explain what is meant by \( LS \) (Russell-Saunders) coupling.

(b) Briefly discuss the associated electric dipole selection rules.

(c) Explain, in simple terms, why the spin-orbit interaction becomes stronger with increasing \( Z \).

(d) What happens when \( LS \) coupling breaks down?

(e) What observations would enable you to determine whether an atom obeyed LS coupling?

15 Assuming \( LS \) coupling holds, list all the possible spectral terms \( 2S+1L \) which result from the following electronic configurations:

\[
\begin{align*}
(a) \ (ns, n's) & \quad (b) \ (ns, n'p) & \quad (c) \ (ns, n'd) & \quad (d) \ (np, n'd)
\end{align*}
\]

List all the corresponding fine structure terms: \( 2S+1LJ \).

[Hint: \( n' \) is also a (general) principal quantum number but \( \neq n \)]
The two 'optically active' or 'valence' electrons in an atom have quantum numbers: \( n_1 = 4, \ell_1 = 0, s_1 = 1/2, \) and \( n_2 = 3, \ell_2 = 2, s_2 = 1/2. \)

(a) What is their configuration?
(b) Using \( LS \) coupling, determine all the fine structure levels. Order the levels in energy, and label each one using spectroscopic notation.
(c) Using the Landé interval rule to predict the ratio of the splittings in each fine structure multiplet.
(d) If this is an excited configuration of calcium, use the electric dipole selection rules to determine which transitions, if any, are allowed to the \( \text{Ca} \, ^1S_0 \) ground state.

Using the Ornstein, Burger, Dorgelo sum rule find the relative intensities for the spectral lines between the following systems:

(a) \( ^2S_{1/2} \) and \( ^2P_{3/2,1/2} \)
(b) \( ^2D_{3/2,5/2} \) and \( ^2P_{3/2,1/2} \)
(c) \( ^2D_{3/2,5/2} \) and \( ^2F_{5/2,7/2} \)
(d) \( ^3S_1 \) and \( ^3P_{0,1,2} \)

18 (a) What condition must be fulfilled for an atom to display the "normal" rather than the "anomalous" Zeeman effect?
With the aid of a suitable diagram, explain why the red line of cadmium \( (^1D_2 \rightarrow ^1P_1 : \lambda = 643.85\text{nm}) \) displays the "normal" Zeeman splitting. Determine the frequency difference, and hence the wavelength difference, between the three components in an applied field of 0.01 T.

19 (a) The yellow sodium doublet arises from transitions between \( ^3P_{3/2,1/2} \) and the ground state \( ^3S_{1/2} \). Draw diagrams to illustrate the Zeeman splitting of the two lines in a weak external magnetic field, and show that this results in 6 and 4 separate “lines” (wavelengths).
(b) Draw diagrams to illustrate the sodium doublet splitting in a strong magnetic field and the resulting transitions. (Paschen-Back effect.)
(c) What are the 'good' quantum numbers in these two situations, and how do they arise?

SECTION 4: MOLECULES

State the expressions for the angular momentum and energy for a (rigid) rotating diatomic molecule. The rotational spectrum of \( ^1H^{35}\text{Cl} \) contains the following successive transition wavelengths in microns (\( \mu \text{m} \)): 120.3, 96.0, 80.4, 68.9 and 60.4.

(a) Use the data to determine the mean energy between the \( J = 0 \) and \( J = 1 \) levels.
(b) Calculate the equilibrium distance between the nuclei.
(c) Identify the rotational quantum numbers \( J_n \) for each transition.
(d) By stating and discussing the validity of any assumptions you make, calculate the rotational splitting between the \( J = 0 \) and \( J = 1 \) of DCl.

[Masses of \(^1\text{H}, \text{D}, \) and \(^{35}\text{Cl} \) are \( 1.67 \times 10^{-27} \) kg, \( 3.35 \times 10^{-27} \) kg and \( 58.45 \times 10^{-27} \) kg]
21 (a) Show that, for a diatomic gas in thermal equilibrium at temperature $T$, the ratio of the number of molecules in rotational level $J$ to the number with $J = 0$ is a maximum when:

$$J = \sqrt{\frac{kT}{\hbar^2} - \frac{1}{2}}$$

(b) What is the most populated $J$ level for CO at 1000K?

(c) What is the relative population of $\nu = 1$ to $\nu = 0$ levels at 1000K?

(d) At what temperature would there be enough thermal energy to dissociate the molecule?

[CO data: Bond length = 0.113nm, $^{12}$C mass = 1.99 x 10$^{-26}$ kg, $^{16}$O mass = 2.66 x 10$^{-26}$ kg, SHM spring constant = 1903 N/m, Dissociation energy = 9.60eV]

22 Find the dissociation energy, $D_0$, for the deuterium molecule D$_2$ and the lowest vibrational energy spacing, given that their corresponding values for H$_2$ are 4.48 eV and 0.545 eV. Hence determine the anharmonicity constant for both H$_2$ and D$_2$. Which vibrational series converges most rapidly per vibrational quantum?

**SECTION 5: NUCLEAR PHYSICS**

1 $u$ (atomic mass unit) = 1.660540 x 10$^{-27}$ kg

23 (a) In Rutherford scattering what is the distance of closest approach for 10 MeV alpha particles colliding with stationary nuclear targets of (a) aluminium and (b) lead? What is the fundamental assumption underlying Rutherford's analysis?

(b) Estimate (stating your assumptions) the incident energy at which you would expect deviations from Rutherford back-scattering to become apparent when alpha particles are used to bombard $^{63}$Cu. Assume that the nuclear radius is given by $R = aA^{1/3}$, with $a = 1.07 F$.

(c) 420 MeV electrons are scattered from $^{12}$C nuclei resulting in a diffraction pattern with the first minimum at 50$^\circ$. Estimate the size of the charge distribution radius of the $^{12}$C nucleus. How does your value compare with that obtained using the formula in part (b)? State any assumptions used.

24 (a) Determine the Q-values (in MeV) for the following reactions and comment on their relevance for nuclear fusion reactors and stellar interiors.

$$D(D, ^1H)T \quad D(D, n)^3He \quad D(T, n)^4He \quad ^1H(^1H, e^+ + \nu)D$$

[Use: $^1H = 1.007825u$; $^2H = 2.014102u$; $T = 3.016050u$; $^3He = 3.006029u$; $^4He = 4.002603u$; $e = 0.000549u$; $n = 1.008665u$]

(b) In their old age, heavy stars obtain part of their energy from the reaction:

$$^4He + ^{12}C \rightarrow ^{16}O$$

How much energy does each such event give off? [$^{12}C = 12.00000u$; $^{16}O = 15.994915u$]
25 (a) Determine the binding energy of $^4\text{He}$ in MeV.

(b) By treating the $\alpha$ particle as an indivisible unit, derive an expression for the Q-value in $\alpha$ particle decay using the semi-empirical mass formula. (Make the large Z approximation and use the $a$ coefficients given in the lectures.) Hence calculate the Q-value for alpha decay of $^{212}_{84}\text{Po}$. The measured alpha particle energy is 8.78 MeV, discuss any discrepancy in your results.

$^{1}\text{H} = 1.007825u; \quad n = 1.008665u$

26 Use the Liquid Drop model to explain why many nuclei which are energetically unstable to fission have a very long lifetime.

Determine and compare the Q-value for the following induced fission reaction:

$$^{235}\text{U} + n \text{(thermal)} \rightarrow ^{236}\text{U} \rightarrow ^{93}\text{Rb} + ^{141}\text{Cs} + 2n$$

(a) By considering their atomic masses: $^{235}\text{U} = 235.043925u$, $^{93}\text{Rb} = 92.92172u$, $^{141}\text{Cs} = 140.91949u$, $n = 1.008665u$, $^{236}\text{U} = 236.045563u$.

(b) By considering only the Coulomb and surface energy terms in the semi-empirical mass formula. (Ignore the free neutrons.)