

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 alkalis 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 ± 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 λ_2 of the second line in the series (3s – 4p).

Sodium atoms are illuminated with light of wavelength around λ_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 λ_1 and λ_2 . Two of the others have wavelengths of 1.14 μm and 2.21 μm . 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 λ_2 .

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

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

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 $\mathbf{B}$ -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 $-\boldsymbol{\mu} \cdot \mathbf{B}$, 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 $1.72 \times 10^3 \text{ m}^{-1}$. 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?

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

To: James Sadler

B3 Atomic Physics Problem Set 1

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(7) In many electron systems, a major part of the repulsion between one electron and the others acts towards the centre. The potential due to ~~neutral~~ ^{the} nucleus is also towards the centre. So we replace the $1/r$ hydrogen-like potential with an effective potential due to the nucleus and the centrally acting part of the $1/r_{ij}$ repulsion term. We put the rest terms into a perturbation. ~~and~~ ~~this~~ This central zeroth-order Hamiltonian gives separable equations that approximate the real solutions. This is the Central Field Approximation. ✓

(8) Under Central Field Approximation, for multi-electron systems, the lower angular momentum states have the electrons spending more times close to the ~~not~~ nucleus. Thus they are less screened from the nucleus so they are ~~tight~~ more tightly bounded and thus have lower energy. ~~Then~~ So n and l determine the energy of a state. By principle of least energy, ~~the~~ the states are filled from low to high energies. ~~Thus the~~ By Pauli exclusion principle, no more than 1 electron can occupy the ~~se~~ same state. So the way quantum states are filled for the electrons inside an ~~at~~ atom is the atom's electron configuration ✓

States $|n L M_L S M_S\rangle$ or alternative basis $|n L S J M_J\rangle$

Pauli ~~Excl~~ Exclusion Principle:

No more than 1 Fermions can be in the same quantum state. ✓

For Fermions: $\psi(1,2) = -\psi(2,1)$

~~$\psi(1,2)$ = Probability amplitude for particle 1 in state 1 and particle 2 in state 2~~

~~$\psi(2,1)$ = Probability amplitude for particle 1 in state 2 and particle 2 in state 1~~

indistinguishable two $\checkmark$ fermions ~~has~~ have their overall wavefunctions

$$\psi_{mm'}(\underline{x}, \underline{x}') = -\psi_{m'm}(\underline{x}', \underline{x}) = \langle \underline{x}, \underline{x}', m, m' | \psi \rangle$$

(m indicates spin, $\underline{x}$ indicates position)

Assume overall ~~wave~~ state of two Fermions to be

$$|\psi\rangle = \sum_{nn'} a_{nn'} |n\rangle |n'\rangle$$

(superposition of product states)

$$\psi_{mm'}(\underline{x}, \underline{x}') = \langle \underline{x}, \underline{x}', m, m' | \psi \rangle = \sum_{nn'} a_{nn'} \langle \underline{x}, m | n \rangle \langle \underline{x}', m' | n' \rangle \quad (1)$$

$$\langle \underline{x}, \underline{x}', m, m' | = \langle \underline{x}, \underline{x}' | \langle m, m' |$$

$\Rightarrow$ Swap $\underline{x}, m$ with $\underline{x}', m'$, we have

$$\psi_{m'm}(x', x) = \sum_{n, n'} a_{nn'} \langle x', m' | n \rangle \langle x, m | n' \rangle \quad (2)$$

$$(1) + (2) \Rightarrow$$

$$0 = \sum_{n, n'} a_{nn'} \langle x, m | n \rangle \langle x', m' | n' \rangle +$$

$$\sum_{n, n'} a_{n'n} \langle x, m | n \rangle \langle x', m' | n' \rangle$$

exchange
index being
summed
over

$$= \sum_{n, n'} \langle x, m | n \rangle \langle x', m' | n' \rangle (a_{nn'} + a_{n'n}) \quad (3)$$

$\sum_{n, n'} = \sum_{n, n'}$
order of
summation
doesn't
matter

$\therefore (3)$ is true for all x, x', m, m'

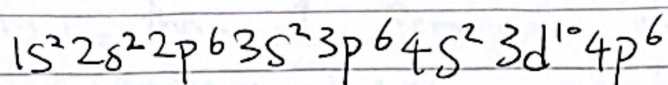
$$\therefore a_{nn'} = -a_{n'n} \quad \therefore a_{nn} = 0$$

$\Rightarrow$ Probability for particles being in state

$|n\rangle|n\rangle$ is 0

$\Rightarrow$ Two Fermions cannot occupy the same identical quantum state.

→ Up to $Z=36$, the order of filling of electrons is



Normally energy increase with n , and when n is the same the larger l the larger energy because ϕ larger l means electrons are further away from nucleus and thus more shielding effect. ✓

Chromium has $4s^1 3d^5$

→ The ~~spec~~ special case ^{is about} $3d$ and $4s$ orbitals. $3d$ ($n=3, l=2$) ~~the~~ electrons are ~~further away~~ has very strong shielding effect such that their energy is higher than $4s$ electrons.

→ The ionisation energy (IE) of Cl is less than that of Ar because the nucleus of Ar has 1 more nuclear charge than Cl. The attraction is stronger for the outer electron in Ar than in Cl.

Also since to ionise Cl and Ar we take an electron out from the same energy level (~~3p~~) ($3p$), the difference in shielding effect can be neglected

⇒ Cl has less IE ✓

~~Potassium~~ Potassium has ^{less} ~~higher~~ IE than Cl because although it has 2 more nuclear charge than Cl, its outermost electron is sitting in $4s$ orbital along

also 4s is very far from the nucleus $\rightarrow \frac{-Ze^2}{4\pi\epsilon_0 r}$ is less

All other electrons in K shield the nuclear attraction from the 4s electron. ✓

$\Rightarrow$ very easy to take out this electron

$\Rightarrow$ K has less IE than Cl. ✓

$\rightarrow$ Cl^+ has outer shell $3p^4$
 Ar^+ has outer shell $3p^5$
 K^+ has outer shell $3p^6$

They all have same outer shell (just different number of electrons filled in that shell). So nuclear charge ~~alone~~ alone determines IE

$\Rightarrow$ 2nd IE: $\text{Cl}^+ < \text{Ar}^+ < \text{K}^+$ ✓

IE from lighter to heavier alkalis for a given l , the IE increases as the core is less and less

hydrogen-like. (away from Hydrogen in periodic table)

Ground state configuration for Na is

also it is very hard to find

All other electrons in k shell. the number
attraction from the $+2$ electron
is very small + the electron
is k has less $I.E.$ than Cl

→ Cl has more $I.E.$ than K has
more $I.E.$ than Cl has
 K has more $I.E.$ than Cl has

They all have same number of electrons
different number of electrons that
spells a negative charge, which is
different $I.E.$

$I.E. : Cl < K$

⑧ Considering the outermost electron, the Alkalies ~~metals~~ are very hydrogen-like. The energy levels are same as that of Hydrogen if we ignore the effect of lower l orbital electron penetrating the inner shells. So we approximate the energy levels of Alkalies metals to be

$$E_n = -\frac{R}{(n^*)^2} \quad \text{where } n^* = n - S(l)$$

$S(l)$ is the quantum defect ~~that~~ ✓

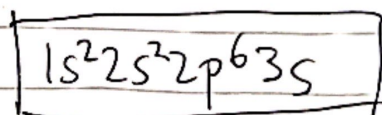
(i) from lower to higher l , $S(l)$ will decrease, the higher the l , the larger because ✓

the energy E_n (and thus n^*) needs to be ~~is~~ in order to approach the energy of Hydrogen atom with the same n .

(ii) from lighter to heavier alkalis for a given l , the $S(l)$ increases as the core is less and less

Hydrogen-like. (Away from Hydrogen in periodic table) ✓

→ Complete configuration for Na is



$$-\frac{R}{(n - \delta_{LS})^2} = -5.14 \text{ eV} \quad \text{for } n=3$$

$$R = 13.6 \text{ eV}$$

$$-\frac{R}{n^2} = -\frac{13.6 \text{ eV}}{3^2} = -1.51 \text{ eV}$$

$$(3 - \delta_{LS})^2 = \frac{13.6}{5.14} = 2.646$$

$$\Rightarrow \boxed{\delta_{LS} = 1.37} \quad \checkmark$$

9) series limit is / ($3s \rightarrow np$ as $n \rightarrow \infty$)

$$\therefore E_{\infty} = -\frac{R}{n^2} \Big|_{n \rightarrow \infty} = 0$$

$$\frac{hc}{\lambda} = \frac{R}{n^2} = \frac{R}{(3-\delta(s))^2} = 5.14 \text{ eV}$$

$$\therefore \lambda = \frac{6.63 \times 10^{-34} \times 3.0 \times 10^8}{5.14 \times 1.6 \times 10^{-19}} = \boxed{242 \text{ nm}}$$

$$\frac{hc}{\lambda_1} = R \left(\frac{1}{(3-\delta(s))^2} - \frac{1}{(3-\delta(l))^2} \right)$$

$$\therefore 5.14 \text{ eV} - \frac{hc}{\lambda_1} = \frac{R}{(3-\delta(l))^2}$$

$$\cancel{5.14} \quad 5.14 \text{ eV} - 2.11 \text{ eV} = \frac{13.6 \text{ eV}}{(3-\delta(l))^2}$$

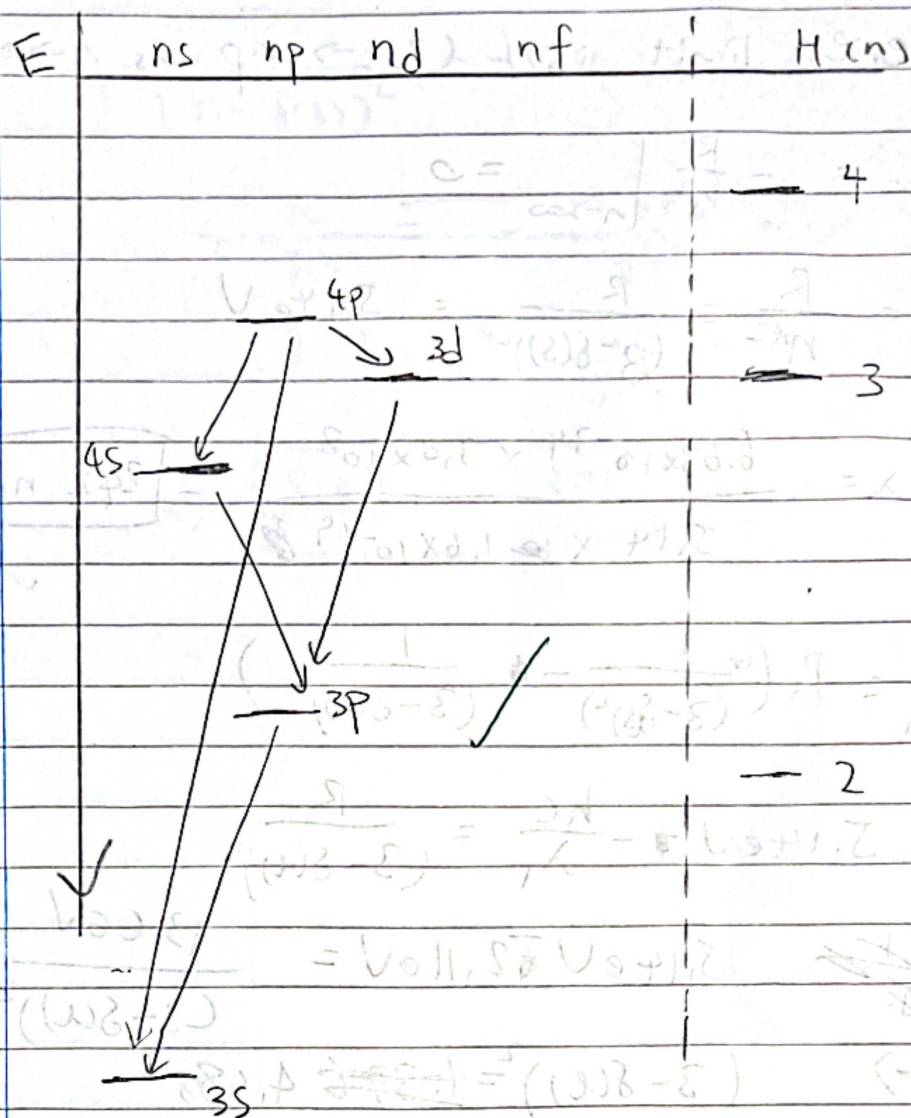
$$\Rightarrow (3-\delta(l))^2 = \cancel{1.876} 4.488$$

$$\Rightarrow \delta(l) = \cancel{1.63} \quad \boxed{\delta(l) = 0.88}$$

For ~~4p~~ $3s-4p$

$$\frac{hc}{\lambda_2} = R \left(\frac{1}{(3-\delta(s))^2} - \frac{1}{(4-\delta(l))^2} \right) = R(0.2736)$$

$$\therefore \lambda_2 = \frac{hc}{0.2736R} = \boxed{334 \text{ nm}} \quad 332 \text{ nm}$$



selection rule $\Rightarrow \Delta l = \pm 1$

Rough comparing estimated values we know:

$\rightarrow 1.14 \mu\text{m}$ corresponds to transition $4s \rightarrow 3p$

$\rightarrow 2.21 \mu\text{m}$ corresponds to transition $4p \rightarrow 4s$

We also know that

$\rightarrow 589 \text{ nm}$ corresponds to transition $3p \rightarrow 3s$

$\therefore$ Energy difference between $4s$ and $3s$ is

$$\Delta E = hc \left(\frac{1}{1.14 \mu\text{m}} + \frac{1}{2.21 \mu\text{m}} + \frac{1}{589 \text{ nm}} \right) = \frac{hc}{\lambda_2}$$

$$\therefore \frac{1}{\lambda_2} = \frac{1}{1140} + \frac{1}{2210} + \frac{1}{589} \Rightarrow \lambda_2 = 330 \text{ nm}$$

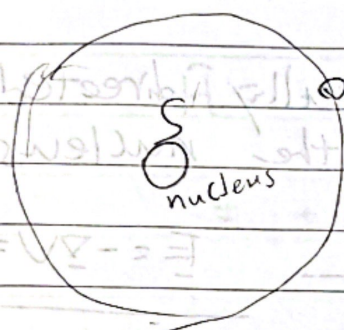
is a better estimate

(10) Lorentz Transformation for general $\underline{E}$ and $\underline{B}$ fields between two frames S and S' with relative velocity $\underline{V} = (0, V, 0)^T = V\hat{y}$ is given by:

$$\underline{E}'_{\parallel} = \underline{E}_{\parallel} \quad \underline{B}'_{\parallel} = \underline{B}_{\parallel}$$

$$\underline{E}'_{\perp} = \gamma(\underline{E}_{\perp} + \underline{V} \times \underline{B}_{\perp}) \quad \underline{B}'_{\perp} = \gamma(\underline{B}_{\perp} - \frac{1}{c^2} \underline{V} \times \underline{E}_{\perp})$$

If $\overset{\text{rest}}{V}$ frame of H nucleus is S and $\overset{\text{rest}}{V}$ frame of electron is S'



then $\underline{B} = 0$

$$\therefore \underline{B}'_{\parallel} = \underline{B}_{\parallel} = 0$$

$$\underline{B}'_{\perp} = \gamma(\underline{B}_{\perp} - \frac{1}{c^2} \underline{V} \times \underline{E}_{\perp})$$

$$= 0 - \gamma \frac{1}{c^2} \underline{V} \times \underline{E}_{\perp}$$

$$\underline{V} = (0, V, 0)^T \quad \underline{E}_{\perp} = (E_x, 0, E_z)^T$$

$$\therefore \underline{V} \times \underline{E}_{\perp} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ 0 & V & 0 \\ E_x & 0 & E_z \end{vmatrix} = \hat{x}(VE_z) - \hat{z}(VE_x)$$

$$\therefore \underline{B}' = \underline{B}'_{\parallel} + \underline{B}'_{\perp} = -\frac{\gamma V}{c^2} (E_x \hat{z} - E_z \hat{x})$$

$$\underline{E}'_{\perp} = \gamma(\underline{E}_{\perp} + \underline{V} \times \underline{B}_{\perp}) = \gamma \underline{E}_{\perp}$$

$$\underline{V} \times \underline{E}' = \underline{V} \times \gamma \underline{E}_{\perp} = \gamma \underline{V} \times \underline{E}_{\perp}$$

$$\underline{E}' \times \underline{V} = 0 \quad \underline{V} \times \underline{E}' = \underline{V} \times \underline{E}'$$

$$\therefore \underline{B}' = \underline{B}_\perp' = -\gamma \frac{1}{c^2} \underline{v} \times \underline{E}_\perp = -\frac{1}{c^2} (\underline{v} \times \underline{E}_\perp)$$

$$= -\frac{1}{c^2} \underline{v} \times \underline{E}'$$

$\therefore$ in the rest frame of electron

$$\boxed{\underline{B} = -\frac{1}{c^2} \underline{v} \times \underline{E}} \rightarrow \text{the electron experiences}$$

a magnetic field due to its motion.

The electric field is radially directed towards the centre of the nucleus

$$\underline{E} = -\frac{1}{e} \frac{\partial V}{\partial r} \hat{r} = -\frac{1}{e} \frac{\partial V}{\partial r} \frac{\underline{r}}{r} \quad \underline{E} = -\nabla V = -\frac{\partial V}{\partial r} \hat{r}$$

where V is the ^{electrostatic} potential ~~energy~~ of the electron.

electrostatic energy $U = -eV$ for electron

$$\therefore \underline{E} = \frac{1}{e} \frac{\partial U}{\partial r} \hat{r} = \frac{1}{e} \frac{\partial U}{\partial r} \frac{\underline{r}}{r}$$

$$\therefore \underline{B} = -\frac{1}{c^2} \underline{v} \times \underline{E} = \frac{1}{c^2} \underline{E} \times \underline{v}$$

$$= \frac{1}{c^2} \frac{1}{e} \frac{\partial U}{\partial r} \frac{1}{r} (\underline{r} \times m \underline{v}) \frac{1}{me}$$

$$= \frac{1}{me c^2} \left(\frac{1}{e r} \frac{\partial U}{\partial r} \right) \underline{L}$$

~~intrinsic~~ intrinsic magnetic moment of an electron due to its spin is

$$\underline{N} = -g_s \mu_B \underline{S} \quad (g_s \approx 2) \quad \checkmark$$

$$\cancel{\mu_B = \frac{e\hbar}{2me}} \quad \mu_B = \frac{e\hbar}{2me}$$

Hamiltonian for the electron in magnetiz field is

$$\hat{H} = -\underline{N} \cdot \underline{B}$$

$$= -(-g_s \mu_B \underline{S}) \cdot \left(\frac{1}{me^2 c^2} \left(\frac{1}{r} \frac{\partial U}{\partial r} \right) \underline{L} \right)$$

$$= g_s \frac{1}{2me^2 c^2} \frac{1}{r} \frac{\partial U}{\partial r} \underline{L} \cdot \underline{S}$$

To Thomas precession replaces $g_s \approx 2$ with $g_s - 1 \approx 1$

$$\rightarrow \boxed{\hat{H}_{so} = \frac{1}{2me^2 c^2} \frac{1}{r} \frac{\partial U(r)}{\partial r} \underline{L} \cdot \underline{S}} \quad \checkmark$$

To find the energy shift we take the expectation value using basis states $|n, l, m_l, s\rangle$
~~energy states for Hydrogen are degenerate~~

$$\Delta E = \langle n, l, m_l, s | \hat{H}_{so} | n, l, m_l, s \rangle$$

$$= \frac{1}{2me^2 c^2} \frac{Ze^2}{4\pi\epsilon_0} \left\langle \frac{1}{r^3} \right\rangle \langle \underline{L} \cdot \underline{S} \rangle$$

$$\left(\begin{aligned} U &= -\frac{Ze^2}{4\pi\epsilon_0 r} \\ \frac{1}{r} \frac{\partial U}{\partial r} &= \frac{Ze^2}{4\pi\epsilon_0 r^3} \end{aligned} \right)$$

$$\left\langle \frac{1}{r^3} \right\rangle = \int_0^\infty \frac{1}{r^3} R_{nl}^2(r) r^2 dr$$

$$= \frac{1}{1(1+\frac{1}{2})(1+1)} \left(\frac{Z}{a_0 n} \right)^3$$

$$\hat{L} \cdot \hat{S} = \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$$

$$\therefore \langle \hat{L} \cdot \hat{S} \rangle = \frac{\hbar^2}{2} (j(j+1) - l(l+1) - s(s+1))$$

$$\therefore \Delta E = \frac{1}{2m_e^2}$$

To Thomas
Precession

$$\text{The coefficient} = \frac{g_s}{2m_e^2} \frac{Ze^2}{4\pi\epsilon_0} \left(\frac{Z}{a_0 n} \right)^3 \times \frac{1}{2}$$

$$= 2g_s \mu_B \epsilon_0 \left(\frac{e\hbar}{2m_e} \right)^2 \frac{1}{4\pi\epsilon_0} \cdot \frac{1}{2} Z^4 \frac{1}{n^2 a_0^3}$$

$$= \frac{\mu_B}{4\pi} Z^4 g_s \mu_B^2 \frac{1}{n^3 a_0^3}$$

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

$$(a) \quad \therefore \underline{B} = \frac{1}{m^2 c^2} \frac{1}{e r} \frac{Z e^2}{4 \pi \epsilon_0 r^2} \underline{L}$$

$\therefore \underline{B}$ is parallel to $\underline{L}$

$$\therefore \underline{N} = -g_s \mu_B \underline{S}$$

$\therefore \underline{N}$ is antiparallel to $\underline{S}$

$$(b) \quad \Delta E = -\underline{N} \cdot \underline{B}, \text{ Based on (a)}$$

If $\underline{L} \cdot \underline{S} > 0$ then $\underline{N} \cdot \underline{B} < 0 \rightarrow \Delta E > 0$

If $\underline{L} \cdot \underline{S} < 0$ then $\underline{N} \cdot \underline{B} > 0 \rightarrow \Delta E < 0$

$\therefore$ the case that $j = l + 1/2$, which

corresponds to $\underline{L} \cdot \underline{S} > 0$, has higher energy.

This agrees with the expression for ΔE

(c) Z^1 comes from the potential energy $U = \frac{-Z e^2}{4 \pi \epsilon_0 r}$

Z^3 comes from the expectation value $\langle \frac{1}{r^3} \rangle$. Together gives Z^4 dependence

$$(v) \quad \frac{1}{B} = \frac{1}{\frac{1}{\frac{1}{55} + \frac{1}{10}}} = \frac{1}{\frac{1}{55} + \frac{1}{10}}$$

$\frac{1}{B}$ is parallel to $\frac{1}{A}$

$$y = -0.15x + 2$$

y is perpendicular to z

$$(p) \quad \frac{1}{B} = -\frac{1}{A} \quad \text{Point on line}$$

If $\frac{1}{B} > 0$ then $\frac{1}{A} < 0 \rightarrow \frac{1}{B} > 0$

If $\frac{1}{B} < 0$ then $\frac{1}{A} > 0 \rightarrow \frac{1}{B} < 0$

the case is that $\frac{1}{B} = \frac{1}{A}$

randomly to $\frac{1}{B} > 0$ or $\frac{1}{B} < 0$

the expression

$$(b) \quad \frac{1}{B} = \frac{1}{\frac{1}{\frac{1}{55} + \frac{1}{10}}}$$

randomly

value from the expression

$$\frac{1}{B} = \frac{1}{\frac{1}{\frac{1}{55} + \frac{1}{10}}}$$

(11.) Hydrogen $Z=1$, $g_s=2$, $g_l=2$

2P configuration $n=2$, $l=1$

Q. $\therefore \Delta E(3/2) = \mu_B = 4\pi \times 10^{-7} \rightarrow \frac{\mu_B}{4\pi} = 1 \times 10^{-7}$
 $a_0 = 5.29 \times 10^{-11} \text{ m}$
 $\mu_B = \frac{e}{2m_e} = \frac{1.6 \times 10^{-19}}{2(9.11 \times 10^{-31})}$

~~$\frac{\mu_B}{4\pi} g_s g_l \frac{1}{a_0^3} = 1.48 \times 10^{-24} \text{ J}$~~

~~$\Delta E = \frac{\beta}{\hbar}$~~ $\Delta E = \frac{1}{2} \beta_{nl} [j(j+1) - l(l+1) - s(s+1)]$

where $\beta_{nl} = \frac{\hbar^2}{2me^2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{(na_0)^3 l(l+1/2)(l+1)}$

~~$\beta_{2p,1}$~~ For Hydrogen

$\beta = \beta_{2p,1} = \frac{\hbar^2}{2me^2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{(2a_0)^3 (\frac{3}{2})(2)}$

$= 4.78 \times 10^{-24} \text{ J}$

$\Delta E(3/2) = \frac{\beta}{2} \left[\frac{3}{2} \cdot \frac{5}{2} - 1 \cdot 2 - \frac{1}{2} \cdot \frac{3}{2} \right]$
 $= \frac{1}{2} \beta = \boxed{2.39 \times 10^{-24} \text{ J}}$

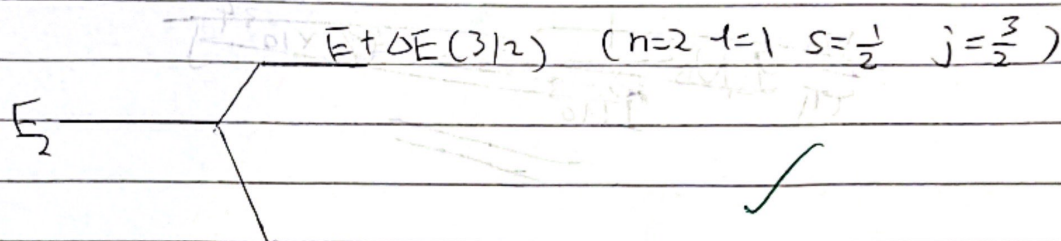
$\Delta E(1/2) = \frac{\beta}{2} \left[\frac{1}{2} \cdot \frac{3}{2} - 1 \cdot 2 - \frac{1}{2} \cdot \frac{3}{2} \right] = -\beta$
 $= \boxed{-4.78 \times 10^{-24} \text{ J}}$

$$\therefore \Delta E \equiv \text{splitting} = \Delta W = \frac{\Delta E(3/2) - \Delta E(1/2)}{h}$$

$$= \frac{2.39 - (-4.78)}{6.63 \times 10^{-34}} \times 10^{-24}$$

$$= 1.08 \times 10^{10} \text{ Hz}$$

$$\approx \boxed{11 \text{ GHz}}$$



$$\beta \propto \frac{1}{n^3} \therefore \frac{\Delta W_{3p}}{\Delta W_{2p}} = \frac{2^3}{3^3} = \frac{8}{27}$$

$$\rightarrow \Delta W_{3p} = \frac{8}{27} \times 11 \text{ GHz} = \boxed{3.26 \text{ GHz}}$$

$$\begin{aligned} |\Delta E(3/2)| &= \frac{1}{2} \beta & \therefore \frac{|\Delta E(3/2)|}{|\Delta E(1/2)|} &= \frac{1}{2} \\ |\Delta E(1/2)| &= \beta \end{aligned}$$

$\rightarrow$ half the displacement

~~number of states with J~~

degeneracy of $J=3/2$ is 4

$$(m_J = 3/2, 1/2, -1/2, -3/2)$$

degeneracy of $J=1/2$ is 2

$$(m_J = 1/2, -1/2)$$

$$\text{Average Splitting } \bar{\Delta E} = 4 \times \Delta E(3/2) + 2 \times \Delta E(1/2)$$

$$= 4 \times \beta/2 + 2 \times (-\beta)$$

$$= 0$$

$\rightarrow \therefore$ mean energy ~~un~~ unaffected.

the atomic number Z for sodium is
 $Z=11$

splitting for Na is

$$\Delta E_{Na} = hc\bar{\nu} = h\omega_{Na}$$

$$\therefore \omega_{Na} = c\bar{\nu} = (3 \times 10^8) (1.72 \times 10^3)$$
$$= \boxed{5.2 \times 10^{11} \text{ Hz}}$$

$$\text{ratio} = \frac{\Delta w(3p, Na)}{\Delta w(3p, H)} = \frac{5.2 \times 10^{11}}{3.26 \times 10^9}$$

~ 160 times larger ✓

For purely hydrogenic atoms, $\Delta w \sim \Delta E \sim Z^4$
and should scale like Z^4

But due to screening effect we need to split the Z^4 into an effective

$Z_{in}^2 \cdot Z_{out}^2$ that describes ~~the~~ the fact

that when electron is inside inner orbitals it experience more attraction than when it is outside ~~the~~ when it feels the shielding.

For rough estimate $Z_{in} \sim Z$, $Z_{out} \sim 1$

$\therefore \Delta w \sim Z^2 = |Z|$ (roughly close to 160) ✓

12. In the $n=2$ manifold:

$\therefore$ for $l=0$ there is no spin-orbit interaction

$\therefore n=2, l=1$, we focus on $2p$ orbital

~~$B_{2p, Z} = (4.78 \times 10^{-24} \text{ J}) \times Z^4$~~

energy difference in terms of frequency

of ~~the~~ $= 1.1 \times 10^{10} \text{ Hz} \times Z^4$

we want $(1.1 \times 10^{10} \text{ Hz}) Z^4 = \frac{c}{\lambda}$

(where $\lambda = 600 \text{ nm}$)

$\therefore Z = \left(\frac{3 \times 10^8}{600 \times 10^{-9} \times 1.1 \times 10^{10}} \right)^{1/4} \approx 14.6$ ✓

$\therefore$ we choose $Z = 15$, which corresponds to

the element ~~silicon~~ ~~phosphorus~~ phosphorus ✓

13. In the $N=5$ manifold

for $\lambda=0$ there is no spin-orbit interaction

$N=5, \lambda=1$ we focus on spin-orbit

$$B_{\text{spin-orbit}} = \frac{1}{2} \hbar^2 \lambda(\lambda+1)$$

energy difference in terms of temperature

$$\Delta E_{\text{spin-orbit}} = 1.1 \times 10^{-4} \text{ MeV} \times \frac{1}{k_B T}$$

$$\frac{1}{k_B T} = \frac{1}{(1.38 \times 10^{-23} \text{ J/K}) \times T}$$

(where $\lambda = 1$)

$$F = \frac{(1.1 \times 10^{-4} \text{ MeV})}{(1.38 \times 10^{-23} \text{ J/K}) \times T}$$

we choose $T = 10^9 \text{ K}$, which corresponds to

the energy of the photon

(13) $\hat{H} = \hat{H}_{\text{gross}} + \hat{H}_1 + \hat{H}_2$ for multi electron atoms

→ $\hat{H}_1$ is due to residual electrostatic effects

→ $\hat{H}_2$ is due to ~~LS coupling~~ spin-orbit interaction ✓

A configuration is determined from $\hat{H}_{\text{gross}}$

For not too large Z , ~~H_1~~ $H_1 \gg H_2$

Hence we first apply H_1 as a perturbation. The energy levels split ~~into~~ according to the sum of orbital and spin angular momenta L and S

∴ ~~L and S~~ L and S specify terms ✓

Then we apply perturbation to H_2 . The energy levels of each term split again into different levels due to spin-orbit interaction ~~into~~

∴ spin-orbit interaction ~~splits~~ splits terms into levels labelled by J , the total angular momentum.

LS coupling is the interaction between overall spin angular momentum and overall orbital angular momentum. (~~L and S~~ (S and L))

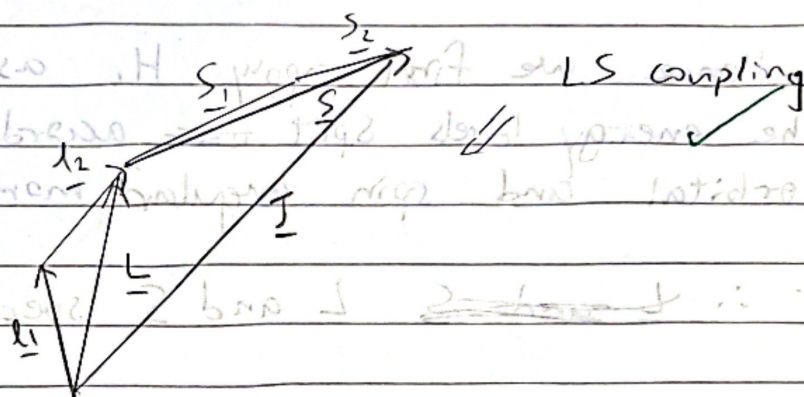
In the LS coupling ~~scheme~~ scheme:

l_1 and l_2 couple to give L } ~~the~~ the residual
 s_1 and s_2 couple to give S } due to ~~electrostatic~~ electrostatic ✓

then L and S couple to give J .

The condition for LS coupling is $H_1 \gg H_2$
 i.e. the electrostatic effect is stronger
 than the spin-orbit interaction.

Also we need spin-spin interaction to not be
 too strong such as in Helium.



Ca ($Z=20$)

~~4s~~

~~4s²~~

4s²: ¹S₀ (No ³S₁ due to Pauli exclusion principle)

4s4p: ¹P₁ ³P_{0,2} ³P₁ ³P₀

4s5s: ¹S₀ ³S₁

symbol explained

2s+1
L
J

Interval Rule

order:

decreasing energy

$$\Delta E_{so} = \langle \hat{H}_2 \rangle \propto \left\langle \left(\frac{1}{r} \frac{\partial V}{\partial r} \right) (\hat{L} \cdot \hat{S}) \right\rangle$$

$$\hat{S} \cdot \hat{L} = \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$$

$$\rightarrow \Delta E_J = \frac{\beta_{nl}}{2} (J(J+1) - L(L+1) - S(S+1))$$

$$\rightarrow \Delta E_{J-1} = \frac{\beta_{nl}}{2} (J(J-1) - L(L+1) - S(S+1))$$

for same
L and S

$$\Rightarrow \boxed{\Delta E_J - \Delta E_{J-1} = \beta_{nl} J}$$

is the interval rule

It applies to 4s4p but not to 4s5s
because for 4s5s, ~~S=0~~, there is no
L=0

Spin-orbit coupling.

For Hydrogen: X not exist ✓ exist

$$3f \ ^2F_{3/2} \rightarrow n=3 \ l=3 \quad X \text{ also } J=3 \pm \frac{1}{2} \neq \frac{3}{2}$$

$$3p \ ^2P_{3/2} \rightarrow S=\frac{1}{2} \ l=1 \ J=\frac{3}{2} \quad \checkmark$$

$$3s \ ^2S_{3/2} \rightarrow S=\frac{1}{2} \ l=0 \ J=\frac{3}{2} \quad X$$

$$3d \ ^3D_2 \rightarrow S=1 \quad X$$

$$2p \ ^2D_{3/2} \rightarrow S=\frac{1}{2} \ l=1, l=2 \quad X$$

Explain why ✓

$$\Rightarrow \Delta E_T = \frac{p_{\text{out}}}{2} (2C_T + 1) - (C_T + 1) - 2C_T + 1$$

$$\Delta E_T = \frac{p_{\text{out}}}{2} (2C_T + 1) - (C_T + 1) - 2C_T + 1$$

$$\Rightarrow \boxed{\Delta E_T - \Delta E_{T-1} = p_{\text{out}}}$$

is the interval rule

It applies to Δp but not to ΔT
 because for ΔT there is no
 L=0

spin-orbit coupling

For hydrogen: χ has axis $\sqrt{6 \times 18}$

$$3d \text{ } \chi_{\text{axis}} \rightarrow N=3 \text{ } l=2 \text{ } \chi_{\text{axis}} = \sqrt{6 \times 18} \pm \frac{1}{2}$$

$$3d \text{ } \chi_{\text{axis}} \rightarrow N=3 \text{ } l=2 \text{ } \chi_{\text{axis}} = \sqrt{6 \times 18} \pm \frac{1}{2}$$

$$3d \text{ } \chi_{\text{axis}} \rightarrow N=3 \text{ } l=2 \text{ } \chi_{\text{axis}} = \sqrt{6 \times 18} \pm \frac{1}{2}$$

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$$3d \text{ } \chi_{\text{axis}} \rightarrow N=3 \text{ } l=2 \text{ } \chi_{\text{axis}} = \sqrt{6 \times 18} \pm \frac{1}{2}$$

B3 Test 1

$$E = -\frac{Z^2 R}{n}$$

$$\langle r \rangle = \frac{n^2}{Z}$$

$$|n, l, m\rangle$$

$$1 \leq n$$

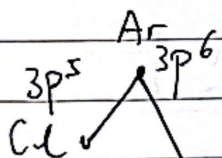
$$0 \leq l \leq n-1$$

$$-l \leq m \leq l$$

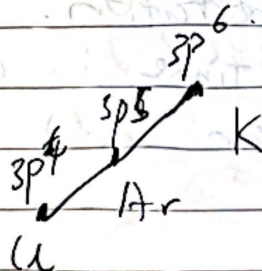
$$x_1, x_2 \quad \psi(x_1, \uparrow, x_2, \downarrow)$$

$$\psi(x_1, \downarrow, x_2, \uparrow)$$

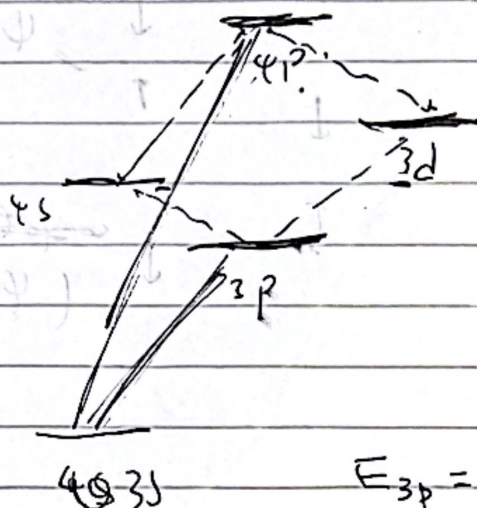
$$(\psi(x_2, \downarrow, x_1, \uparrow))^2$$



K 4s (much further away
electron less tightly bound)



$$8. \quad -\frac{R}{(n-\delta_u)^2} = 5.14 \Rightarrow -\delta_s = 1.37$$



$$\lambda_{00} = 241 \text{ nm}$$

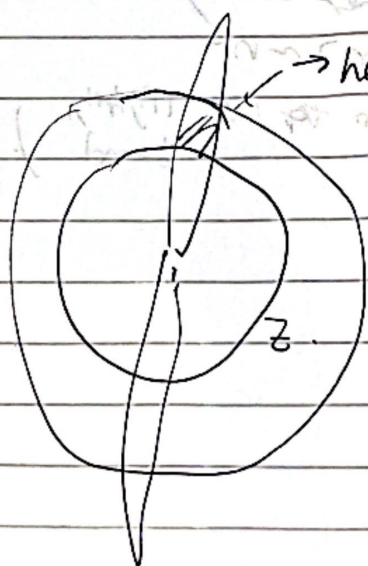
$$E_{3p} = -\frac{R}{(n-\delta_p)^2}$$

$$\delta_p = 0.88$$

$$\delta_d \approx 0$$

$$\lambda_2 = 332 \text{ nm}$$

$$\lambda_2 = 330 \text{ nm}$$



→ heavier element

→ more penetration.

→ more time in cladding

→ larger $S(u)$

$$\underline{B} \parallel \underline{L} \quad \underline{B} \parallel -\underline{S}$$

$$\begin{array}{ll} 1 & Z \\ 3 & Z \end{array} \quad \frac{Ze^2}{4\pi\epsilon_0 r} \quad \left(\frac{1}{r}\right)^*$$

$$|nLS \pm MJ\rangle$$

average energy unchanged

$\Rightarrow$ magnetic force cannot do work on the atom.

$$\left(\frac{n^3}{Z_{out}}\right) / \left(\frac{n^{*3}}{Z_{in}}\right)$$

$$\left(\frac{2.07}{4.54 \times 10^{-5}}\right)^{\frac{1}{4}} = 15$$

$4s^2$ state $\Rightarrow$ wavefunction symmetric
 $\Rightarrow$ spin ~~is~~ antisymmetric

$\therefore 4s^2 \Rightarrow {}^1S_0$ only singlet

$4s4s \Rightarrow$ singlet and triplet.

$4s4p \Rightarrow {}^3P_{2,1,0}$
 $\& {}^1P_1$

2-11-11

$$\frac{595}{4164} = \frac{1}{5.3}$$

10-2-12

10-2-12

10-2-12

$$\frac{1}{5.3} = \frac{1}{5.3}$$

$$\frac{1}{5.3} = \frac{1}{5.3}$$

10-2-12

10-2-12

10-2-12

10-2-12

10-2-12