2703

SECOND PUBLIC EXAMINATION

Honour School of Physics Part B: 3 and 4 Year Courses

Honour School of Physics and Philosophy Part B

B3. QUANTUM, ATOMIC AND MOLECULAR PHYSICS

TRINITY TERM 2014

Thursday, 19 June, 2.30 pm – 4.30 pm

10 minutes reading time

Answer **two** *questions.*

Start the answer to each question in a **fresh book.**

A list of physical constants and conversion factors accompanies this paper.

The numbers in the margin indicate the weight that the Examiners expect to assign to each part of the question.

Do NOT turn over until told that you may do so.

$\int dr\, r^2$ $\quad \int dr\, r^2 \frac{1}{r_{12}} \sim$ $\quad r \to 2r$ $\quad \frac{1}{r}\, dr\, r^2$

$\psi_a(\underline{r}_1)\psi_b(\underline{r}_2) \neq$
$\neq \psi_a(\underline{r}_2)\psi_b(\underline{r}_1)$

1. Under certain assumptions the time independent Schrödinger equation for the helium atom can be written in the form

$$\left(-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)\psi = E\psi$$

where r_1 and r_2 are the radial coordinates of the two electrons and r_{12} is their separation. Discuss the physical origin of each of the terms in this expression. [4]

When the term $e^2/4\pi\varepsilon_0 r_{12}$ is ignored, a solution of the form $\psi_{a,b} = \psi_a(\mathbf{r_1})\psi_\mathbf{b}(\mathbf{r_2})$ can be found, where a and b are labels for the states occupied by electrons 1 and 2. Explain why such a wave function is not in general acceptable for two identical particles. Discuss the symmetry properties of the wave functions that describe the $1s^2$ and $1s2p$ configurations, and sketch an energy level diagram for helium showing the terms that arise from them. [9]

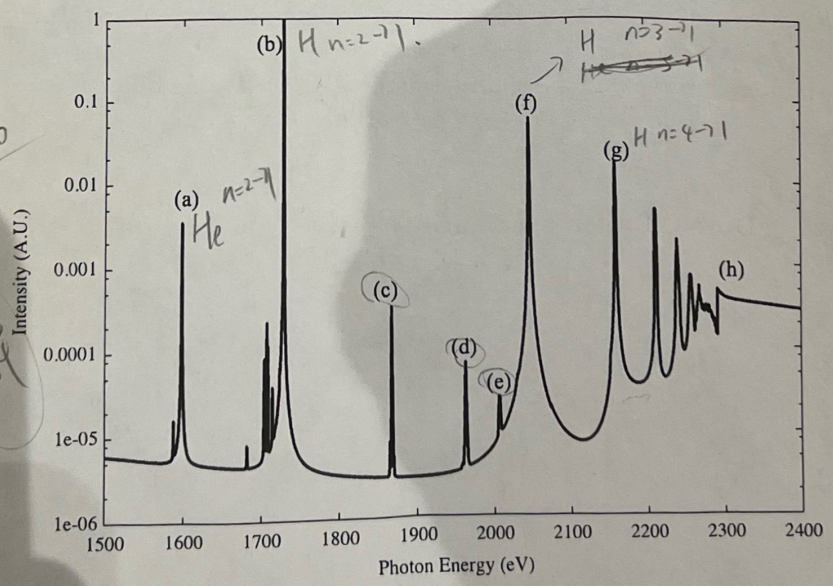
Without detailed calculation, state how would you expect the expectation value of $1/r_{12}$ to scale with Z for a helium-like ion. [3]

The energy required to remove an electron from the ground state of atomic helium is approximately 25 eV. For the helium-like ion N^{5+} the corresponding energy is approximately 551 eV. Estimate, giving your reasoning, the corresponding energy for the helium-like ion Al^{11+}, and the hydrogenic ion, Al^{12+}. The figure below shows a soft X-ray spectrum of the emission from a hot plasma created by shining an intense pulsed laser beam onto an Al target, producing highly ionised material. Identify the ionic species and configurations involved in each of the transitions marked (a) through to (g) inclusive, and discuss the origin of the feature marked (h). [9]

He 1632 1591 1885 1598 1598 1964 2036 2043

H 1591 1723 2023 2184

$V_0 Z^2 \sim \frac{Z}{4\pi\epsilon_0} \frac{e^2}{r}$



$^1P_1$

$^3P_{2,1,0}$

$^1S_0$

7

$\beta \underline{L} \cdot \underline{S}$

2. Explain what is meant by the *LS coupling approximation.* State the selection rules for electric dipole radiation between terms for which this approximation is valid. [7]

Consider a fine-structure level of an atom which is well described within the *LS* coupling approximation. Show that in the presence of weak magnetic flux density **B** the degeneracy in M_J may be lifted, and the energy shift of the states is given by

$$\Delta E = g_J \mu_B B M_J \quad ,$$

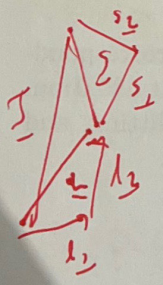
and obtain an expression for g_J. State the selection rules for Zeeman transitions. What is meant by a 'weak' magnetic flux density in this context? [8]

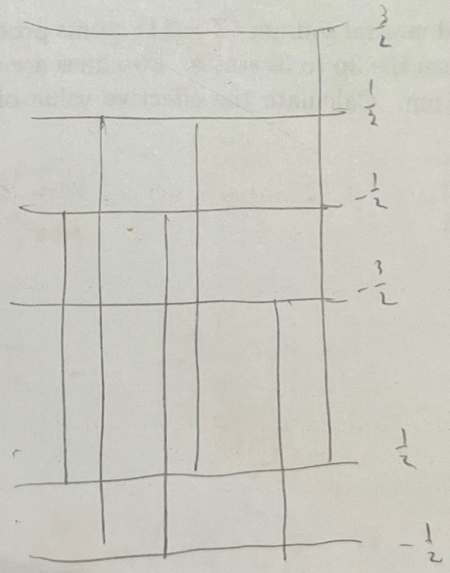
$L=2$ $^2D_{\frac{3}{2}}$

A transition in an alkali atom ($S=\frac{1}{2}$) has an upper level denoted by $^{2S_2+1}D_{J_2}$ and a lower level denoted by $^{2S_1+1}L_{1J_1}$, where S_2 and S_1 are the spin quantum numbers of the upper and lower levels respectively, J_2 and J_1 (where $J_2 > J_1$) are the total angular momentum quantum numbers of the upper and lower levels respectively, and L_1 is the orbital angular momentum quantum number of the lower level. In the presence of a weak magnetic flux density **B** of magnitude 0.5 T, four emission lines are observed when observing parallel to **B**, and six emission lines are observed when observing perpendicular to **B**. What are the values of L, S, and J for the upper and lower levels? Calculate the positions of the lines relative to those in the absence of an applied magnetic field, and sketch them on a relative wavenumber scale in units of cm^{-1}, indicating which transitions are seen as a function of direction of observation. [10]

$S=\frac{1}{2}$ $L=1$

$^2P_{\frac{1}{2}}$





$LSJM_J$

$\mu_B B \ll \beta \underline{L} \cdot \underline{S}$

3. State what the fine structure constant α would represent in the simple Bohr model of the atom. Calculate the value of $\alpha^2 m_e c^2/2$, where m_e is the rest mass of the electron, and comment on the result. [4]

Explain why you would expect the magnitude of fine structure splittings in hydrogen to scale as α^4 times the rest mass energy of an electron. [4]

The spin–orbit interaction within a single-electron atom can be represented by a term in the Hamiltonian

$$\frac{1}{2m_e^2c^2}\frac{1}{r}\frac{\partial V(r)}{\partial r}\,\mathbf{l}\cdot\mathbf{s}$$

where r is the radial coordinate of the electron, m its mass, $\mathbf{l}$ the angular momentum operator and $\mathbf{s}$ the electron spin operator. $V(r)$ is the central electrostatic potential energy. Give simple arguments that justify the form of the above expression. [6]

For hydrogenic ions of atomic number Z, and assuming a point nucleus, for a 3p electron

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{81}\left(\frac{Z}{a_0}\right)^3$$

where $a_0 = (4\pi\epsilon_0\hbar^2)/(m_e e^2)$ is the Bohr radius. Show that under the above assumptions the 3p spin-orbit splitting is given by

$$E_{j=3/2} - E_{j=1/2} = \frac{1}{108}(Z\alpha)^4 m_e c^2$$

and evaluate this splitting for hydrogen. [6]

Light from excited neutral sodium ($Z = 11$) atoms produces emission corresponding to transitions between the 3p to 3s states. Two lines are observed, one at 589.0 nm, and the other at 589.6 nm. Calculate the effective value of Z for this splitting, and comment on the result. [5]

* small signal coefficient ∝ population inversion ①

~~too~~ I ↑ more stimulated emission reduces pop inversion

4. Why does the input signal level influence the gain of a laser amplifier? [4]

→ saturation

Gain depends intensity of amplifier

A homogeneously broadened laser amplifier operates on a transition from an upper level 2 and a lower level 1, which have degeneracies g_2 and g_1 respectively. The excitation rates into the respective levels are S_2 and S_1, and the effective lifetimes τ_2 and τ_1 (where τ_2 includes radiative decay to level 1). The Einstein coefficient for spontaneous emission between the two levels is A_{21}. Show that the gain coefficient $\alpha(\omega)$ for a signal with angular frequency ω varies along the length of the amplifier, such that at a point within the amplifying medium where its intensity is I the value of $\alpha(\omega)$ is given by

$$\alpha(\omega) = \frac{\alpha_0(\omega)}{1 + I/I_{\text{sat}}}$$

where

$$\alpha_0(\omega) = \sigma(\omega)\left[S_2\tau_2\left(1 - \frac{g_2 A_{21}\tau_1}{g_1}\right) - \frac{g_2}{g_1}S_1\tau_1\right]$$

and $\sigma(\omega)$ is the gain cross section of the transition. Obtain an expression for the saturation intensity I_{sat}. [12]

Two identical laser amplifiers, of the same length and small signal gain coefficient, are placed one after another, so that light is amplified by them successively. A monochromatic signal of intensity I_0 is input into the first amplifier. At the end of the first amplifier, the signal has been amplified to 100 I_0, and after exiting the second amplifier the final output is 300 I_0. Deduce a value of I_{sat} in terms of I_0. [9]

$N_2 B_{21} \rho \qquad N_1 B_{12} \rho$

$$\alpha(\omega) = \frac{\alpha_0(\omega)}{1 + I/I_{sat}} \qquad \frac{1}{I_{sat}} = \frac{\sigma}{\hbar\omega}\left[\tau_2 + \frac{g_2}{g_1}\tau_1 - \frac{g_2}{g_1}A_{21}\tau_2\tau_1\right]$$

$$\frac{dI}{dz} = \alpha I = \frac{\alpha_0 I}{1 + \frac{I}{I_{sat}}}$$

$$\int \frac{1}{I} + \frac{1}{I_{sat}}\, dI = \int \alpha_0\, dz$$

$$= \ln\left(\frac{I_2}{I_1}\right) + \frac{I_2 - I_1}{I_s} = \alpha_0 L$$

$$\ln(100) + \frac{100 I_0 - I_0}{I_s} = \alpha_0 L$$

$$\ln(3) + \frac{300 I_0 - 100 I_0}{I_s} = \alpha_0 L.$$

$$\frac{I_s}{I_0} = 28.8$$

14B30

14B3Q1

$$\left(-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)\psi = E\psi$$

kinetic energy of first electron

kinetic energy of second electron

electrostatic energy between 1st electron and nucleus

electrostatic energy between 2nd electron and nucleus

electrostatic energy between 1st and 2nd electrons.

For two identical electrons, probability for 1 in position $\underline{r_1}$ and 2 in position $\underline{r_2}$ should equal to if they swap.

$$\therefore |\psi(\underline{r_1}, \underline{r_2})|^2 = |\psi(\underline{r_2}, \underline{r_1})|^2$$

$$\therefore \psi(\underline{r_1}, \underline{r_2}) = e^{i\alpha}\psi(\underline{r_2}, \underline{r_1})$$

swap again $\psi(\underline{r_1}, \underline{r_2}) = e^{2i\alpha}\psi(\underline{r_1}, \underline{r_2})$

$$\therefore (e^{i\alpha})^2 = 1 \qquad \therefore e^{i\alpha} = \pm 1$$

$$\therefore \psi(\underline{r_1}, \underline{r_2}) = \pm\psi(\underline{r_2}, \underline{r_1})$$

ψ needs to be either symmetric or antisymmetric

But $\psi_{a,b} = \psi_a(\underline{r_1})\psi_b(\underline{r_2})$ if swap

$$\psi_{b,a} = \psi_b(\underline{r_1})\psi_a(\underline{r_2}) \neq \psi_{a,b}$$

$\therefore$ No symmetry, not work for identical particles.

- symmetry properties

For $1s^2$ orbital, by pauli exclusion principle, the spin wavefunction must be antisymmetric because the spins must point to opposite directions.

→ Spatial wavefunction should be symmetric.

$$\psi(\underline{r}_1, \underline{r}_2) = \psi_0^1(\underline{r}_1)\,\psi_0^1(\underline{r}_2)$$

ψ_l^n is the single electron wavefunction of n, l

both the ground states.

(overall antisymmetric ⇒ spin antisymmetric $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$)

For the 1s2p orbital:

terms arise because the spins can point in the same or opposite directions.

Use degenerate perturbation theory for degenerate states

$$\psi_a(\underline{r}_1)\,\psi_b(\underline{r}_2) \quad \text{and} \quad \psi_b(\underline{r}_1)\,\psi_a(\underline{r}_2)$$

on the perturbation Hamiltonian $\frac{e^2}{4\pi\varepsilon_0 r_{12}} = \hat{H}_{res}$

try $\psi(\underline{r}_1, \underline{r}_2) = a\,\psi_a(\underline{r}_1)\,\psi_b(\underline{r}_2) + b\,\psi_b(\underline{r}_1)\,\psi_a(\underline{r}_2)$

then

$$\begin{pmatrix} J & K \\ K & J \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \Delta E \begin{pmatrix} a \\ b \end{pmatrix}$$

where $J = \int d^3\underline{r}_1 d^3\underline{r}_2 \left|\psi_a(\underline{r}_1)\right|^2 \left|\psi_b(\underline{r}_2)\right|^2 \hat{H}_{res}$

$$= \int d^3\underline{r}_1 d^3\underline{r}_2 \left|\psi_a(\underline{r}_2)\right|^2 \left|\psi_b(\underline{r}_1)\right|^2 \hat{H}_{res}$$

$$K = \int d^3\underline{r}_1 d^3\underline{r}_2 \, \psi_a^*(\underline{r}_1)\psi_a(\underline{r}_2)\psi_b^*(\underline{r}_2)\psi_b(\underline{r}_1) \hat{H}_{res}$$

$$= \int d^3\underline{r}_1 d^3\underline{r}_2 \, \psi_a^*(\underline{r}_2)\psi_a(\underline{r}_1)\psi_b^*(\underline{r}_1)\psi_b(\underline{r}_2) \hat{H}_{res}$$

And $(J - \Delta E)^2 - K^2 = 0$

$\therefore (J + K - \Delta E)(J - K - \Delta E) = 0$

$\therefore \Delta E = J + K$ or $J - K$

In this case $\psi_a = \psi_0^1$ $\psi_b = \psi_1^2$

$\therefore$ Non perturbed energy $E_0 = E_1 + E_2$

$\left(E_1 = -\frac{Z^2 R_y}{1^2}, \; E_2 = -\frac{Z^2 R_y}{2^2} \right)$

$\therefore$ overall energy $E = E_1 + E_2 + J \pm K$

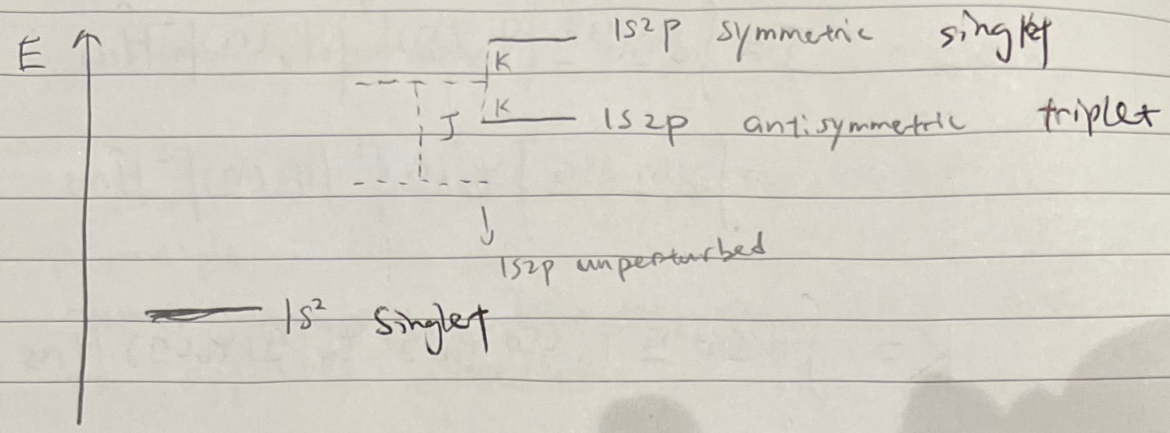
overall wavefunction

$\Delta E = J + K \Rightarrow \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$ ~~symmetric~~ ~~antisymmetric~~ antisymmetric

$\Rightarrow$ symmetric (spin antisymmetric $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$).

$\Delta E = J - K \Rightarrow \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix} \Rightarrow$ antisymmetric

(spin symmetric $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$, $|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$).



— expectation of $\frac{1}{r_{12}}$ should be <u>proportional to Z</u>

This is because in the radial part of the wavefunction, coordinate r always appears as $\frac{r}{a_Z}$ where $a_Z = \frac{a_0}{Z}$ (a_0 = Bohr radius)

$$\therefore \frac{r}{a_Z} = \frac{rZ}{a_0}$$

$$\left\langle \frac{1}{r_{12}} \right\rangle = \int dr \cdot r^2 \, \psi^*_{(rZ)} \left(\frac{1}{r_{12}}\right) \psi(rZ)$$

in wavefunction ψ there is a normalisation factor $\propto \frac{1}{a_Z^{3/2}} \propto Z^3$

$dr \cdot r^2 \rightarrow \frac{1}{Z^3} d(rZ)(rZ)^2$, this $\frac{1}{Z^3}$ cancells with the Z^3 in normalisation

$$\frac{1}{r_{12}} \sim \frac{1}{r} \sim \frac{Z}{rZ}$$

so if we replace all r by rZ in the integral, we would get the same result as if $Z=1$ except a factor of Z

in front because $\frac{1}{r_{12}} \sim \frac{Z}{r_Z}$

$\therefore \langle \frac{1}{r_{12}} \rangle \propto Z$

- Qualitatively, the Bohr radius is decreased by a factor of Z, so all length scales should be shrinked by Z, so $\frac{1}{r_{12}}$ should be increased by a factor of Z

- the $\frac{e^2}{4\pi\varepsilon_0 r_{12}}$ term is repulsive, so it gives a contribution to the binding energy $\propto -Z$ ("$-$" is indicates repulsion, $\frac{1}{r_{12}} \propto Z$)

The nuclear-electron interaction for the ~~seco~~ outer electron is given by the term $-\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2}$

$\because \langle \frac{1}{r_2} \rangle \sim Z$, $\therefore$ this term ~~$\propto Z^2$~~ gives a contribution $\propto Z^2$ to the binding energy

So the ~~binding~~ Ionization energy B is approximately given by

$$B \propto Z^2 - Z$$

- This can also be understood by noting that the outer electron is effectively ~~shelt~~ shielded by the inner electron from the Coulomb potential of the nucleus. The effective charge of nucleus

On the outer electron is then $Z-1$

$\because$ the ~~rad~~ $(\text{distance})^{-1}$ between outer electron and nucleus scales as Z

$\therefore$ ~~Binding~~ Ionization energy B scales as

$$B \propto Z(Z-1) \propto Z^2 - Z$$

We check this with data given in the problem.

~~Bex~~ $$\frac{B(N^{5+})}{B(He)} = \frac{7^2-7}{2^2-2} = 21 \text{ is expected}$$

~~in reali~~

The data given is

$$\frac{\bar{B}(N^{5+})}{\bar{B}(He)} = \frac{551\,eV}{25\,eV} = 22.04$$, close enough to 21, so we proceed with this formula:

~~Ionisation of Al^{11+} (A Helium like ion)~~

$$B^{(1)}(Al^{11+}) = \frac{13^2-13}{2^2-2} \times 25\,eV = 1950\,eV$$

$$B^{(2)}(Al^{11+}) = \frac{13^2-13}{7^2-7} \times 551\,eV = \cancel{2046}\ 2047\,eV$$

$\therefore$ ~~Average~~ gives

$$B(Al^{11+}) \simeq \boxed{2000\,eV}.$$

~~Al^{12+} is a Hydrogen-like ion. so ionisation energy is just the energy of ground state hydrogen with $Z = 13$ (but positive)~~

~~$\therefore B(Al^{12+}) = \frac{(13.6eV)(13)^2}{1^2} = 2300\ eV$~~

Without the $\frac{1}{r_{12}}$ term, the ionisation energy of ~~outer~~ outer electron is simply the hydrogenic energy (but positive) $+\frac{Ry\ Z^2}{n^2} = +\frac{(13.6eV)Z^2}{1^2} = (13.6eV)Z^2$

$\therefore$ for the $Z^2 - Z$ dependence, we assume the proportionality constant is still $13.6eV$

$\therefore B = (13.6eV)(Z^2 - Z)$ is the ionisation energy for outer electron in $1s^2$ state of Helium-like ions.

check: $B(He) = 13.6(2^2-2) = 27.2eV \simeq 25eV$

$B(Na^+) = 13.6(7^2-7) = 571.2eV \simeq 551eV$

$\therefore B(Al^{11+}) = 13.6(13^2-13) = 2120\ eV$

- Al^{12+} is a Hydrogen-like ion so ~~to~~ ionisation energy is just the energy of ground state with $Z=13$

$\therefore B(Al^{12+}) = 13.6(13^2) = 2300\ eV$

- The figure describes the transition spectra of Al^{11+} and Al^{12+} ions:

- The energy of outer electron in Helium like ions can be calculated:

If outer electron in ground state, then its energy equal to the ionisation energy calculated above (but negative)

$$E_1 = -R_y(Z^2 - Z)$$

If outer electron is in an excited state, then it feels an effective charge of $Z-1$ from the nucleus, so its energy is

$$E_n = -\frac{R_y(Z-1)^2 Z}{n^2} = -\frac{R_y}{n^2}(Z^2 - Z)$$

- The energy of hydrogen like ion is simpler:

$$E_n = -\frac{R_y Z^2}{n^2} \qquad (Z = 13,\ R_y = 13.6\,eV)$$

- Identify the peaks:

(a) transition of Al^{11+} from $n=2$ to $n=1$

photon energy $\Delta E = -(13.6)\frac{(13^2-13)}{2^2} - (-13.6(13^2-13))$

$= \underline{\underline{1591\,eV}}$

(on graph $\Delta E \sim 1600\,eV$)

(b) transition of Al^{12+} from $n=2$ to $n=1$

photon energy $\Delta E = -13.6\left(\frac{13^2}{2^2}\right) - (-13.6)\left(\frac{13^2}{1^2}\right)$

$= \underline{\underline{1724\ eV}}$

(on graph $\Delta E \sim 1730\ eV$)

(c) transition of Al^{11+} from $n=3$ to $n=1$

$\Delta E = -13.6\,(13^2-13)\left(\frac{1}{3^2}-1\right) = \underline{\underline{1886\ eV}}$

(on graph $\Delta E \sim 1870\ eV$)

(d) transition of Al^{11+} from $n=4$ to $n=1$

$\Delta E = -13.6\,(13^2-13)\left(\frac{1}{4^2}-1\right) = \underline{\underline{1989\ eV}}$

(on graph $\Delta E \sim 1970\ eV$)

(e) transition of Al^{11+} from $n=5$ to $n=1$

$\Delta E = -13.6(13^2-13)\left(\frac{1}{5^2}-1\right) = \underline{\underline{2036\ eV}}$

(on graph $\Delta E \sim 2010\ eV$)

(f) transition of Al^{12+} from $n=3$ to $n=1$

$\Delta E = -13.6\,(13^2)\left(\frac{1}{3^2}-1\right) = \underline{\underline{2043\ eV}}$

(on graph $\Delta E \sim 2040\ eV$)

(g) transition of Al^{12+} from $n=4$ to $n=1$

$$\Delta E = -13.6(13^2)\left(\frac{1}{4^2}-1\right) = \underline{\underline{2154\ eV}}$$

(on graph $\Delta E \sim 2150\ eV$)

- (a), (c), (d), (e) are Al^{11+} transitions to the ground state, (b), (f), (g) are Al^{12+} transitions to the ground state

Al^{12+} transitions typically have larger intensity, probably because more Al^{12+} are in the sample of Al than Al^{11+}. Within a certain ion, ~~bec~~ higher transition frequencies corresponds to smaller intensity. In X-ray transitions, the α-lines (transition between neighbouring n) ~~is~~ are the most intense ones because the transition states are close to each other.

- The feature in (h) is the Bremsstrahlung, i.e. the "braking radiation"

This is due to that the photon energy is high enough to completely ionise Al^{12+} into Al^{13+}, i.e. the Al nucleus. There are many free electrons in the plasma due to this ionisation. Free electrons collide and decelerate, according to classical ~~Electromag~~ electrodynamics, they radiate energy. ~~Some of this~~ This radiation is continuous in energy and generates a spectrum looks like (h). ~~Similarly we can see they~~ This occurs at photon energy $\Delta E \sim 2300\ eV$, the

ionisation ~~of~~ energy of Al^{12+}.

Similarly we observe that at energy ~ 2120 eV, the background continuous radiation increases, this is due to the ionisation and Bremsstrahlung of Al^{11+}.

(h) is the radiation omitted by the ~~inte~~ interaction between free electrons and ions. The spectrum is continuous.

14 B3 Q2

the overall Hamiltonian of multi-electron atoms is

$$H = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_{j>i}^{N} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \right].$$

In central field approximation, central potential

$$\cancel{V_{CF}} = V_{CF}(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + S(r)$$

Central Hamiltonian

$$H_{CF} = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m} \nabla_i^2 + V_{CF}(r_i) \right]$$

this allows separable solutions $\psi = \psi_1 \psi_2 \cdots \psi_N$

replace $V_{CF}(r_i) = \frac{Z_{eff} e^2}{4\pi\varepsilon_0 r_i}$, the same

quantum number ~~arises~~ n, l, m arises for each electron.

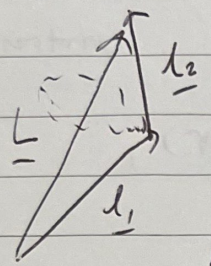
The quantum numbers n, l, m are assigned to each electron according to Pauli exclusion principle, gives the configuration of atom.

$$H = H_{CF} + \underbrace{\sum_{i=1}^{N} \left(\sum_{j>1}^{N} \left(\frac{e^2}{4\pi\varepsilon_0 r_{ij}} \right) - S(r_i) \right)}_{H_{rel}}$$

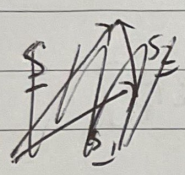
where H_{rel}, the residual electrostatic interaction, acts as a perturbation relative to H_{CF}. This H_{rel} Hamiltonian perturbs the configuration and gives terms

with ~~this~~ the addition of H_{rel}, the individual angular momentum of each electron $\underline{l_i}$, (orbital & spin)

are not conserved quantities any more, instead, the total angular momenta (orbital and spin) $\underline{L} = \sum_i \underline{l_i}$, and $\underline{S} = \sum_i \underline{s_i}$, are conserved and thus are good quantum numbers of the system.



($\underline{S_i}$ is also conserved but we choose $\underline{S}$ to be quantum number to antisymmetrize wavefunction)



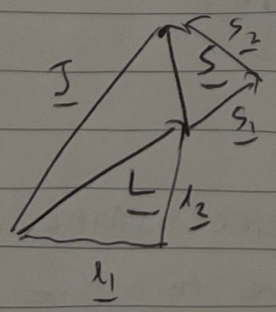
$\underline{l_1}, \underline{l_2}$ are not conserved, their magnitude remains the same, but precesses around $\underline{L}$ (direction changes)

Quantum state is $|L M_L S M_S\rangle$

This is LS coupling scheme.

~~splitting due to B~~

Spin-orbit ~~coupling~~ interaction in LS coupling



$\underline{L}$ and $\underline{S}$ precess around $\underline{J}$ more slowly than $\underline{l_1}, \underline{l_2}$ precess around $\underline{L}$

The good quantum numbers are

$|L S J M_J\rangle$

- selection rules for dipole radiation

  - $\Delta J = 0, \pm 1$ $\quad (J=0 \not\leftrightarrow 0)$
  - $\Delta M_J = 0, \pm 1$ $\quad (M_J = 0 \not\leftrightarrow M_J = 0 \text{ if } \Delta J = 0)$
  - parity ~~between int~~ needs to change between initial & final states
  - single electron jump
  - $\Delta l = \pm 1$ for that electron
  - $\Delta L = \pm 1, 0$ $\quad (L=0 \not\leftrightarrow 0)$
  - $\Delta S = 0$

- Zeeman effect.

The atoms total magnetic moment

$$\underline{\mu} = -\mu_B \underline{L} - g_s \mu_B \underline{S}$$

Hamiltonian for magnetic moment in an external $\underline{B}$ field

$$H_z = -\underline{\mu} \cdot \underline{B}$$

$\therefore$ H_z acts as a perturbation to states $|JM_J LS\rangle$

$\therefore$ We project $\underline{L}$ and $\underline{S}$ onto $\underline{J}$ in the vector model since one component of $\underline{J}$ is certain. And thus we can choose this direction to be parallel to the $\underline{B}$ field (z direction)

$$\therefore H_z = -\underline{\mu} \cdot \underline{B} = -\frac{\langle \underline{\mu} \cdot \underline{J} \rangle}{J(J+1)} \underline{J} \cdot \underline{B}$$

$$= \frac{\langle \underline{L} \cdot \underline{J} \rangle + g_s \langle \underline{S} \cdot \underline{J} \rangle}{J(J+1)} \mu_B B J_z$$

$\cancel{\langle L \cdot J \rangle = \frac{1}{2}[J(J+1)]}$ $\because \underline{S} = \underline{J} - \underline{L} \therefore \underline{S}^2 = \underline{J}^2 + \underline{L}^2 - 2\underline{J}\cdot\underline{L}$

$$\langle \underline{L} \cdot \underline{J} \rangle = \frac{1}{2}\left[J(J+1) + L(L+1) - S(S+1)\right]$$

Similarly $\langle \underline{S} \cdot \underline{J} \rangle = \frac{1}{2}\left[J(J+1) + S(S+1) - L(L+1)\right]$

we take $g_s \simeq 2$

$$\Rightarrow \quad \hat{H}_{ZE} = g_J \mu_B B \hat{J}_z$$

where $g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$

$$\Delta E = \langle J M_J L S | \hat{H}_{ZE} | J M_J L S \rangle$$

$$= g_J \mu_B B M_J$$

- weak means $H_Z \ll H_{SO}$

spin orbit interaction in LS coupling

i.e. $\mu_B B \ll$ fine structure splitting (the β_{LS} in $\beta_{LS}\langle \underline{L} \cdot \underline{S} \rangle$).

- selection rule for Zeeman.

$\Delta M_J = 0, \pm 1$ (not $0 \to 0$ if $\Delta J = 0$)

$\Delta M_J = 0 \Rightarrow \pi$ transitions (not observed // to $\underline{B}$)

$\Delta M_J = \pm 1 \Rightarrow \sigma$ transition (observed // and $\perp$ to $\underline{B}$)

- Zeeman pattern of Alkali atom

$\because$ 6 lines observed $\perp$ to $\underline{B}$
4 lines observed $\parallel$ to $\underline{B}$

$\therefore$ 2 π transitions , 4 σ transitions
$\Downarrow$ $\Downarrow$
$\Delta m_J = 0$ $\Delta m_J = \pm 1$

upper level $L_2 = D = 2$

Alkali metal $\Rightarrow$ one valence electron $\therefore S = \frac{1}{2}$

$J_2 = \frac{5}{2}$ or $\frac{3}{2}$, $J_2 > J_1$
$\swarrow$ $\searrow$
degeneracy = 6 degeneracy = 4

$\because$ 2 π transitions , 4 σ transitions.

$\therefore$ try $J_2 = \frac{3}{2}$, $J_1 = \frac{1}{2}$

$\because$ $\because S = \frac{1}{2}$ still , $\therefore L_1 = 1, 0$

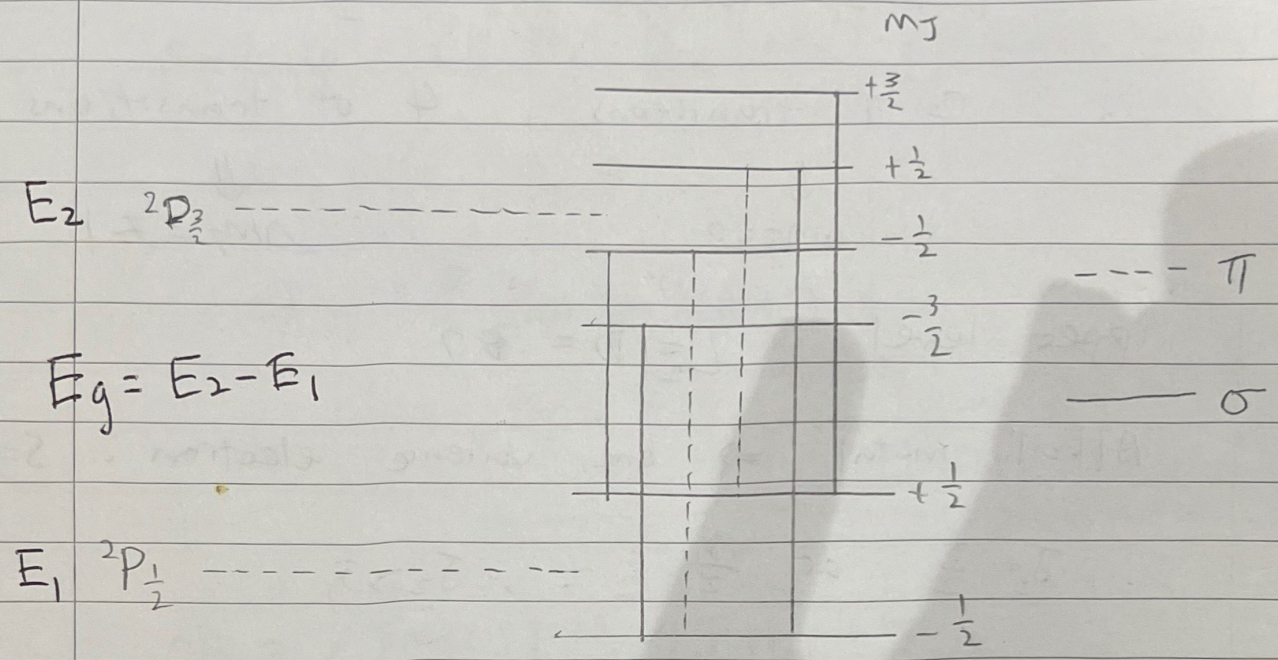
$\because \Delta L = 0, \pm 1$, $L_2 = 2$ $\therefore L_1 = 1$.
$S_1 = S_2 = \frac{1}{2}$ $2S+1 = 2$

$\therefore$ upper state ;
$^2D_{3/2}$ $g_J = \frac{4}{5}$

lower state : $^2P_{1/2}$ $g_J = \frac{2}{3}$

~~Pull up~~

$\therefore$ $S_1 = \frac{1}{2}$ $L_1 = 1$ $J_1 = \frac{1}{2}$ $S_2 = \frac{1}{2}$ $L_2 = 2$ $J_2 = \frac{3}{2}$



$E_g = E_2 - E_1$

indeed 2π, 4σ

For level 2 :

$$\Delta E_J^{(2)} = \frac{11}{5}\mu_B B M_J = \frac{11}{5}(9.274\times10^{-24}\,\frac{J}{T})(0.5\,T)\,M_J$$

$$= \frac{11}{5}(9.274\times10^{-24}\times0.5)\,(M_J)$$

$$= \cancel{(1.02\times10^{-23}\,J)\,M_J} = (3.7\times10^{-24})\,M_J$$

For level 1 :

$$\Delta E_J^{(1)} = \frac{2}{3}(9.274\times10^{-24}\times0.5)\,M_J = \cancel{(1.08\times10^{-23}\,J)\,M_J}$$

$$= (3.09\times10^{-24})\,M_J$$

σ transitions:

$\Delta M_J = -1$:

$\rightarrow \Delta E(\frac{3}{2} \rightarrow \frac{1}{2}) = E_g + \Delta E^{(2)}_{3/2} - \Delta E^{(1)}_{1/2}$ (set $E_g = 0$)

$= (10^{-24})[3.71 \times \frac{3}{2} - 3.09 \times \frac{1}{2}]$

$\frac{1}{\lambda} = \frac{E}{hc}$

$= \cancel{0.99 \times 10^{-23} J} = 4.02 \times 10^{-24} J$

$= \boxed{0.202 \text{ cm}^{-1}}$

$= \cancel{2.01 \text{ cm}^{-1}}$ $\cancel{3.14 \times 10^4 \text{ cm}^{-1}}$

(use $\cancel{\frac{hc}{\lambda} = E}$ $\cancel{\therefore \lambda = \frac{hc}{E}}$ $\cancel{(c = \frac{E}{hc})}$)

$\rightarrow \Delta E(\frac{1}{2} \rightarrow -\frac{1}{2}) = (10^{-24})[3.71 \times \frac{1}{2} - 3.09 \times \frac{1}{2}]$

$= 3.4 \times 10^{-24} J = \boxed{0.170 \text{ cm}^{-1}}$

$\cancel{= 1.05 \times 10^{-23} J = 1.89 \text{ cm}^{-1}}$

$\cancel{= 3.33 \times 10^4 \text{ cm}^{-1}}$

$\Delta M_J = +1$:

$\rightarrow \Delta E(-\frac{1}{2} \rightarrow \frac{1}{2}) = (10^{-24})[3.71(-\frac{1}{2}) - 3.09(\frac{1}{2})]$

$= -3.4 \times 10^{-24} J = \boxed{-0.170 \text{ cm}^{-1}}$

$\cancel{= 1.05 \times 10^{-23} J = -1.89 \text{ cm}^{-1}}$

$\cancel{= -3.33 \times 10^4 \text{ cm}^{-1}}$

$\Delta E(-\frac{3}{2} \rightarrow -\frac{1}{2}) = 10^{-24}[3.71(-\frac{3}{2}) - 3.09(-\frac{1}{2})]$

$= -4.02 \times 10^{-24} = \boxed{-0.202 \text{ cm}^{-1}}$

$\cancel{= -0.99 \times 10^{-23} J = -2.01 \text{ cm}^{-1}}$

$\cancel{= -3.33 \times 10}$

$\cancel{= -3.14 \times 10^4 \text{ cm}^{-1}}$

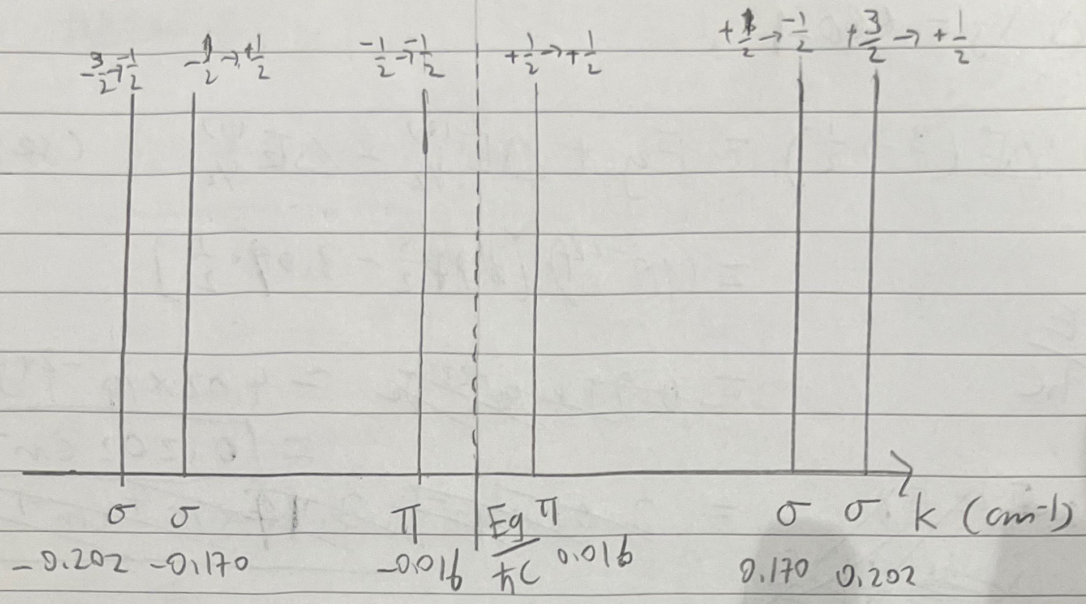
π transitions :

$\rightarrow \Delta E(\frac{1}{2} \rightarrow \frac{1}{2}) = (10^{-24})[3.71(\frac{1}{2}) - 3.09(+\frac{1}{2})]$

$= 0.31 \times 10^{-24} J = \boxed{0.016 \text{ cm}^{-1}}$

$\cancel{= 0.314 \times 10^{-23} J = 952 \text{ cm}^{-1}}$

$\rightarrow \Delta E(-\frac{1}{2} \rightarrow -\frac{1}{2}) = \cancel{+952 \text{ cm}^{-1}}$ $\boxed{-0.016 \text{ cm}^{-1}}$



both
// and ⊥ B

⊥ B only

both // and ⊥ B

14B3Q3

- In Bohr model Hydrogen, $\alpha = \frac{v}{c}$

v = orbital velocity of electron
c = speed of light

$\alpha = \frac{1}{137}$ & $m_e c^2 = 0.511\ MeV$

$\therefore \frac{\alpha^2}{2} m_e c^2 = \frac{1}{2}\left(\frac{1}{137}\right)(0.511 \times 10^6)\ eV$

$= 13.6\ eV$ (the binding energy of H)
$\simeq \frac{1}{2} m v^2$

- α^4 dependence $= (-\text{total energy})$

the fine structure splitting is a relativistic effect.

the γ factor is $\gamma = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}}$

in its taylor expansion the first term $\propto \left(\frac{v}{c}\right)^2$, which is the kinetic energy of the particle.

The second term $\propto \left(\frac{v}{c}\right)^4$, which is this fine structure splitting $\because \alpha = \frac{v}{c}$

$\therefore$ fine structure splitting $\propto \alpha^4$

- spin orbit interaction:

An electron moving through an electric field $\underline{E}$ experiences a magnetic field

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

Electric field is the gradient of potential energy

$$\underline{E} = \frac{1}{e}\frac{\partial V}{\partial r}\frac{\underline{r}}{r}$$

So $$\underline{B} = \frac{1}{m_e c^2}\left(\frac{1}{er}\frac{\partial V}{\partial r}\right)\underline{r} \times m_e \underline{v}$$

$$= \frac{1}{m_e c^2}\left(\frac{1}{er}\frac{\partial V}{\partial r}\right)\underline{l}$$

intrinsic magnetic moment of electron is

$$\underline{\mu} = -g_s \mu_B \underline{S}/\hbar \quad (g_s \simeq 2)$$

Hamiltonian $$H = -\underline{\mu}\cdot\underline{B} = \frac{g_s \mu_B}{\hbar}\underline{S}\cdot\frac{1}{m_e c^2}\left(\frac{1}{er}\frac{\partial V}{\partial r}\right)\underline{l}$$

$$\left(\mu_B = \frac{e\hbar}{2m_e}\right)$$

take into account of Thomas precession

replace g_s by $g_s - 1 \simeq 1$

we have $$H = \frac{1}{2m_e^2 c^2}\frac{1}{r}\frac{\partial V}{\partial r}\underline{l}\cdot\underline{S}$$

$$\left(V = -\frac{Ze^2}{4\pi\varepsilon_0 r}\right)$$

- spin-orbit splitting for 3p electron, $\left(\frac{1}{r}\frac{\partial V}{\partial r} = \frac{Ze^2}{4\pi\varepsilon_0 r^3}\right)$

$$E_3 = \langle H \rangle = \frac{1}{2m_e^2 c^2}\frac{e^2 Z}{4\pi\varepsilon_0}\left\langle\frac{1}{r^3}\right\rangle\langle \underline{S}\cdot\underline{l}\rangle$$

$$= \frac{1}{2m_e^2 c^2}\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{81}\left(\frac{Z}{a_0}\right)^3\langle \underline{S}\cdot\underline{l}\rangle$$

$$\langle \underline{s}\cdot\underline{l}\rangle = \langle \tfrac{1}{2}(\underline{j}^2-\underline{s}^2-\underline{l}^2)\rangle = \tfrac{\hbar^2}{2}[j(j+1)-s(s+1)-l(l+1)]$$

for $\underline{j} = \underline{l}+\underline{s}$ = total angular momentum.

$$\therefore E_j = \frac{1}{2m_e^2c^2}\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{8}\cdot\frac{\hbar^2}{2}\left(\frac{Z}{a_0}\right)^3\left[j(j+1)-s(s+1)-l(l+1)\right]$$

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \qquad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = \left(\frac{4\pi\varepsilon_0\hbar c}{e^2}\right)\frac{\hbar}{cm_e} = \frac{\hbar}{\alpha m_e c}$$

$$\therefore E_j = \frac{1}{2m_e^2c^2}\frac{e^2}{4\pi\varepsilon_0}\frac{1}{8}\frac{\hbar^2}{2}\left(\frac{m_e c}{\hbar}\right)^3 Z^4\alpha^3\left[j(j+1)-s(s+1)-l(l+1)\right]$$

$$= \underbrace{\left(\frac{e^2}{4\pi\varepsilon_0\hbar c}\right)}_{\alpha}\cdot\frac{1}{2}\cdot\frac{1}{8}\cdot\frac{1}{2}m_e c^2 Z^4\alpha^3\left[j(j+1)-\tfrac{1}{2}(\tfrac{1}{2}+1)-(1(1+1)\right]$$

$$= \frac{1}{2}\cdot\frac{1}{2}\cdot\frac{1}{8}(Z\alpha)^4 m_e c^2\left[j(j+1)-\frac{3}{4}-2\right].$$

$$= \frac{1}{32}(Z\alpha)^4 m_e c^2\left[j(j+1)-\frac{11}{4}\right].$$

$$\therefore E_{j=3/2}-E_{j=1/2} = \frac{1}{32}(Z\alpha)^4 m_e c^2\left[\frac{3}{2}(\tfrac{5}{2})-(\tfrac{1}{2})(\tfrac{3}{2})\right]$$

$$= \frac{1}{32}\cdot 3(Z\alpha)^4 m_e c^2 = \underline{\underline{\frac{1}{108}(Z\alpha)^4 m_e c^2}}$$

- effective Z

$$\frac{1}{108}(Z_{eff})^4\left(\frac{1}{137}\right)^4 m_e c^2 = \frac{hc}{589\,nm} - \frac{hc}{\cancel{566}\ 588.6\,nm}$$

$$= 0.00214\ eV$$

$m_e c^2 = 0.511\ \text{MeV}$

$$\therefore \frac{1}{108}(Z_{eff}^4)\left(\frac{1}{137}\right)^4 \underset{\times 10^6}{0.511} = 0.00214$$

$$\therefore Z_{eff} = \left(\frac{0.00214}{10^6 \times 0.511} \times 108 \times 137^4\right)^{\frac{1}{4}}$$

$$= \underline{\underline{3.6}}$$

- electrons in the inner filled shells shield nuclear charge.

- Splitting for H: $Z = 1$.

$$E_{3/2} - E_{1/2} = \frac{1}{108}\left(\frac{1}{137}\right)^4 (0.511 \times 10^6\ \text{eV})$$

$$= \underline{\underline{1.34 \times 10^{-5}\ \text{eV}}}$$

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$$\frac{dI}{dz} = \frac{\alpha_0 I}{1 + \frac{I}{I_s}}$$

input signal level

~~increasing the input signal level increases both absorption and stimulated emission~~

- Small signal gain coefficient is ~~pos~~ proportional to the population inversion

- increasing the input signal level ~~increases~~ increases stimulated emission and thus reduces population inversion, reducing the gain coefficient. This is gain saturation.

- Gain depends on the intensity of amplifier as well.

- population inversion $N^* = N_2 - \frac{g_2}{g_1} N_1$

rate equations

$$\frac{dN_2}{dt} = S_2 - \cancel{N_2 A_{21}} - \frac{\sigma I N^*}{\hbar\omega} - \frac{N_2}{\tau_2}$$

$$\frac{dN_1}{dt} = S_1 + N_2 A_{21} + \frac{\sigma I N^*}{\hbar\omega} - \frac{N_1}{\tau_1}$$

Steady state $\frac{dN_1}{dt} = \frac{dN_2}{dt} = 0$

$$\therefore \quad S_2 - \frac{\sigma I N^*}{\hbar\omega} - \frac{N_2}{\tau_2} = 0 \qquad ①$$

$$S_1 + \frac{\sigma I N^*}{\hbar\omega} - \frac{N_1}{\tau_1} + N_2 A_{21} = 0 \qquad ②$$

$$① + ② \Rightarrow \quad S_1 + S_2 - \frac{N_2}{\tau_2} - \frac{N_1}{\tau_1} + N_2 A_{21} = 0$$

$$\therefore \quad N_1 = \tau_1 \left(S_1 + S_2 - \frac{N_2}{\tau_2} + N_2 A_{21} \right) \qquad ③$$

$$③ \rightarrow ② \Rightarrow \cancel{S_1} + \frac{\sigma I N^*}{\hbar\omega} - \cancel{S_1} - S_2 + \frac{N_2}{\tau_2} - \cancel{N_2 A_{21}} + \cancel{N_2 A_{21}} = 0$$

$$\therefore \quad \frac{\sigma I N^*}{\hbar\omega} - S_2 - \frac{N_2}{\tau_2} = 0$$

$$\therefore \quad N_2 = \tau_2 \left(\frac{\sigma I N^*}{\hbar\omega} - S_2 \right)$$

$$N_1 = \tau_1 \left(S_1 + S_2 - \frac{\sigma I N^*}{\hbar\omega} + S_2 + \right.$$

$$N^* = N_2 - \frac{g_2}{g_1} N_1$$

$$= N_2 - \frac{g_2 \tau_1}{g_1} \left(S_1 + S_2 - \frac{N_2}{\tau_2} + N_2 A_{21} \right)$$

$$① \Rightarrow \quad N_2 = \tau_2 \left(S_2 - \frac{\sigma I N^*}{\hbar\omega} \right).$$

$$N^* = \tau_2 \left(S_2 - \frac{\sigma I N^*}{\hbar\omega} \right)$$

$$- \frac{g_2}{g_1} \tau_1 \left(S_1 + \cancel{S_2} - \left(\cancel{S_2} - \frac{\sigma I N^*}{\hbar\omega} \right) \right.$$

$$\left. + \tau_2 A_{21} \left(S_2 - \frac{\sigma I N^*}{\hbar\omega} \right) \right)$$

$$\therefore N^* = \tau_2 S_2 - \tau_2 \frac{\sigma I}{\hbar\omega} N^*$$

$$- \frac{g_2}{g_1} \tau_1 S_1 - \frac{g_2}{g_1} \tau_1 \frac{\sigma I N^*}{\hbar\omega}$$

$$- \frac{g_2}{g_1} \tau_1 \tau_2 A_{21} S_2 + \frac{g_2}{g_1} \tau_1 \tau_2 A_{21} \frac{\sigma I N^*}{\hbar\omega}$$

$$\therefore N^* \left[1 + \tau_2 \frac{\sigma I}{\hbar\omega} + \frac{g_2}{g_1} \tau_1 \frac{\sigma I}{\hbar\omega} - \frac{g_2}{g_1} \tau_1 \tau_2 A_{21} \frac{\sigma I N^*}{\hbar\omega} \right]$$

$$= \tau_2 S_2 - \frac{g_2}{g_1} \tau_1 S_1 - \frac{g_2}{g_1} \tau_1 \tau_2 A_{21} S_2.$$

$$\cancel{\therefore N^* = \tau_2 S_2 \left(1 - \frac{g_2}{g_1} \tau_1 A_{21} \right) - \frac{g_2}{g_1} \tau_1 S_1}$$

$$N^* = \frac{S_2 \tau_2 \left(1 - \frac{g_2}{g_1} \tau_1 A_{21} \right) - \frac{g_2}{g_1} \tau_1 S_1}{1 + \frac{\sigma I}{\hbar\omega} \left(\tau_2 + \frac{g_2}{g_1} \tau_1 - \frac{g_2}{g_1} \tau_1 \tau_2 A_{21} \right)}$$

$$= \frac{N^*(0)}{1 + I / I_{sat}}$$

$$N^*(0) \equiv S_2\tau_2\left(1 - \frac{g_2}{g_1}A_{21}\tau_1\right) - \frac{g_2}{g_1}S_1\tau_1$$

$$I_{sat} \equiv \frac{\hbar\omega}{\sigma}\left[\tau_2 + \frac{g_2}{g_1}\tau_1 - \frac{g_2}{g_1}\tau_1\tau_1 A_{21}\right]^{-1}$$

$$\alpha(\omega) = \cancel{N^*(0)}\, N^*\sigma(\omega)$$

$$= \frac{N^*(0)\,\sigma(\omega)}{1 + I/I_{sat}}$$

$$= \frac{\alpha_0(\omega)}{1 + I/I_{sat}} \qquad (\alpha_0 = N^*(0)\sigma)$$

Amplification:

$$\frac{dI}{dz} = \alpha I \qquad \therefore \cancel{\frac{dI}{\alpha I} = dz}$$

$$\therefore \frac{dI}{dz} = \frac{\alpha_0 I}{1 + I/I_{sat}}$$

$$\therefore \left(1 + \frac{I}{I_{sat}}\right)\frac{1}{I}\,dI = \alpha_0\,dz$$

$$\therefore \frac{dI}{I} + \frac{dI}{I_{sat}} = \alpha_0\,dz$$

first amplifier :

length of both amplifiers.

$$\int_{I_0}^{100 I_0} \frac{dI}{I} + \frac{dI}{I_{sat}} = \alpha L$$

$$\Rightarrow \ln\left(\frac{100 I_0}{I_0}\right) + 99 \frac{I_0}{I_{sat}} = \alpha L$$

Second amplifier :

$$\int_{100 I_0}^{300 I_0} \frac{dI}{I} + \frac{dI}{I_{sat}} = \alpha L .$$

$$\therefore \ln\left(\frac{300 I_0}{100 I_0}\right) + 200 \frac{I_0}{I_{sat}} = \alpha L$$

$$\therefore \ln(100) + 99 \frac{I_0}{I_{sat}} = \ln(3) + 200 \frac{I_0}{I_{sat}}$$

$$\therefore 101 \frac{I_0}{I_{sat}} = \ln(100) - \ln(3)$$

$$= 3.5$$

$$\therefore \frac{I_{sat}}{I_0} = \frac{101}{3.5} = \underline{\underline{28.8}}$$