

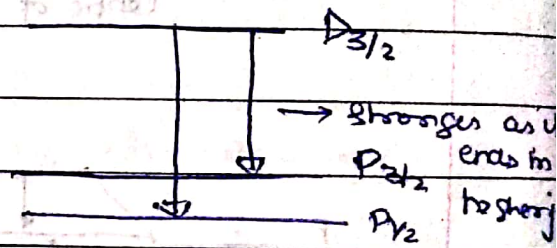
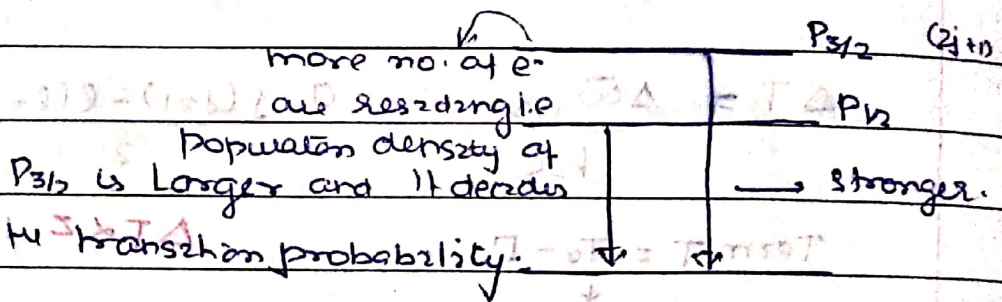
Intensities of doublet lines:

Rules:

① Strongest lines are observed when the change in total angular momentum & angular orbital momentum is same. i.e. j and l changes by same way

eg: $\Delta j = 1, \Delta l = 1$

② If more than one ~~lines~~ transitions are involved in the doublet structure, then the line with largest j will be stronger.



$2P_{1/2} \rightarrow 2D_{3/2}$

$\Delta l = -1$

$\Delta j = -1$

} follows first rule and hence its strong line

$2P_{3/2} \rightarrow 2D_{5/2}$

$\Delta l = -1$

$\Delta j = -1$

} → strong.

$2P_{3/2} \rightarrow 2D_{3/2}$

$\Delta l = -1$

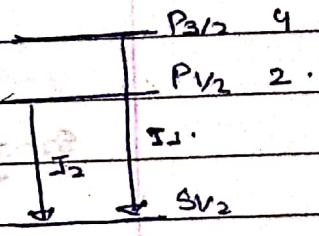
$\Delta j = 0$

} → weaker.

Quantitative rules for intensity of doublet lines:

- ① The sum of the intensities of these lines of a doublet from a common initial level is proportional to the quantum weight $(2j+1)$ of that level.
- ② The sum of intensities of these lines which ends on a common level is proportional to the quantum weight of that level.

$$\frac{I_1}{I_2} = \frac{2(3/2+1)}{2(1/2+1)} = \frac{2}{1}$$



Hamiltonian of electron:

$$H = H_0 + H_C + H_{S.S.}$$

H_0 : K.E.
 H_C : Coulomb
 $H_{S.S.}$: Spin

$$= H^0 + \Delta H_{L.S.}$$

↳ perturbation caused by s-o coupling.

Two electron atom:

He (Z=2)

Possible configurations

- ↑↑
- ↑↓
- ↓↑
- ↓↓

$$\Psi(H) = \Psi(1s)\Psi(1s)$$

↳ antisymmetric with to exchange of electrons because as per Pauli exclusion principle

Ortho Helium → spins are parallel

Para " → " " antiparallel

Electrons in the same orbit are called equivalent electrons.

sp electrons → s = one from here spherically from atom

sp electrons → s = one from here spherically from atom
 p electrons → p equivalent e⁻

all spin
 Date: / /

$$S = \uparrow\uparrow \delta_1 + \delta_2$$

$$= 1$$

Spin degeneracy $\Rightarrow (2S+1) = 3$ Triplet State

$$\uparrow\downarrow S = \frac{1}{2} - \frac{1}{2} = 0 = \delta_1 - \delta_2$$

$$S = (2S+1) = 1$$
 Singlet State

Singlet $\not\leftrightarrow$ Triplet \equiv It needs to flip the spin which requires energy & hence not possible

Singlet \leftrightarrow Singlet

Triplet \leftrightarrow Triplet

$\Rightarrow \Delta S = 0$ / Singlet-Singlet

Selection rule for triplet-triplet transition: $\Delta L = \pm 1, \Delta J = 0, \pm 1$

In terms of Singlet & Triplet: $1p, 3p$

{ Two e^- only when far away from each other can have same spin }

Exercise 3 electrons:

$$\uparrow\uparrow\uparrow \quad \boxed{0 \ 0 \ 0}$$

$$S = \frac{1}{0} \quad \frac{1}{2} \quad \frac{3}{2} \rightarrow \text{doublet}$$

$3e^-$ system will always give a doublet:

eg. C atoms : $4e^-$
 Singlet & triplet

Spin coupling takes place due to interaction of mag. fields
 \rightarrow The two electrons have their magnetic fields and they interact with each other and hence spin-spin interaction takes place.

① Spin-Spin Correlation

→ magnetic field

} strong.

② Spins (electrons) are also orbiting around the nucleus. and hence see a weak coupling due to ~~strong~~ orbital motion.
→ Angular momentum correlation

→ electrostatic in nature

$$\vec{L} = \vec{l}_1 + \vec{l}_2 \quad (\text{These are vector quantity})$$

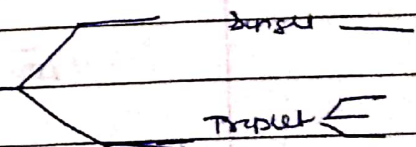
$$l_1 - l_2, \dots, l_1 + l_2$$

$$\text{if } \vec{L} = 0 \Rightarrow S$$

$$\text{if } l_1 = 1, l_2 = 1, L = 0, 1, 2$$

$$\begin{matrix} \downarrow & \downarrow & \downarrow \\ S & P & D \end{matrix}$$

③ Spin-orbit interaction



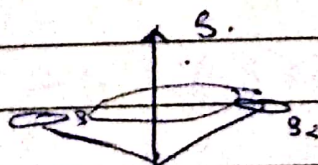
↓ Lower in energy

because it forms when they are very far from each other.

→ Ground state of He is singlet, though triplet is more stable because e- can't have to be accommodated in same orbit.

$$1s^1 | 2s^1 2p \dots$$

↳ Triplet (3s) but it is not the ground state.



$$\cos(\theta_{12}) = \frac{S^2 - s_1^2 - s_2^2}{2(s_1 s_2)}$$

Selection rule:

$$\Delta S = 0$$

$$\Delta L = \pm 1$$

Ⓟ

Two electron system

$l_1 l_2$
 $s_1 s_2$



So, only valence electrons contribute to it

The two electrons are identical and hence they are indistinguishable and so according to Pauli exclusion principle they must have atleast one quantum no. different \Rightarrow spin different \Rightarrow Triplet

The statistical weight of S can never be 0.

Spin-Spin Interaction - Two spins of each electron couple together and is magnetic in nature.

The magnetic field due to spin is larger than orbital

$$\Delta E = a \cos(\theta, \phi)$$

where $a = \frac{4\pi^2 q^2}{h^3 R(R+1)(L+1/2)}$

$$\cos(\theta, \phi) = \frac{L(L+1) - L(L+1) - S(S+1)}{2L^*S^*}$$

$\Delta E_1 = a_1 \cos(\theta_1^*, \theta_2^*)$ spin spin coupling S — ①

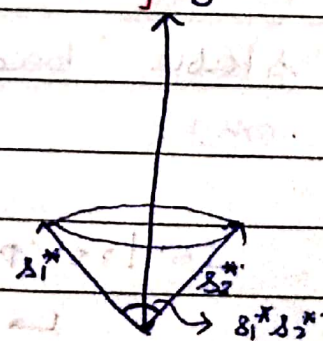
$\cos(\theta_1^*, \theta_2^*)$: projection

$$\cos(\theta_1^*, \theta_2^*) = \frac{S^{*2} - S_1^{*2} - S_2^{*2}}{2S_1^*S_2^*}$$

$$S_1^* = \sqrt{S_1(S_1+1)}$$

$$S_2^* = \sqrt{S_2(S_2+1)}$$

$$S^* = \sqrt{S(S+1)}$$



l-l. coupling:

$\Delta E_2 = a_2 \cos(\theta_1^*, \theta_2^*)$ — ②

Spin-orbit:

$\Delta E_3 = a_3 \cos(\theta_1^*, \theta_1^*)$ — ⑤

$\Delta E_4 = a_4 \cos(\theta_2^*, \theta_2^*)$ — ④

$$\begin{aligned} \Delta \bar{\nu}_5 &= a_5 \cos(\theta_1^* \theta_2^*) \quad \text{--- ⑤} \\ \Delta \bar{\nu}_6 &= a_6 \cos(\theta_1^* \theta_2^*) \quad \text{--- ⑥} \end{aligned} \left. \begin{array}{l} \text{Spin orbit} \\ \text{--- weaker} \end{array} \right\}$$

Schemes:

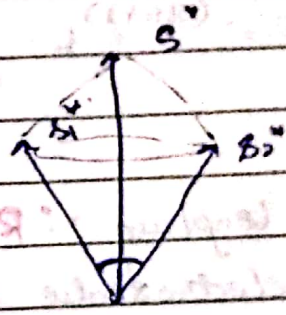
① LS coupling:
 $\Delta \nu_1, \Delta \nu_2 \gg \Delta \bar{\nu}_3, \Delta \bar{\nu}_4$

② J-J coupling:
 $\Delta \nu_3, \Delta \nu_4 \gg \Delta \bar{\nu}_1, \Delta \bar{\nu}_2$

③ Spin Spin Interaction:

$$\Delta \nu_1 = a_1 \cos(\theta_1^* \theta_2^*)$$

$$\cos(\theta_1^* \theta_2^*) = \frac{S^2 - S_1^2 - S_2^2}{2 S_1 S_2}$$



$$= \frac{S(S+1) - S_1(S_1+1) - S_2(S_2+1)}{2 S_1 S_2}$$

$$\therefore S_1 = 1/2, S_2 = 1/2$$

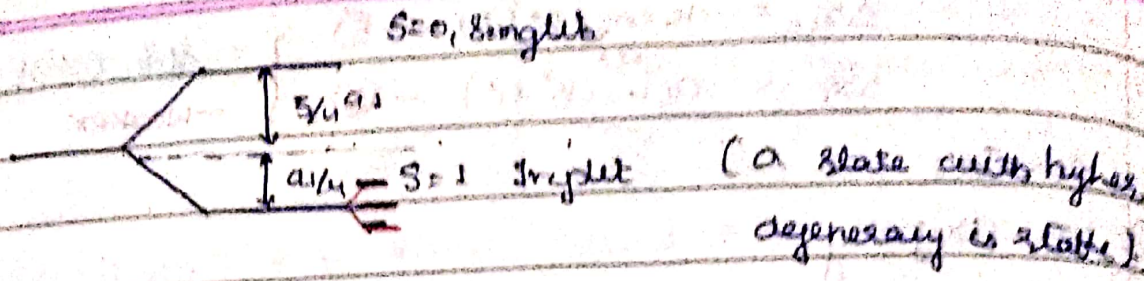
$$\therefore \cos(\theta_1^* \theta_2^*) = \frac{S(S+1) - \frac{1}{2} \cdot \frac{3}{2} - \frac{1}{2} \cdot \frac{3}{2}}{2 \cdot \frac{1}{2} \cdot \frac{1}{2}}$$

$$\Delta \nu_1 = \frac{a}{2} \cos \theta_1^* \theta_2^* \left\{ \frac{S(S+1) - 3/2}{2 \cdot \frac{1}{2} \cdot \frac{1}{2}} \right\}$$

$$\therefore \Delta \nu_1 = \frac{a}{2} \left\{ S(S+1) - 3/2 \right\}$$

Singlet $S=0$
 $\Delta \nu_1 = -3/4 a$

Triplet $S=1$
 $\Delta \nu_1 = a/4$



$\Rightarrow a_1 \text{ is } -ve$

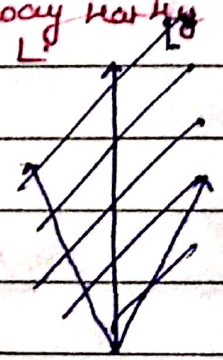
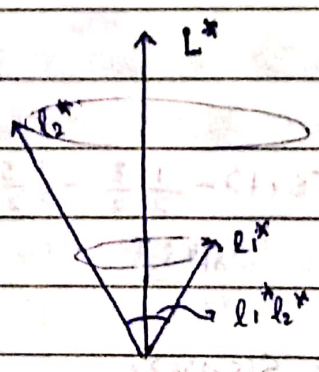
Degeneracy = $(2s+1) \cdot \dots$ Cause of degeneracy is
couple of orbital angular momenta each spin and hence
these levels have different angular momentum value.

$\Delta \bar{2} \bar{1} > \Delta \bar{2} \bar{2} >> \Delta \bar{2} \bar{3}, \Delta \bar{2} \bar{4}$

$(2s+1)_L \quad 3p, 3s, 1d, 3d, 1d$

LL Coupling : Russell-Saunders Coupling $\equiv L_1$ and L_2 are quantized
with respect to one other in such a way that they can
- electrostatic in nature form a resultant L^*

$\Delta \bar{2} \bar{2} = a_2 L_1^* L_2^* \cos(L_1^* L_2^*)$



$$\cos(L_1^* L_2^*) = \frac{L^{*2} - L_1^{*2} - L_2^{*2}}{2 L_1^* L_2^*}$$

$$= \frac{L(L+1) - L_1(L_1+1) - L_2(L_2+1)}{2 L_1^* L_2^*}$$

Where $L_1^* = \sqrt{L_1(L_1+1)}$
 $L_2^* = \sqrt{L_2(L_2+1)}$
 $L^* = \sqrt{L(L+1)}$

$$\therefore \Delta \psi_2 = \frac{a_2}{2} [L(L+1) - l_1(l_1+1) - l_2(l_2+1)]$$

eg:

(i) s-s electron - Helium atom
 $l_1 = l_2 = 0$

$$\Delta \psi_2 = \frac{a_2}{2} \times 0 = 0$$

(ii) sp-electrons (≠ps)

$$l_1 = 0, l_2 = 1$$

$$L = l_2$$

$$\Delta \psi_2 = 0$$

This is true for sd, sf, ...

(iii) pd electron

$$l_1 = 1, l_2 = 2$$

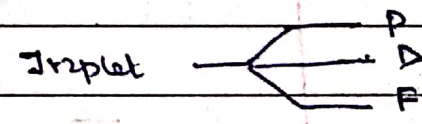
$$L = |l_1 - l_2| \dots |l_1 + l_2|$$

$$= 1, 2, 3$$

Term $\begin{matrix} \square & \square & \square \\ \downarrow & \downarrow & \downarrow \\ P & D & F \end{matrix}$

$$\Delta \psi_2 = \frac{a_2}{2} [L(L+1) - 6]$$

L	1	2	3
$\Delta \psi_2$	$-3a_2$	$-a_2$	$2a_2$



highest degeneracy is more stable.

(iv) pp electron

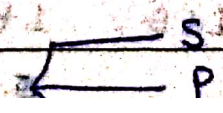
$$l_1 = 1, l_2 = 1$$

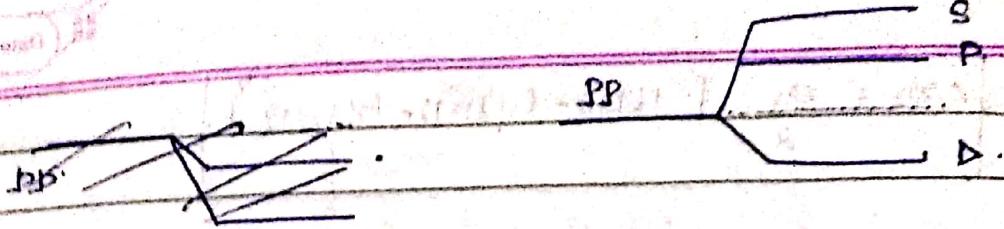
$$L = 2, 1, 0$$

D P S

$$\Delta \psi_2 = \frac{a_2}{2} [L(L+1) - 4]$$

L	0	1	2
$\Delta \psi_2$	$-2a_2$	$-a_2$	a_2



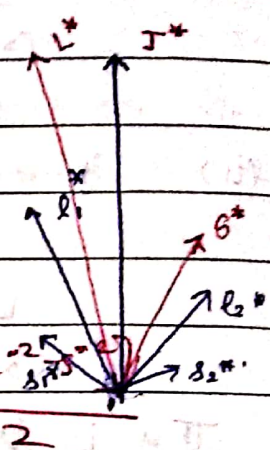


③ LS coupling (Spin orbit interaction)

$\Delta\bar{S}_3, \Delta\bar{S}_4$ - energies term

$$\Delta\bar{S}_3 = \alpha_3 l_1^* s_1^* \cos(l_1^*, s_1^*)$$

$$\Delta\bar{S}_4 = \alpha_4 l_2^* s_2^* \cos(l_2^*, s_2^*)$$



average $\Delta\bar{S}_{l_1, l_2} = \Delta\bar{S}_3 + \Delta\bar{S}_4 = (\alpha_3 \alpha_3 + \alpha_4 \alpha_4) \left[\frac{J^{*2} - L^{*2} - S^{*2}}{2L^{*2}} \right]$

$$\alpha_3 = \left(\frac{l_1^{*2} - l_2^{*2} + L^{*2}}{2l_1^* l_2^*} \right) \left(\frac{s_1^{*2} - s_2^{*2} + S^{*2}}{2s_1^* s_2^*} \right)$$

$$\alpha_3 = \left[\frac{l_1^{*2} - l_2^{*2} + L^{*2}}{2L^{*2}} \right] \left[\frac{s_1^{*2} - s_2^{*2} + S^{*2}}{2S^{*2}} \right]$$

$$\alpha_4 = \left(\frac{l_2^{*2} - l_1^{*2} + L^{*2}}{2L^{*2}} \right) \left(\frac{s_2^{*2} - s_1^{*2} + S^{*2}}{2S^{*2}} \right)$$

Term: $2S+1 L_J$

$$\boxed{{}^3P_5}, \quad \begin{matrix} S=1 \\ L=1 \\ J=5 \end{matrix}$$

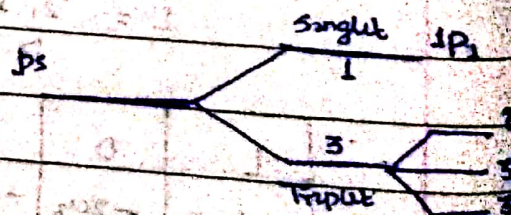
eg: LS coupling in ps electron configuration

$$l_1 = 1, l_2 = 0$$

$$L = 1 \Rightarrow P$$

Singlet: $J = L + S = 1 + 0 = 1$

$1P_1 =$ Singlet state



- Term with highest S value lies lowest and with L value lies...