LS Coupling: for equivalent e⁻s. : Normal arrangement of terms

interval between the different Lines:

$$\Delta E_{S,L} = \frac{a(\vec{L}\cdot\vec{S})h}{2\pi}$$

$$= \frac{a}{2}[J(J+1) - L(L+1) - S(S+1)]\hbar$$

$$\Delta E_{S,L}(J+1) - \Delta E_{S,L}(J) = \frac{a}{2}[(J+1)(J+2) - J(J+1)]\hbar$$

$$= \frac{a}{2}[2(J+1)]\hbar$$

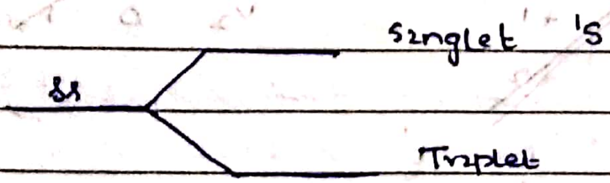
$$\Delta E(J+1) - \Delta E(J) = a(J+1)\hbar$$

$$= A(J+1).$$

This interval energy is proportional to $(J+1)$ i.e. upper level J value.

Two equivalent electrons:

Suppose He. , $l_1 = 0$, $l_2 = 0$, $s_1 = 1/2$, $s_2 = 1/2$, $\boxed{S = 0, 1}$ → always.



(Triplet is more stable since the separation is large and is more likely).

- Ground state of helium is $^1S_0$

Non-equivalent pp e^-

$l_1 = 1, l_2 = 1$

$L = 0, 1, 2$ $S = 0, 1$.

S P D

$\therefore$ ^1S ^1P ^1D

^3S ^3P ^3D

L	S	J
0	0	0
1		1
2		2
0	1	X
1	1	X
2	1	3 ✓

$^3S_1 \rightarrow$ not allowed

$L = 1$. $l_1 = m_l \hbar$

$= M_L \hbar$

m_{l_2} \ m_{l_1}	-1	0	+1
-1	-2	-1	0
0	-1	0	+1
+1	0	+1	+2

S P D

m_{s_2} \ m_{s_1}	-1/2	1/2
-1/2	-1	0
1/2	0	1

Singlet Triplet

For equivalent e^-:

The diagonal terms ~~represent~~ is removed. and then remaining term triplet is allowed. and singlet of others are allowed.

m_{l_2} \ m_{l_1}	-1	0	+1
-1	$\cancel{-2}$	-1	0
0	-1	$\cancel{0}$	+1
+1	0	+	$\cancel{+2}$

m_{s_2} \ m_{s_1}	-1/2	1/2
-1/2	$\cancel{-1}$	0
1/2	0	$\cancel{1}$

S P D

Singlet Triplet Singlet

Q Find out for d^2.

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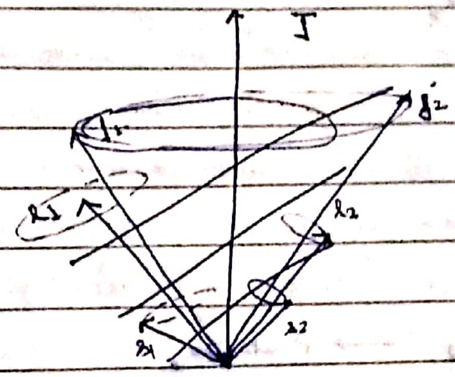
jj coupling:

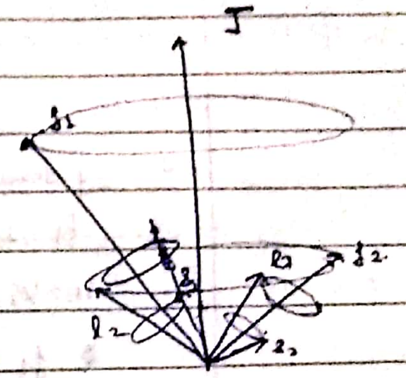
$$\Delta 2\bar{5}_3 = a_3\, l_1^* s_1^* \cos(l_1^* s_1^*)$$

$$\Delta 2\bar{5}_4 = a_4\, l_2^* s_2^* \cos(l_2^* s_2^*)$$

$\Delta 25_1, \Delta 25_2 >> \Delta 25_3\ \Delta 25_4$ LS scheme.

$\Delta 25_3, \Delta 25_4 >> \Delta 25_1, \Delta 25_2$ jj scheme.





$$J = j_1 \pm j_2$$
$$= |j_1 - j_2| \cdots |j_1 + j_2|.$$

- for jj coupling,

$$\Delta 25_3 = \frac{1}{2} a_3 (j_1^{*2} - l_1^{*2} - s_1^{*2})$$

$$\Delta 25_4 = \frac{1}{2} a_4 (j_2^{*2} - l_2^{*2} - s_2^{*2})$$

$$\Delta 25_1 + \Delta 25_2 = \frac{1}{2} B \left[J^{*2} - j_1^{*2} - j_2^{*2} \right]$$

$$B = a_1\beta_1 + a_2\beta_2$$

$$\beta_1 = \left(\frac{s_1^{*2} + j_1^{*2} - l_1^{*2}}{2 j_1^{*2}} \right) \left(\frac{s_2^{*2} + j_2^{*2} -}{2 j_2^{*2}} \right.$$

$$\beta_2 = \left(\frac{l_1^{*2} + j_1^{*2} - s_1^{*2}}{2 j_1^{*2}} \right) \left[\frac{l_2^{*2} + j_2^{*2}}{2 j_2^{*}} \right.$$

We have seen that,

$$\Delta 25_3 + \Delta 25_4 = \frac{1}{2} A (J^{*2} - L^{*2} - S^{*2})$$

$$A = a_3\alpha_3 + a_4\alpha_4$$

Selection rules:

LS coupling

$\Delta S = 0$

$\Delta L = 0, \pm 1$

jj coupling

$\Delta j_1 = 0$

$\Delta j_2 = 0 \pm 1$

$\Delta J = 0, \pm 1 (0 \to 0 X)$

Scanned with CamScanner

Eg: ps electrons.

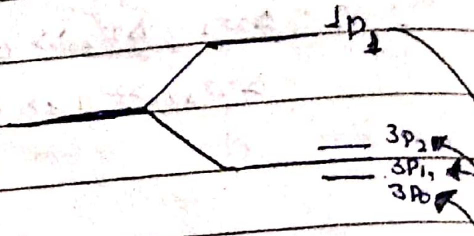
In LS scheme:

$l_1 = 1,\ l_2 = 0$

$L = 1 \Rightarrow P$ term.

$S = 0, 1.$

${}^3P_{0,1,2}$ ${}^1P_1$



jj scheme:

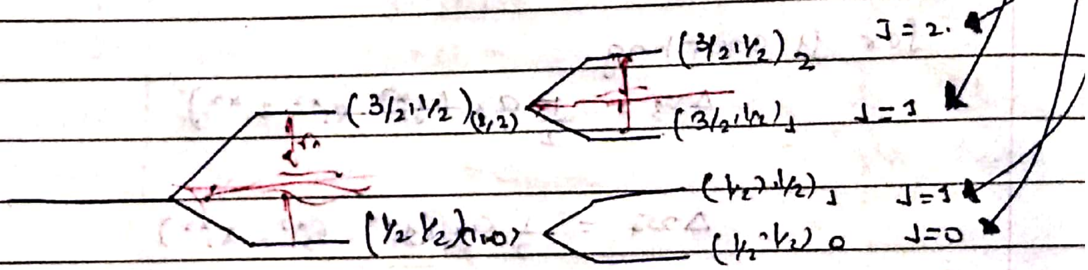
$l_1 = 1,\ l_2 = 0.$

$s_1 = 1/2,\ s_2 = 1/2$

$j_1 = 3/2, 1/2 \longrightarrow$ P electron

$j_2 = 1/2, 1/2 \longrightarrow$ s electron.

$j = 2, 1, 0.$



Total angular momentum remains conserved

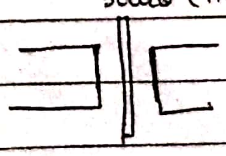
22/08/13

$H' = H_0 + H_1 + H_{SO} + H_B$

↳ hyperfine structure.

Apply magnetic field in presence of magnetic field (weak field)

Source (Na/Cd lamps).

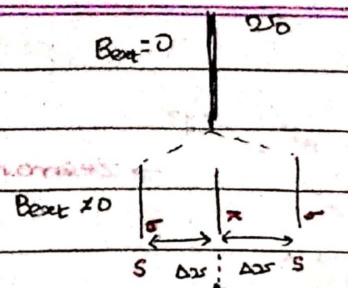


$B_{internal} > B_{ext}$

Zeeman effect.

$B_{ext} = 0$

250



Normal zeeman effect.

p ⟶ plane polarised and polarised along mag. field direction

Normal zeeman effect ≡ - only three components is observed and the three components are proportional to the magnetic field. These lines are polarised.

p-component - parallel comp.

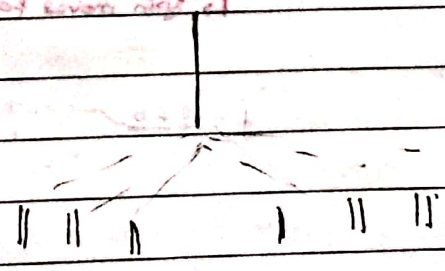
S - " ≡ perpendicular to the direction of magnetic field

- sum of the intensities of lines = intensity without magnetic field
- intensity of the central one = sum of intensities of other two

Observations:

1. $B \neq 0$, the line splits into 3 components.
2. These components are plane polarised such that central component is parallel to $\vec{B}$ and other two in the direction ⊥ to B.
3. Intensity ~~of~~ p = Intensity in the absence of B.

Anamolous



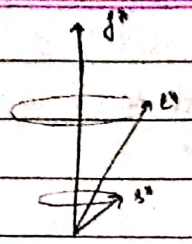
Anamolous zeeman effect

The three components split ~~into~~ in many components.

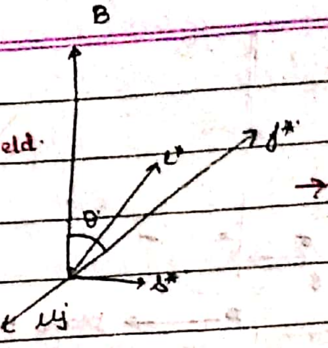
- In case of singlets, S = 0 and it gives rise to normal zeeman effect i.e 3 components.
- In case of Triplet S = 1, spin further interact with magnetic field and split into more lines.

Quantum mechanically,

$H_2 = -\vec{\mu}_B \cdot \vec{B}$ (perturbation due to external magnetic field).



Weak field.

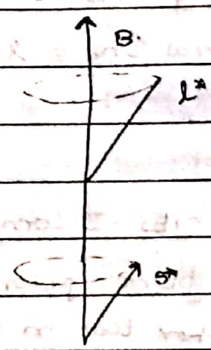


→ zeeman effect

$B_{ext} < B_{int}$ B is small enough not to break the coupling between l^*, s^* and j^* i.e B doesn't interact with l^* and s^*.

$B_{ext} > B_{int}$ Direct coupling b/w l, s and magnetic field takes place and is called Paschen - Back effect.

Strong field



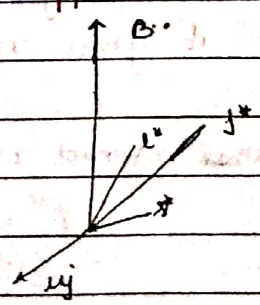
→ Paschen Back effect.

$$\frac{\mu_l}{|l|} = \frac{e}{2mc}, \quad \frac{\mu_s}{|s|} = 2\left(\frac{e}{2mc}\right)$$

↳ spin moves faster than orbital

$$\frac{\mu_j}{|j|} = \frac{e}{2mc}, \quad j = l \pm s$$

Zeeman effect:



$$\frac{\mu_l}{|l|} = \frac{e}{2mc}$$

$$\frac{\mu_s}{|s|} = 2 \cdot \frac{e}{2mc}$$

$$\mu_l = l^* \frac{h}{2\pi}\left(\frac{e}{2mc}\right)$$

$$= \sqrt{l(l+1)}\ \hbar \left(e/2mc\right)$$

$$\mu_s = 2 s^* \frac{h}{2\pi}\left(\frac{e}{2mc}\right)$$

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Projection on j^*

$$\mu_l = l^* \frac{h}{2\pi}\left(\frac{e}{2mc}\right) \cos(l^* j^*)$$

{ Angle between l^* & s^* and j^* doesnot change :) θ doesnot change and here effect of mag. field is only to process } }..

$$\mu_s = 2 s^* \frac{h}{2\pi}\left(\frac{e}{2mc}\right) \cos(s^*, j^*)$$

$$\mu_j = \left[l^* \cos(l^* j^*) + 2 s^* \cos(s^* j^*)\right] \frac{h}{2\pi} \left(\frac{e}{2mc}\right)$$

$$\therefore \mu_j = g\, j^* \underbrace{\left(\frac{h}{2\pi}\frac{e}{2mc}\right)}_{\text{Bohr magneton}}$$

↓ Lande g-factor (constant b/w 1-2)
↳ strength of interaction

$$g \cdot j^* = \left[l^* \cos(l^* \cdot j^*) + 2 s^* \cos(s^* j^*)\right]$$

$$s^{*2} = l^{*2} + j^{*2} - 2 l^* j^* \cos(l^* j^*)$$

$$l^* \cos(l^* s^*) = \frac{j^{*2} + l^{*2} - s^{*2}}{2 j^*}$$

$$s^* \cos(s^* j^*) = \frac{j^{*2} + s^{*2} - l^{*2}}{2 j^*}$$

$$g = 1 + \frac{j^{*2} + s^{*2} - l^{*2}}{2 j^{*2}}$$

$$= 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2 (j)(j+1)}.$$

s term, $l = 0$, $j = s$. so, it has a g-factor of 2.

g-factor gives the strength of coupling with the external magnetic field

Magnetic Interaction energy:

$$\Delta W = \omega_L\, j^* \frac{h}{2\pi} \cos(j \cdot B).$$

$$= \omega_L\, \mu_j$$

Se'lection rule for zeeman effect of 2e systems are:

Viewed ⊥ to the field; $\Delta M \pm 1$: Plane Pol. ⊥ to H → s comp
ΔM 0 : ∥ , ∥ to H → p comp

Viewed ∥ to the field; $\Delta M = \pm 1$ Circularly Pol. s comp
$\Delta M = 0$ forbidden p comp

or $$\Delta W = B g \frac{e}{2mc} j^* \frac{h}{2\pi} \cos(j^* B)$$

ω_L is the Larmour precession frequency of j^* around B.

$$\omega_L = g B \left(\frac{e}{2mc}\right)$$

Interaction energy:

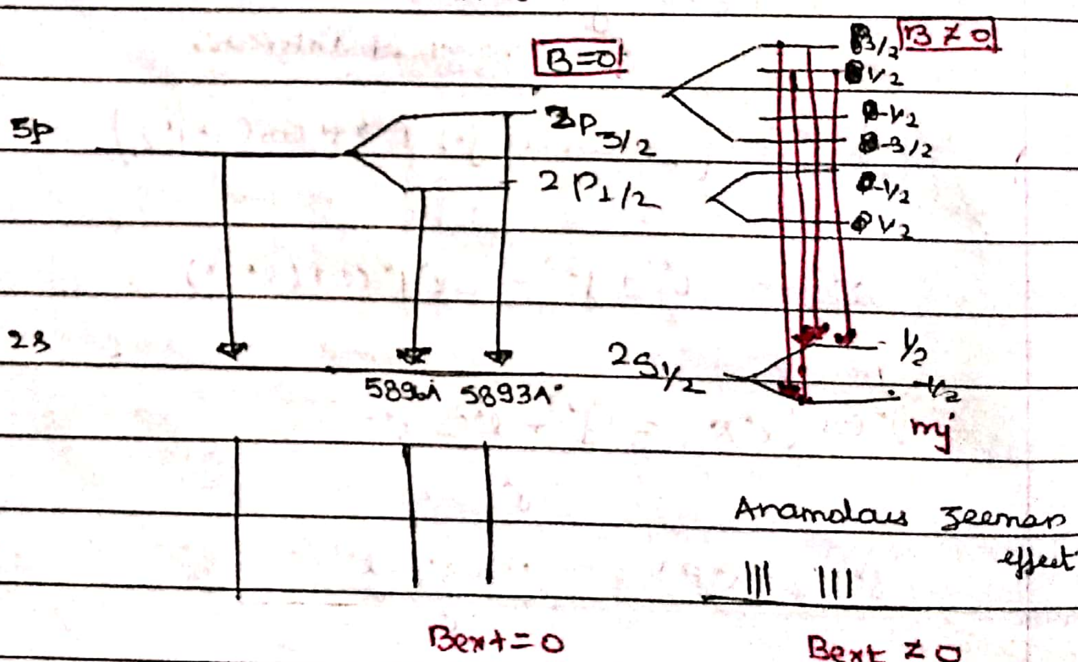
$$\Delta\nu_B = \frac{\Delta W}{hc} = B\cdot g \cdot \underbrace{\boxed{\left(\frac{e}{4\pi mc^2}\right)}}_{L} m_j$$

m_j = magnetic quantum number.

$$\Delta\nu_B = B g m_j L.$$

$\hookrightarrow L = \frac{e}{4\pi mc^2}$ = Larmour unit

Na Doublet:



Selection rule:

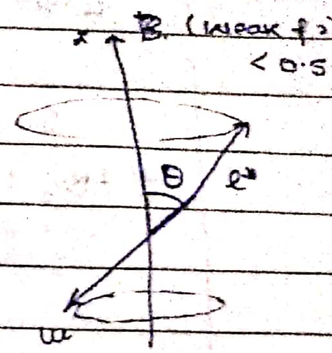
$$\Delta l = \pm 1, \quad \Delta j = 0, \pm 1, \quad \Delta m_j = 0, \pm 1, \cdots$$

The zeeman splitting

$$\boxed{\Delta\nu = B\cdot g\cdot m}$$

3 components — Normal (does not consider spin).

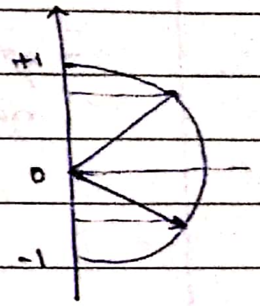
Singlet $\boxed{S=0}$ $\uparrow\downarrow$



$$\frac{|\mu|}{|l^*|} = \frac{e}{2mc}$$

$$\omega_l = \frac{|\mu|}{|l^*|} B$$

$$= \frac{e}{2mc} B.$$



$$\Delta E = \omega_l l_z$$

$$= \left(\frac{e}{2mc} B\right) l_z$$

$$= \left(\frac{e}{2mc} B\right) \sqrt{l(l+1)} \frac{h}{2\pi}$$

$m_l = -l \cdots +l$

↳ magnetic quantum ~~associated with~~ motion

Interaction energy:

$$\Delta E = \left(\frac{eh}{4\pi mc}\right) B m_l$$

Wave number:

$$\Delta\bar{\nu} = \frac{\Delta E}{hc} = \left(\frac{e}{4\pi mc^2}\right) B m_l.$$

$$= \left(\frac{eB}{4\pi mc^2}\right) m_l.$$

$$= m_l L'$$ where L': Lorentz unit

where $L' = 4.67 \times 10^{-5} B.$

m_l only differs by unity,

$$\Delta\bar{\nu}_1 - \Delta\bar{\nu}_2 = L'.$$

Separation between two consecutive terms is same and is e…
L'.

Two electron Atom:

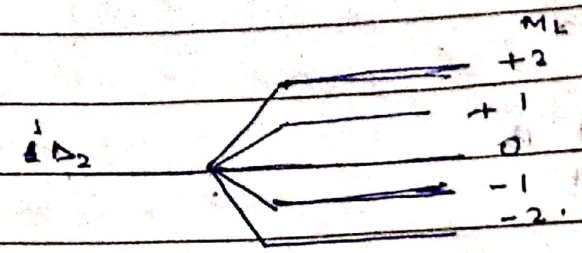
$$\Delta E = \left(\frac{ehB}{4\pi mc}\right) M_L$$

$\Delta\nu = \left(\frac{eB}{4\pi mc^2}\right) M_L$ where $M_L = -L \ldots +L$

& $L = |l_1 - l_2| \ldots |l_1 + l_2|$.

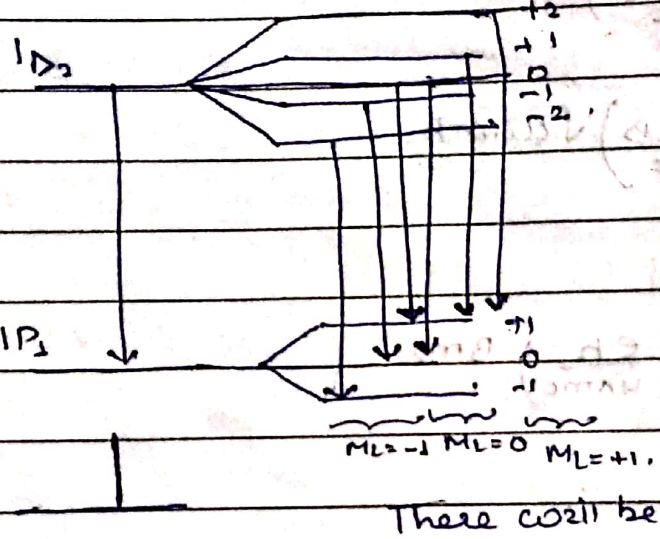
$S = 0$ spins are opposite.

Eg: $^1D_2$:

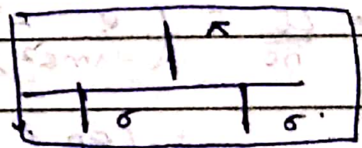


$L = 2,\ M_L = -2, -1, 0, 1, 2$

- separation b/w the levels is equal since we have neglected the spin.



There will be total 9 transitions

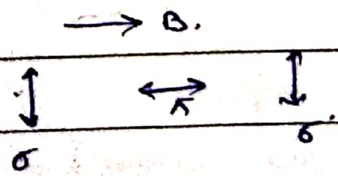


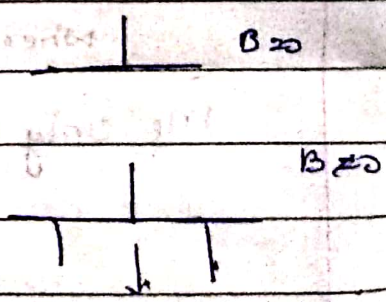
Selection rule:

$M_L = \pm 1 \equiv 6$ transitions

$M_L = 0 \equiv 3$ "

$M_L = 0 \equiv \pi$, $M_L = \pm 1$ σ.



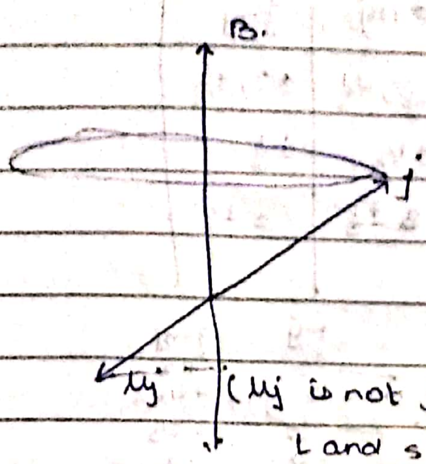


Parally polarised
It corresponds to no change.

Anamolous zeeman effect :

(does not neglect spin)

In presence of B (weak).   absence of B.



(μ_j is not parallel to J because precessional frequency of L and S are not same i.e. $\omega_S = 2\omega_L$).

$\therefore \frac{|\mu_j|}{|j|} = \frac{e}{2mc}$.

Interaction energy :

$\Delta E_j = \omega_j j_z$.

$= \left(\frac{e}{2mc} B\right) \frac{m_j h}{2\pi}$ where $m_j = -j \dots +j$

Degeneracy $(2j+1)$

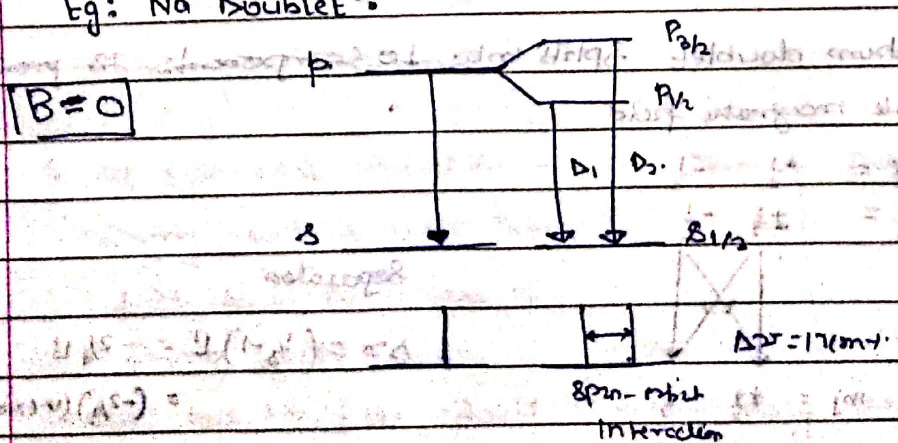
In terms of wave number

$\boxed{\Delta \nu = g m_j L'}$ Where $g = 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}$.

s-level : $l = 0$. $g = 2$.

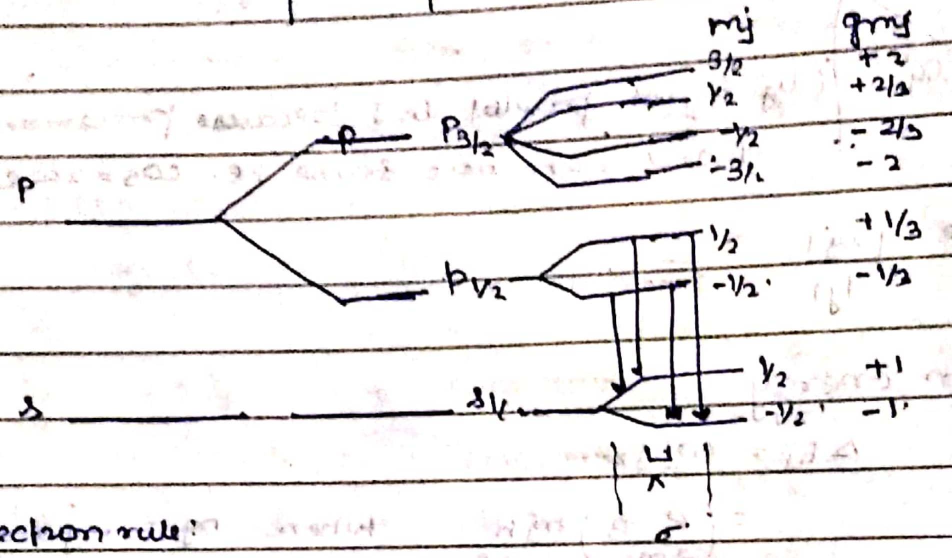
Anamolous effect : g : Lande g-factor split the levels by different amounts.

Eg: Na Doublet :



$B \neq 0$:

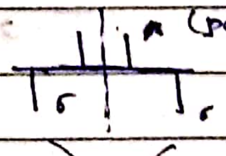
Terms	$(2J+1)$	g	m_j	$g m_j$
$P_{3/2}$	4	$\frac{4}{3}$	$\pm\frac{3}{2}, \pm\frac{1}{2}$	$\pm 2, \pm\frac{2}{3}$
$P_{1/2}$	2	$\frac{2}{3}$	$\pm 1/2$	$\pm\frac{1}{3}$
$S_{1/2}$	2	2	$\pm\frac{1}{2}$	± 1



Section rule:

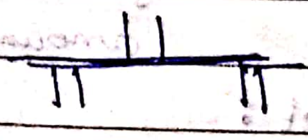
$\Delta m_j = 0$
$\Delta m_j = \pm 1$ } $\Delta J = 0$ is not allowed

D_1:



4-transitions

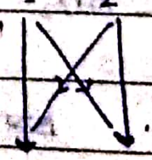
D_2: 6 components



The Sodium doublet splits into 10 components in presence of weak magnetic field

$g m_j$ = $+\frac{1}{3}$ $-\frac{1}{3}$

Upper level: m_j = $+\frac{1}{2}$ $-\frac{1}{2}$



Lower level: m_j = $+\frac{1}{2}$ $-\frac{1}{2}$

$g m_j$ = $+1$ -1

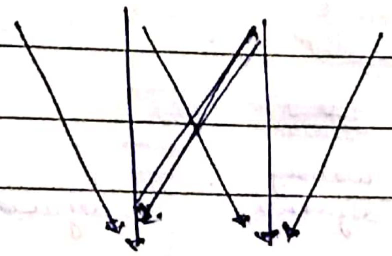
Separation:

$\Delta\nu = \left(\frac{1}{3} - 1\right) L' = -\frac{2}{3} L'$

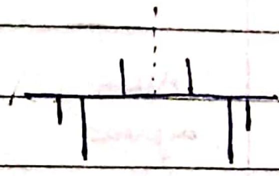
$= \left(-\frac{2}{3}\right)(4.6 \times 10^{-5}) B$

Where B = gauss

$l>2$: m_j $+\frac{3}{2}$ $+\frac{1}{2}$ $-\frac{1}{2}$ $-\frac{3}{2}$

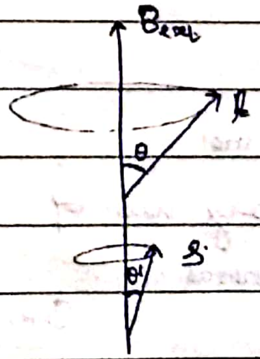


m_j $\frac{1}{2}$ $-\frac{1}{2}$



STRONG FIELD EFFECT: (Paschen Back effect)

(When applied field Becomes stronger than internal magnetic field $B_e > B_{int}$)



Angle b/w l and B_{ext} & s and B_{ext} is constant but b/w l and s is not constant.

$$\omega_l = \left(\frac{e}{2mc}\right)B$$

$$\omega_s = 2\left(\frac{e}{2mc}\right)B$$

In strong field,

$$\Delta E = (\Delta E_l + \Delta E_s)$$

$$= g(m_l + 2m_s)L'$$

$m = m_l + 2m_s$

$$\therefore \Delta E = gmL'$$

Degeneracy : $(2l+1)(2s+1)$