

orbital motion of e^-

$$I = q/T$$

$$T = \frac{2\pi r}{v}, L = mvr$$

$$\vec{\mu}_L = -\frac{e v r}{2}$$

$$\vec{\mu}_L = -\left(\frac{e}{2m}\right) \vec{L}$$

$$\frac{\vec{\mu}_L}{\vec{L}} = \text{constant}$$

$$\therefore \vec{L} = \sqrt{J(J+1)} \hbar$$

$$\mu_L = -\left(\frac{e}{2m}\right) \sqrt{J(J+1)} \hbar$$

$$\mu_L = -\left(\frac{e \hbar}{2m}\right) \sqrt{J(J+1)}$$

$$\mu_L = -\mu_B \sqrt{J(J+1)}$$

Where μ_B is called Bohr magneton.

$$\mu_B = 9.27 \times 10^{-24} \text{ A}\cdot\text{m}^2$$

Z-Component

$$\vec{\mu}_z = -\left(\frac{e}{2m}\right) \vec{L}_z$$

$$\vec{\mu}_z = -\left(\frac{\mu_B}{\hbar}\right) \vec{L}_z$$

$$\vec{\mu}_L = -g_L \left(\frac{\mu_B}{\hbar}\right) \vec{L}$$

vector atom model:-

$$\vec{J} = \vec{L} + \vec{S}$$

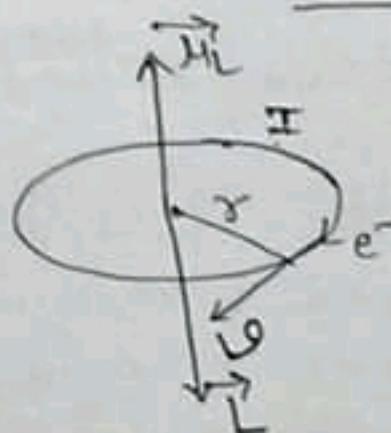
$$J^2 = J(J+1) \hbar^2$$

$$J_z = m_j \hbar$$

$$-j \leq m_j \leq j$$

$$j = |l+s| \text{ to } |l-s|$$

Short notes



$$\boxed{\vec{\mu}_L = -\left(\frac{e}{2m}\right) \vec{L}}$$

Where $\left(\frac{e}{2m}\right)$ is called gyro magnetic ratio

$$\vec{\mu}_L = -g_L \left(\frac{e}{2m}\right) \vec{L}$$

Where $g_L \rightarrow$ Lande factor

for orbital motion of e^- $g_L \rightarrow 1$

NOTE:-

$$\omega = \frac{eB}{2m}$$

$$\boxed{f = \frac{eB}{4\pi m}}$$

Larmor frequency

space quantization:-

$$L_z = L \cos \theta$$

$$\therefore L_z = m_l \hbar \text{ and } L = \sqrt{J(J+1)} \hbar$$

$$\cos \theta = \frac{L_z}{L} = \frac{m_l}{\sqrt{J(J+1)}}$$

$$\theta = \cos^{-1} \left[\frac{m_l}{\sqrt{J(J+1)}} \right]$$

because direction of angular momentum is also fixed.

\Rightarrow electron spin:-

s.g. experiment (concept)

$$\vec{S} = \sqrt{S(S+1)} \hbar$$

$$\vec{\mu}_s = -\left(\frac{e}{2m}\right) \vec{S}$$

$$S_z = m_s \hbar$$

$$\vec{\mu}_s = -g_s \left(\frac{\mu_B}{\hbar}\right) \vec{S}$$

$$g_s \rightarrow 2$$

Z-Component

$$\vec{\mu}_z = -2 \left(\frac{e}{2m}\right) \vec{S}_z$$

$$\mu_z = -2 \frac{\mu_B m_s}{\hbar}$$

$$s = 1/2, m_s = \pm 1/2$$

$$\boxed{(\mu_s)_z = \mp \mu_B}$$

spectroscopy term and their notation := $[n^{2s+1} L_j]$

L-S Coupling:-

NOTE (1) for completely filled

$$S = |s_1 + s_2| \text{ to } |s_1 - s_2|$$

$$L = |l_1 + l_2| \text{ to } |l_1 - l_2|$$

$$j = |l + s| \text{ to } |l - s|$$

$$L=0, \sum m_L=0$$

$$S=0, \sum m_S=0$$

$$L=0, S=0, j=0$$

$$\text{term } 2s+1 L_j \Rightarrow 1s_0$$

NOTE (2)

degeneracy $\sum_{j=|l-s|}^{j=|l+s|} (2j+1) = (2s+1)(2l+1)$

non-equivalent e⁻ Configuration:- $(n's)(n'l's)$
the value of n, n' is different

⇒ equivalent e⁻ Configuration:- $(n's)(n's)$
the value of n, n' is same.

Noto

$S \Rightarrow$ spin quantum number

$S \Rightarrow$ spin Angular momentum

$L =$ orbital Angular momentum

$l \Rightarrow$ azimuthal quantum number

$J \Rightarrow$ Total Angular momentum

$j \Rightarrow$ Angular momentum quantum number

$$S=1, m_S = 2s+1$$

$$L=1, m_L = 2l+1$$

$$j=1, m_j = 2j+1$$

$$\vec{S}_z = m_S \hbar$$

$$\vec{L}_z = m_L \hbar$$

$$\vec{J}_z = m_j \hbar$$

$$\vec{J} = \vec{L} + \vec{S}$$

$$S = \sqrt{S(S+1)} \hbar$$

$$J = \sqrt{J(J+1)} \hbar$$

$$L = \sqrt{L(L+1)} \hbar$$

$$-S \leq m_S \leq +S$$

$$-j \leq m_j \leq +j$$

$$-l \leq m_L \leq +l$$

NOTE: \Rightarrow Configuration $(n\ell)^q$ is same $(n\ell)^{x-q}$ where x is the max. number of e^- $x = 2(2\ell+1)$

\Rightarrow terms of equivalent: \Rightarrow

<u>Configuration</u>	<u>Terms</u>
s^1	$2s_{1/2}$
s^2, p^6, d^{10}	$1s_0$
p^2, p^4	$1s_0, 3p_{0,1,2}, 1d_2$
p^1, p^5	$2p_{1/2, 3/2}$
p^3	$2p_{1/2, 3/2}, 4s_{3/2}, 2d_{3/2, 5/2}$
d^2, d^8	$1s_0, 1d_2, 3p_{0,1,2}, 3f_{4,3,2}, 1g_8$

\Rightarrow Hund Rule: \Rightarrow

- largest multiplicity lies lowest
- multiplicity same, then largest ℓ lies lowest.
- if both are same, then less than $1/2$ filled, lowest j lies lowest
- if more than $1/2$ Half Filled, highest j lies lowest.
- if subcells are $1/2$ filled, then-

For $s-1/2$ Filled $\rightarrow 2s_{1/2}$; for $p-1/2$ Filled $\rightarrow 4s_{3/2}$

for $d-1/2$ Filled $\rightarrow 6s_{5/2}$; for $d-1/2$ Filled $\rightarrow 8s_{7/2}$

\Rightarrow Lande Interval Rule: \Rightarrow

$$E = a[\vec{L} \cdot \vec{S}] \because \vec{J} = \vec{L} + \vec{S}$$

$$E = \frac{a\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)] \quad \text{if } l \text{ and } s \text{ have same values.}$$

$$j \rightarrow j+1$$

$$\Delta E = E_{j+1} - E_j$$

$$\Delta E = E_{j+1} - E_j$$

$$\Delta E = \frac{a\hbar^2}{2} [(j+1)(j+2) - j(j+1)]$$

$$\Delta E \propto (j+1)$$

$\Rightarrow j-j$ Coupling \Rightarrow Degeneracy $\Rightarrow (2j+1)$

(1) non-equivalent e^- possible j
 $H = H_0 + H_2$
 and H_1 as perturb
 $j = |j_1 + j_2|$ to $|j_1 - j_2|$

$\vec{J} = \vec{L} + \vec{S}$

$$\vec{J}_i = \vec{L}_i + \vec{S}_i$$

$$\sum_i \vec{J}_i = \vec{J}_1 + \vec{J}_2 + \dots$$

(2) for equivalent e^- configuration-

if $j_1 \neq j_2$ then $j = |j_1 + j_2|$ to $|j_1 - j_2|$

(3) $j_1 = j_2 = j$ then possible value of

$$j = (2j-1)(2j-3)(2j-5) \dots j \geq 0$$

$$\text{Represent} = (j_1, j_2)_j$$

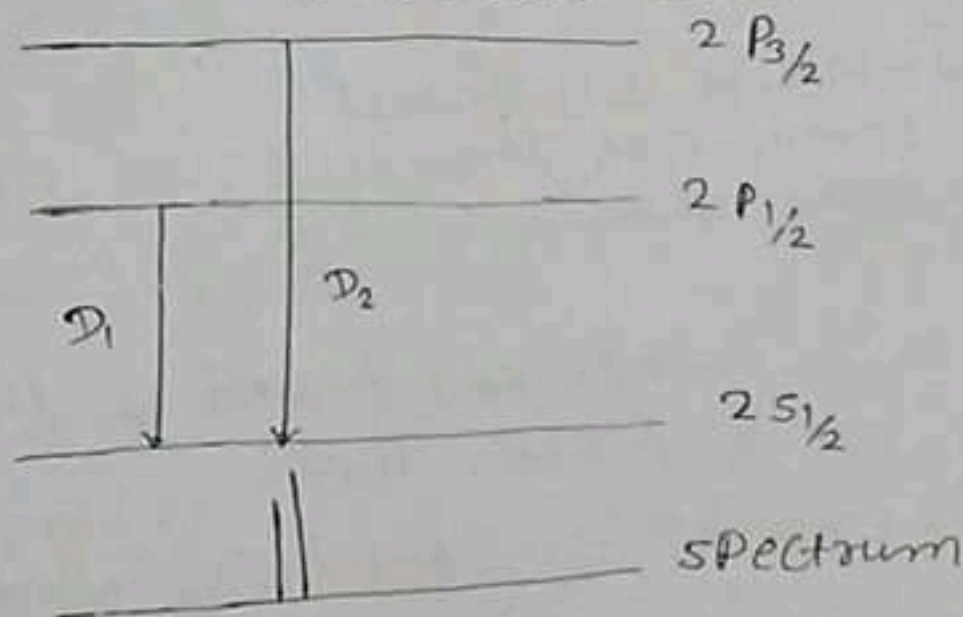
$\Rightarrow Na$ spectrum \Rightarrow

$$11Na = 1s^2, 2s^2, 2p^6, 3s^1$$

ground state $\rightarrow 3s^1 \Rightarrow 2s_{1/2}$

excited state $\rightarrow 3p^1 \Rightarrow 2p_{1/2, 3/2}$

selection Rule $\Rightarrow \Delta j = 0, \pm 1$; $\Delta l = \pm 1$, $\Delta s = 0$



\Rightarrow Intensity Ratio Rule \Rightarrow

(1) j and l changes in same ways

(2) if there is one such lies in one doublet then largest j values is strongest.

(3) sum of intensity those line comes from common initially level is proportional to quantum wave factor $(2j+1)$ of that line and similarly end on a common level.

In sodium spectrum:-

$$I_{D_1} \propto (2J_1 + 1); I_{D_2} \propto (2J_2 + 1)$$

$$\Rightarrow \frac{I_{D_2}}{I_{D_1}} = \frac{2 \times \frac{3}{2} + 1}{2 \times \frac{1}{2} + 1} = \frac{4}{2} = \frac{2}{1}$$

$$I_{D_2} : I_{D_1} = 2 : 1$$

\Rightarrow Hyperfine structure \Rightarrow Finer than Fine that is called Hyperfine structure

\Rightarrow Magnetic Interaction \Rightarrow

magnetic moment of nucleus-

$$\vec{\mu} = g_N \left[\frac{\mu_N}{\hbar} \right] \vec{I}$$

$$\Rightarrow \mu_B = \frac{e\hbar}{2m_e}$$

$$\mu_N = \frac{e\hbar}{2m_p} \text{ nuclear magneton } \text{Now } \frac{\mu_N}{\mu_B} = \frac{m_e}{1836m_e}$$

$$\Rightarrow \boxed{\mu_N = \frac{\mu_B}{1836}}$$

\Rightarrow Interaction of nuclear spin with Angular momentum

$$E = A(\vec{I} \cdot \vec{J})$$

$$\vec{I} \cdot \vec{J} = \frac{1}{2} [F^2 - I^2 - J^2]$$

$$\vec{F} = \vec{I} + \vec{J} \Rightarrow E = \frac{Ah^2}{2} [F(F+1) - I(I+1) - J(J+1)]$$

degeneracy $(2F+1)$

(ii) Interval Rule- $\Delta E \propto (F+1)$ \Rightarrow selection Rule $\Delta f = 0, \pm 1$

$$\Delta E = E_{F+1} - E_F$$

(iii) Possible values of $F \rightarrow |I+J|$ to $|I-J|$

(iv) Intensity $\propto (2F+1)$

\Rightarrow Zeeman effect \Rightarrow splitting of spectral lines in the presence of external magnetic field i.e. is known as Zeeman effect

Two types of Zeeman effect:-

(1) Normal Zeeman -

(2) Abnormal Zeeman -

(1) Normal Zeeman effect \Rightarrow spectral line split into three spectral lines, Zeeman effect does not include spin of e^- split up to three equal spaces line.

magnetic moment - $\vec{\mu}_L = -(\frac{\mu_B}{\hbar}) \vec{L}$
 now energy correction due to external magnetic field -

$$\Delta \vec{E} = -\vec{\mu}_L \cdot \vec{B}$$

$$\Delta E = -\mu_L B \cos \theta \Rightarrow \Delta E = \left(\frac{\mu_B}{\hbar}\right) L \cos \theta$$

$$\Rightarrow \boxed{\Delta E = m_L (\mu_B B)}$$

Now $E_i = E_{0i} + \Delta E_i$ and $E_f = E_{0f} + \Delta E_f$

$$\therefore \Delta E_i = m_{Li} (\mu_B B) \text{ and } \Delta E_f = m_{Lf} (\mu_B B)$$

for transition -

$$h\nu = E_f - E_i \Rightarrow \nu = \frac{(E_{0f} - E_{0i})}{h} + (m_{Lf} - m_{Li}) \left(\frac{\mu_B B}{h}\right)$$

$$\nu = \nu_0 + \Delta m_L \left(\frac{\mu_B B}{h}\right)$$

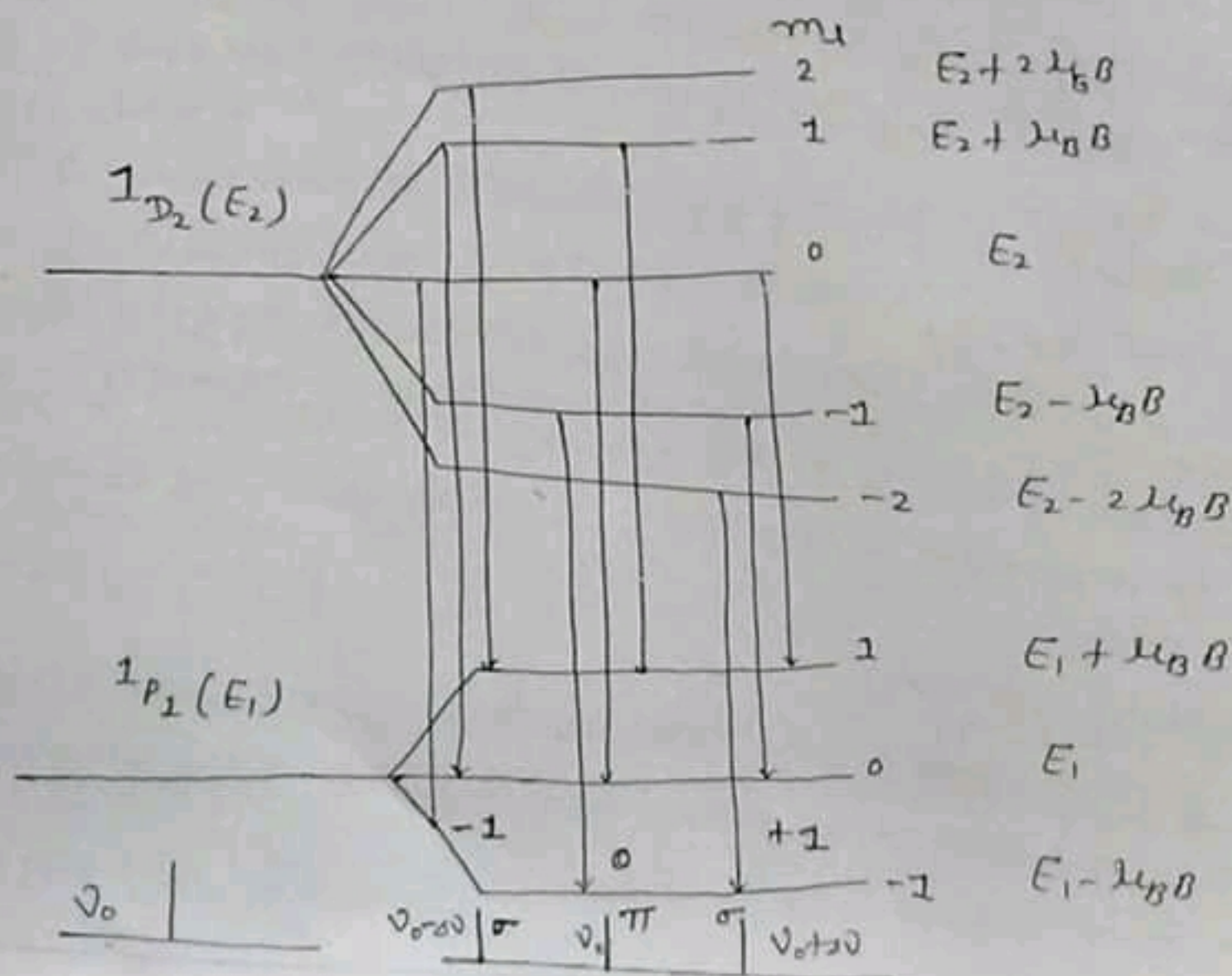
$$\nu = \nu_0 + \Delta m_L \left(\frac{e\hbar}{2m} \cdot \frac{B}{\hbar}\right)$$

$$\boxed{\nu = \nu_0 + \Delta m_L (\Delta \nu)} \text{ where } \Delta \nu = \frac{eB}{4\pi m} \text{ (zeeman shift)}$$

Selection Rule $\Delta m_L = 0, \pm 1$

$$\nu = \nu_0 - \Delta \nu, \nu_0, \nu_0 + \Delta \nu$$

Example: $1D_2 \rightarrow 1P_1$



$m_l = 0$; spectral line parallel to field. (TI-Component)
 $m_l = \pm 1$; spectral line perpendicular to field (σ -Component)
 $\pi \rightarrow$ plane polarised and $\sigma^- \rightarrow$ left circular polarised,
 $\sigma^+ \rightarrow$ right circular polarised.

(2) abnormal Zeeman effect \Rightarrow

splitting of spectral lines in more than three lines.
 (i) including spin of e^- (ii) transition occurs b/w
 multipoles also (iii) spectral lines are unequal spaced

magnetic moment - $\mu_j = -g_j \left(\frac{\mu_B}{\hbar} \right) \vec{J}$

Interaction energy $\Delta E = -\vec{\mu}_j \cdot \vec{B}$

$$\Delta E = -\mu_j B \cos \theta$$

$$\Delta E = g_j \left(\frac{\mu_B}{\hbar} \right) B J \cos \theta \Rightarrow \boxed{\Delta E = g_j m_j (\mu_B B)}$$

Zeeman shift \Rightarrow

$$\Delta \nu = \boxed{(g_f m_{jf} - g_i m_{ji}) \left(\frac{\mu_B B}{h} \right)}$$

Examples - D_1 and D_2 lines -

$$D_1 = 2P_{1/2} \rightarrow 2S_{1/2}, D_2 = 2P_{3/2} \rightarrow 2S_{1/2}$$

(1) $2S_{1/2}$, $s = 1/2$, $j = 1/2$, $l = 0$

$$g_j = \left[1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right]$$

$$g_j = 2, j = 1/2, m_j = \frac{1}{2}, -\frac{1}{2} \Rightarrow -\mu_B B, \mu_B B$$

(2) $2P_{1/2}$, $j = 1/2$, $s = 1/2$, $l = 1$

$$g_j = 2/3, j = 1/2, m_j = \frac{1}{2}, -\frac{1}{2} \Rightarrow -\frac{1}{3}(\mu_B B), \frac{1}{3}(\mu_B B)$$

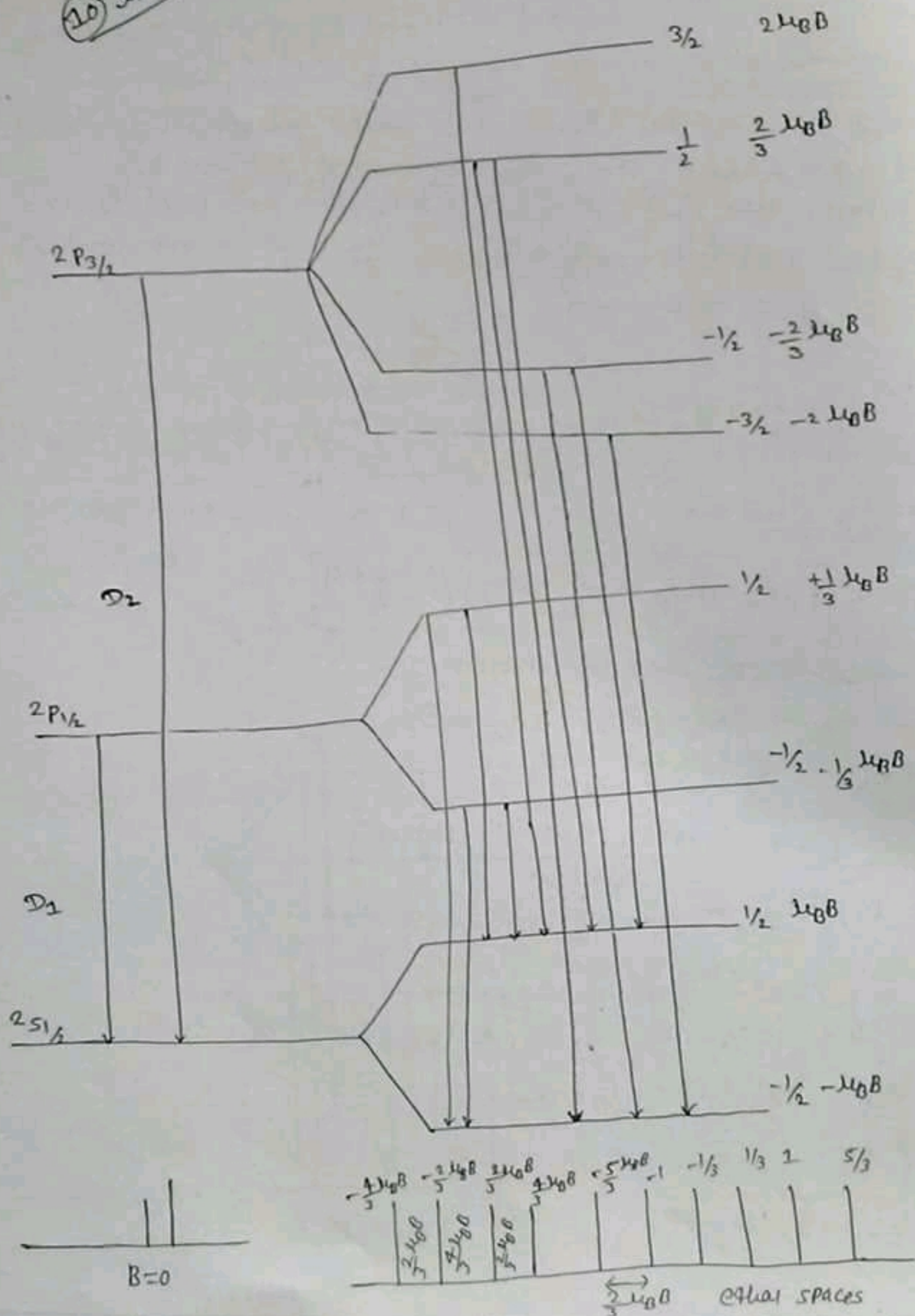
(3) $2P_{3/2}$, $j = 3/2$, $s = 1/2$, $l = 1$

$$g_j = 4/3; j = 3/2, m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$$

$$-2\mu_B B, -\frac{2}{3}\mu_B B, \frac{2}{3}\mu_B B, 2\mu_B B$$

$\Delta m_j = 0, \pm 1$ selection rule :-
(Weak Field)

⑩ lines



PSE-5

→ Paschen back effect:

strong magnetic field, L-S coupling break then total magnetic momentum is sum of \vec{L} and \vec{S} magnetic momentum. $\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S$

where $\vec{\mu}_L = -\left(\frac{\mu_B}{\hbar}\right)\vec{L}$; $\vec{\mu}_S = -2\left(\frac{\mu_B}{\hbar}\right)\vec{S}$

$$\vec{\mu} = -\frac{\mu_B}{\hbar} [\vec{L} + 2\vec{S}]$$

Now energy Interaction $\Delta E = -\vec{\mu} \cdot \vec{B}$

$$\Delta E = \frac{\mu_B}{\hbar} [\vec{L} + 2\vec{S}] \cdot \vec{B} \Rightarrow \frac{\mu_B}{\hbar} [\vec{L} \cdot \vec{B} + 2\vec{S} \cdot \vec{B}]$$

$$\Delta E = \frac{\mu_B B}{\hbar} [L_z + 2S_z] \Rightarrow \Delta E = \left(\frac{\mu_B B}{\hbar}\right) [m_L \hbar + 2m_S \hbar]$$

$$\Delta E = \mu_B B (m_L + 2m_S) \quad \text{and}$$

$$\Delta J = \left(\frac{\mu_B B}{\hbar}\right) [\Delta m_L + 2\Delta m_S]$$

selection Rule := $\begin{cases} \Delta m_L = 0, \pm 1 \\ \Delta m_S = 0 \end{cases}$

$$D_1 = 2P_{1/2} \rightarrow 2S_{1/2} \quad \text{and} \quad D_2 = 2P_{3/2} \rightarrow 2S_{1/2}$$

$$2S_{1/2}, \quad L=0, \quad J=1/2, \quad S=1/2$$

$$m_L=0, \quad m_S = \frac{1}{2}, -\frac{1}{2}$$

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

$$2P_{3/2} = S=1/2, \quad L=1,$$

$$m_S = \frac{1}{2}, -\frac{1}{2}, \quad m_L = 0, -1, 1$$

Page-6

Hydrogen Spectrum: \Rightarrow

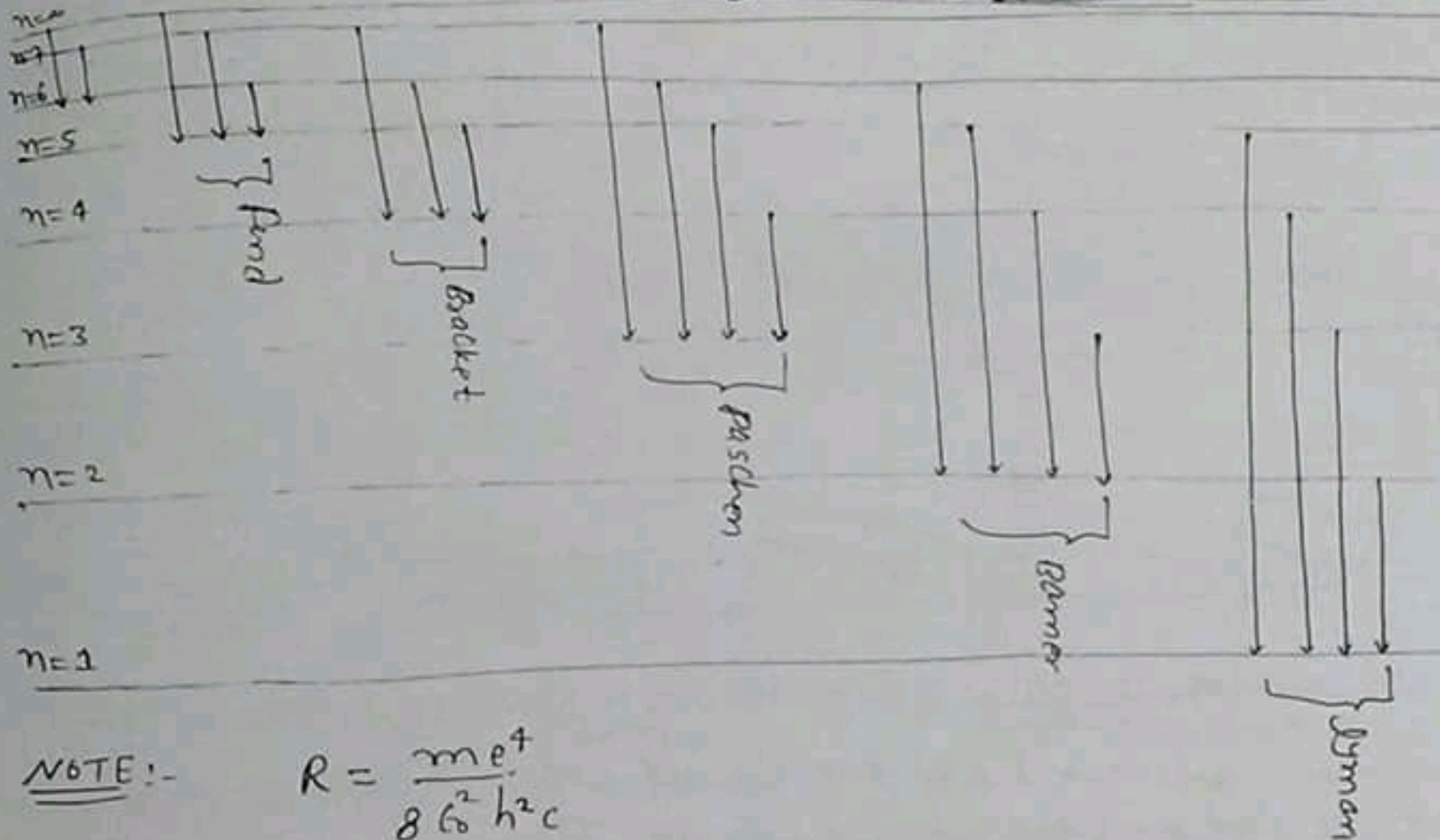
$$E_n = -\frac{13.6 \text{ eV}}{n^2}, n=1, 2, 3, \dots$$

$$\bar{\nu} = RZ^2 \left[\frac{1}{n_i^2} - \frac{1}{n_f^2} \right]$$

\rightarrow Atomic and molecular

- (i) Lyman series $\rightarrow n_i=1, n_f=2, 3, \dots$
- (ii) Balmer series $n_i=2, n_f=3, 4, \dots$
- (iii) Paschen series $n_i=3, n_f=4, 5, \dots$
- (iv) Brackett series $n_i=4, n_f=5, 6, \dots$
- (v) Pfund series $n_i=5, n_f=6, 7, \dots$

\Rightarrow Hydrogen Spectrum



NOTE:- $R = \frac{me^4}{8\epsilon_0^2 h^2 c}$

$R_\infty \propto m$, mass of e^-

$R_M \propto \mu \propto \frac{mM}{m+M}$, $M \rightarrow$ mass of nucleus

$$\frac{R_\infty}{R_M} = 1 + \frac{m}{M}$$

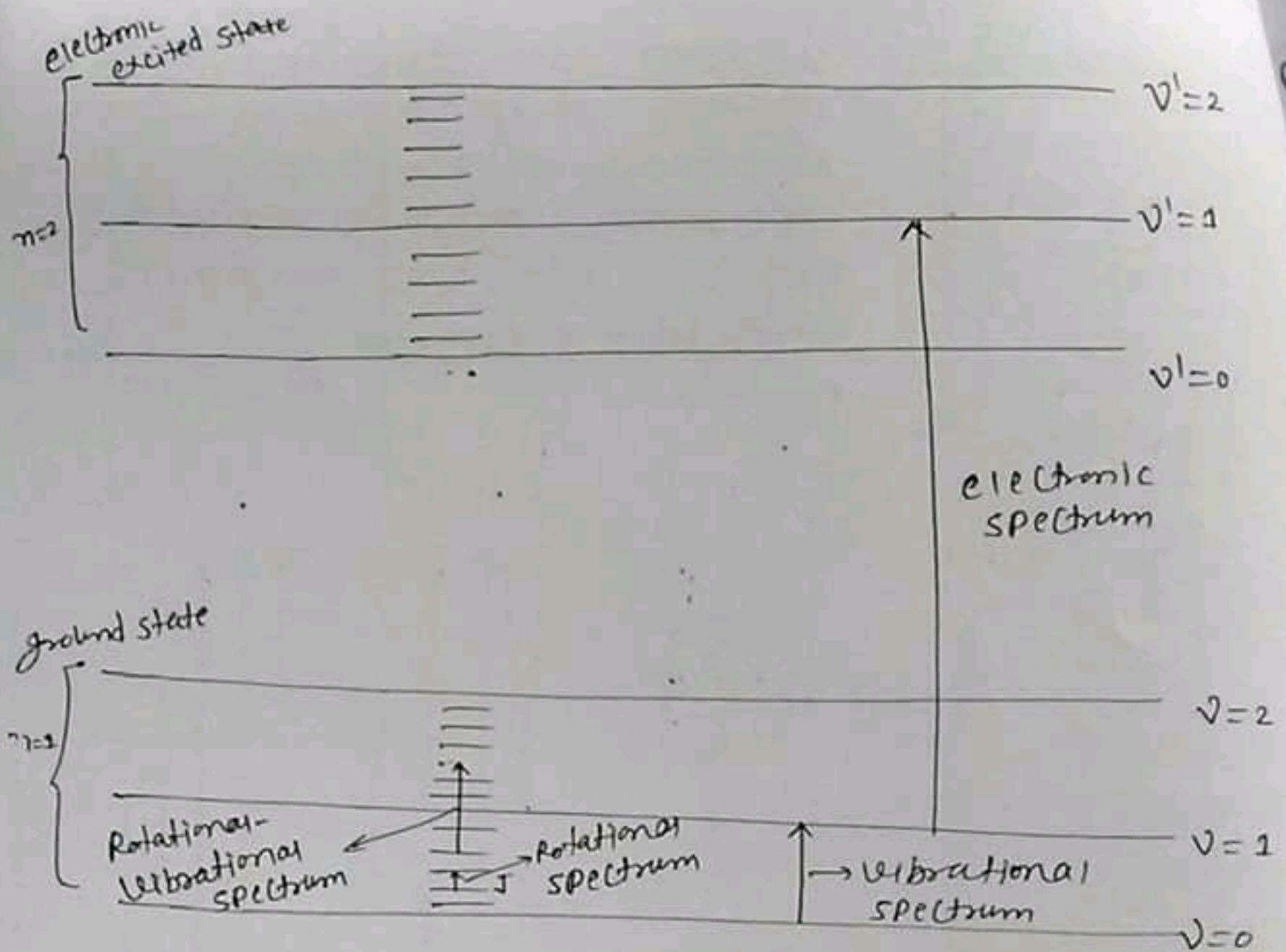
\Rightarrow molecular spectroscopy: \Rightarrow

three types spectrum (EVR)

- (1) electronic spectrum
- (2) vibrational spectrum
- (3) Rotational spectrum

Energy gap: $E > V > R$

10 eV 1 eV 10^{-3} eV
 visible or UV IR (microwave)



⇒ Diatomic molecule: ⇒ ① Homonuclear ② Heteronuclear

① Homo: does not have permanent ^{electric} dipole moment and overlaps -ve and +ve charge centres. $\vec{D} = -e\vec{r}$

$$\langle \psi_i | \vec{D} | \psi_f \rangle = 0$$

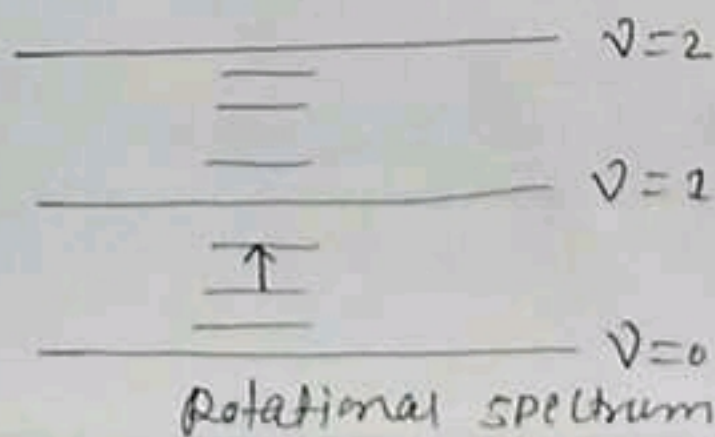
it does not show rotational and vibrational spectrum and only shows electronic spectrum H_2, N_2, O_2

② Hetero: = Permanent dipole moment, -ve and +ve charge centre does not coincide. $\vec{D} = -e\vec{r}$ HCl, NO, HCN

$$\langle \psi_i | \vec{D} | \psi_f \rangle \neq 0$$

it shows rotational and vibrational spectrum.

⇒ Rotational spectrum: = Corresponding to same electronic and vibrational state, but transition b/w rotational levels



Rigid Rotator: \Rightarrow Rigid Rotator means bond length is fix

$$I = \mu r^2 \Rightarrow I = \frac{m_1 m_2 r^2}{m_1 + m_2}$$

Rot energy- $E = \frac{1}{2} I \omega^2 = \frac{J^2}{2I} = \frac{j(j+1) \hbar^2}{2I}$

$$E = \frac{j(j+1) \hbar^2}{2I} \quad \text{then } E_j = \frac{j(j+1) \hbar^2}{2I}, \quad j = 0, 1, 2, 3, \dots$$

so energy levels of rigid rotator is unequal spaced.

$$J = I \omega$$

$$\Rightarrow \sqrt{j(j+1) \hbar} = I \omega \Rightarrow \omega = \sqrt{j(j+1) \frac{\hbar}{2I}}$$

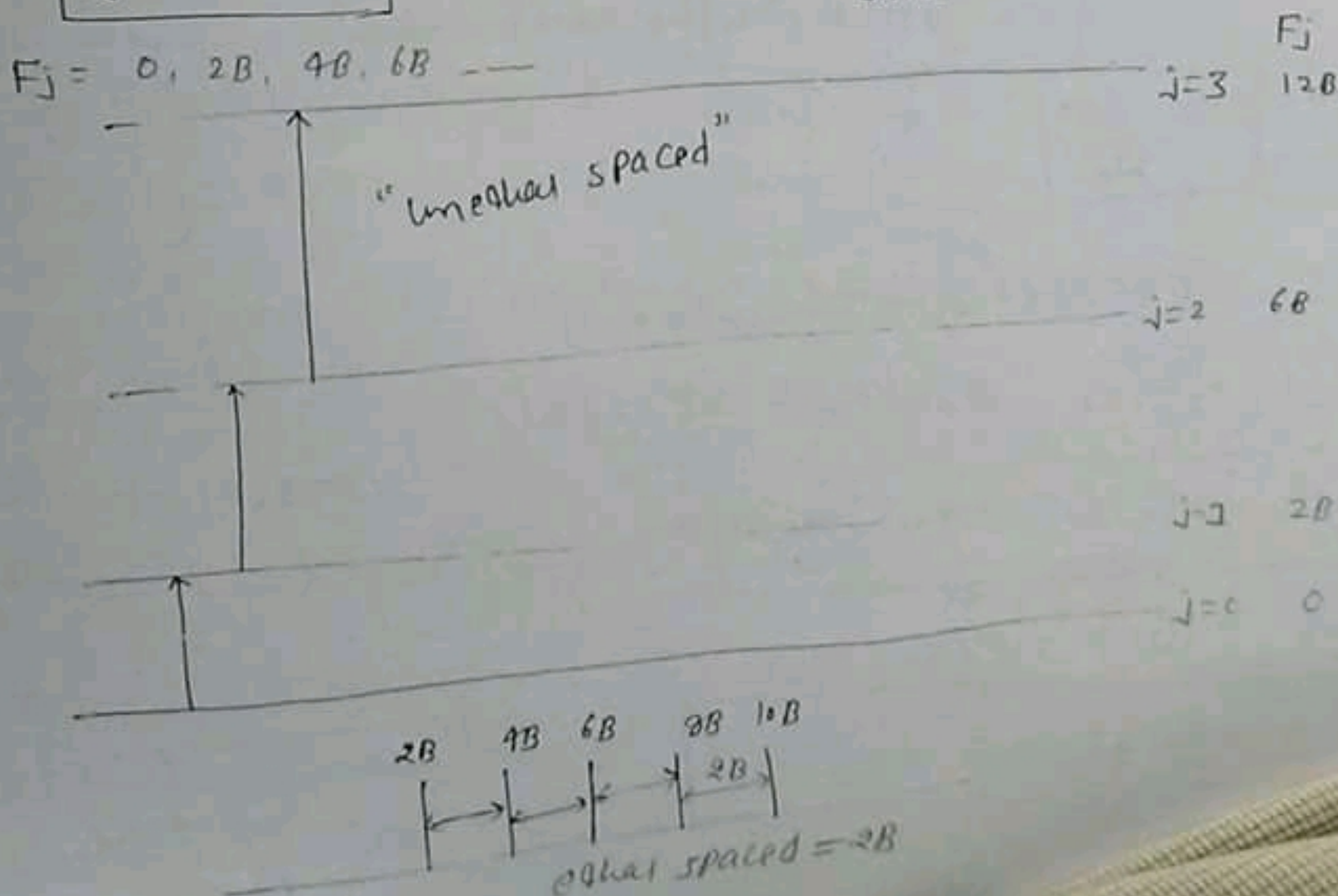
Energy levels diagram: \Rightarrow

$$E_j = \frac{j(j+1) \hbar^2}{2I}$$

$$F_j = \frac{E_j}{hc} = \frac{j(j+1) \hbar^2}{hc \cdot 4\pi^2 I} = \frac{j(j+1) h}{8\pi^2 I c} = \frac{B j(j+1)}{8\pi^2 I c}$$

$$F_j = B j(j+1)$$

Where $B = \frac{h}{8\pi^2 I c}$ cm⁻¹ Rotational Constant



Now $j \rightarrow j+1$

$$\bar{V} = F(j+1) - F(j) = B(j+1)(j+2) - B j(j+1)$$

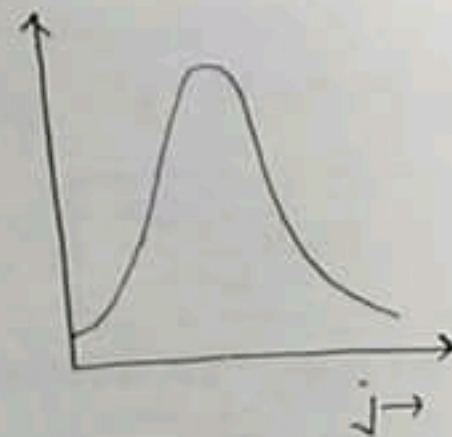
$$\bar{V} = 2B(j+1)$$

NOTE:-

$$N_j = N_0 (2j+1) e^{-(E_j - E_0)/kT} \quad \left(\frac{N_j}{N_0} \right)$$

$$\Rightarrow N_j = N_0 (2j+1) e^{-B j(j+1) hc/kT}$$

$$\frac{dN_j}{dj} = 0 \quad \text{then} \quad j_{\text{max}} = \frac{1}{2} \sqrt{\frac{2kT}{Bhc}} - \frac{1}{2}$$



\Rightarrow Non-Rigid Rotator \Rightarrow (massless spring)

$$E_j = Bhc j(j+1) - (j(j+1))^2 \frac{h^4}{32I^2 \sigma_e^2 k}$$

σ_e = equilibrium

k = spring const

$$E_j = Bhc j(j+1) - Dhc [j(j+1)]^2 \quad \text{where } D = \frac{h^4}{32I^2 \sigma_e^2 k} \cdot \frac{1}{hc}$$

$$D = \frac{h^3}{32I^2 \pi^4 \sigma_e^2 k c}$$

$$\omega = \sqrt{k/\mu} \Rightarrow k = \omega^2 \mu = \mu (2\pi\nu)^2$$

$$k = 4\pi^2 \mu c^2 \omega_e^2 \rightarrow \text{wave number}$$

and $D = \frac{4B^3}{\omega_e^2}$

$$E_j = Bhc j(j+1) - Dhc [j(j+1)]^2$$

$$F_j = \frac{E_j}{hc} = B j(j+1) - D [j(j+1)]^2$$

$$F_j = B j(j+1) - D [j(j+1)]^2$$

$$\bar{V} = F(j+1) - F(j)$$

$$\bar{V} = 2B j(j+1) - 4D (j+1)^3$$

$(D \ll B)$

$j=2$

$j=1$

$j=0$

Rigid
Rotator

Non-Rigid
Rotator

⇒ Diatomic molecule as anharmonic oscillator: ⇒

Potential energy anharmonic oscillator: ⇒

$$V(r) = \frac{\partial^2 V}{\partial r^2} \bigg|_{r=r_0} \left(\frac{r-r_0}{2} \right)^2 + \frac{1}{6} \frac{\partial^3 V}{\partial r^3} \left(\frac{r-r_0}{3} \right)^3 + \dots$$

$$V(r) = f r^2 - g r^3, \quad f \gg g$$

Energy of anharmonic oscillator- ↗ Anharmonicity

$$E(v) = \left(v + \frac{1}{2}\right) h c \omega_e - \left(v + \frac{1}{2}\right)^2 h c \omega_e x_e \rightarrow \text{Anharmonicity Constant}$$

$$G(v) = \frac{E(v)}{h c} = \left(v + \frac{1}{2}\right) \omega_e - \left(v + \frac{1}{2}\right)^2 \omega_e x_e$$

$$G(0) = \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e; \quad v \rightarrow v'$$

$$G(1) = \frac{3}{2} \omega_e - \frac{9}{4} \omega_e x_e \Rightarrow \bar{\nu} = G(v') - G(v)$$

$$\bar{\nu}_{v \rightarrow v'} = \left(v' + \frac{1}{2}\right) \omega_e - \left(v' + \frac{1}{2}\right)^2 \omega_e x_e - \left(v + \frac{1}{2}\right) \omega_e + \left(v + \frac{1}{2}\right)^2 \omega_e x_e$$

$$\boxed{\bar{\nu}_{0 \rightarrow v} = v \omega_e [1 - x_e (1 + v)]}$$

Selection Rule-
 $\Delta v = \pm 1$

$$\bar{\nu}_{0 \rightarrow 1} = \omega_e [1 - 2x_e]$$

First overtone- $\Delta v = \pm 2$

$$\bar{\nu}_{0 \rightarrow 2} = 2 \omega_e [1 - 3x_e]$$

Second overtone- $\Delta v = \pm 3$

$$\bar{\nu}_{0 \rightarrow 3} = 3 \omega_e [1 - 4x_e]$$

⇒ Continuous spectrum and dissociation energy: ⇒

$$D_0 = \sum_{v=0} E(v+1) - E(v)$$

$$D_0 = \sum_{v=0} \frac{E(v+1) - E(v)}{h c} \quad \text{In wave no}$$

Now

$$D_e = D_0 + G(0)$$

$$\boxed{D_e = \frac{\omega_e}{4} \left[\frac{1}{x_e} - x_e \right]}$$

