

Physics - 6

<https://ourstudycircle.in/upscpdf/>

- ① \hat{H} means 'operator H ' i.e. Hamiltonian.
eg. $\hat{P} = -i\hbar \frac{\partial}{\partial x}$

- ② BOSON : Integral spin $s=0, 1, 2, 3, \dots$
eg. Photon, Ground state He atom

FERMION : Half Integral Spin

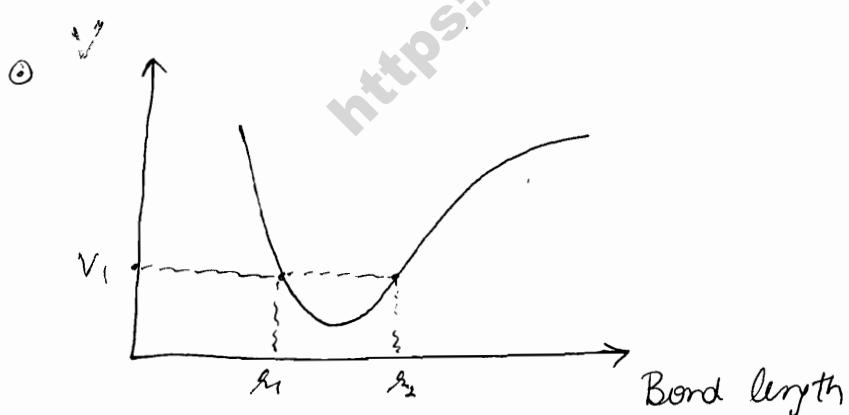
eg. Electron

Proton

Neutron

- ③ $\omega : \frac{1}{\lambda} \Rightarrow E = hc\omega$ and $\gamma = c\omega$

- ④ $\gamma_r = 10^{20} \text{ Hz} \rightarrow \gamma_{x-ray} = 10^{18} \text{ Hz} \rightarrow \gamma_{uv} = 10^{16} \text{ Hz}$
- $\gamma_{radio} = 10^6 \text{ Hz}$
- $I_{MW} = 10^{10} \text{ Hz}$
- $\gamma_{IR} = 10^{12} \text{ Hz}$
- Visible 10^{15} Hz



- ⑥ In deuteron problem,
 $m = \text{reduced mass} = \left(\frac{m_p m_n}{m_p + m_n} \right)$

- ⑦ Value of R_0
 $m_\pi : 1.4 \text{ fm}$

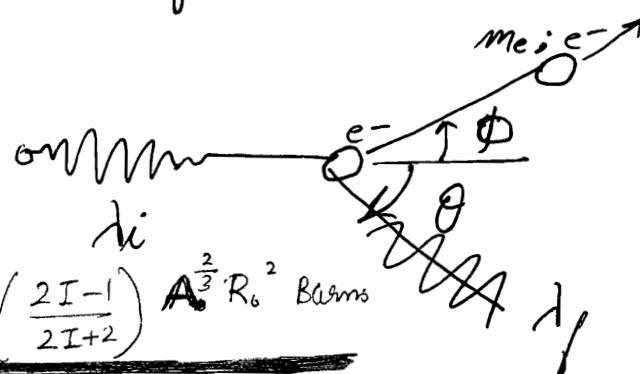
- Fission parameter : 1.5 fm

Note that x component of points on the curve give Bond length. Note that molecule with bond length r_1 and r_2 have same value of Potential Energy V_1 .

- ⑧ Visible light range = 4000 Å - 7000 Å

$$\textcircled{1} \text{ Compton Scattering : } \lambda_f - \lambda_i = \frac{h}{mc^2} [1 - \cos\theta]$$

θ : scattering angle of photon



$$\textcircled{2} Q = \frac{3}{5} \left(\frac{2I-1}{2I+2} \right) A^{\frac{2}{3}} R_b^2 \text{ Barns}$$

$$= \frac{1}{e} \int (3z^2 - r^2) \rho(r) dz$$

NUCLEAR PHYSICS

Lectures	Ch: BT	Ch: Beiser
1, 2, 3	1, 2	11, 12
4	7, 5(b)	
5, 6A	3A	6 of Particle Physics
6B, 7A	3B,	
7B	4, 5(a), 6	

PARTICLE PHYSICS

Lectures	Ch: BT	Ch: Beiser
1, 2, 3	1, 2, 3, 4, 5, 6, 7	13

Atomic Physics

lectures

Chapters
(Raj kumar)

1

1, 2, 3, 4

2, [half of 3]_A

5, 6, 7, 8

[half of 3]_B, [first
page of
4]

9

[rest of 4]

12, 15

Chapter 5 of Bonwell

Molecular Physics

lectures

Chapters

1, 2

17, 18

Chapter 2 of Bonwell

3

19

Chapter 3 of
Bonwell

4

21, 22

Chapter 6

5

20, 23

Chapter 11

↳ Ch - 7, 8, 9 of Bonwell

Atomic Physics

- ✓ Concept of Spin : Stern - Gerlach Experiment ①
- ✓ Fine Structure of Hydrogen atom : Lamb Shift & its significance ①
- ✓ Spectroscopic Notations ; LS & JJ coupling ①
- ✓ Zeeman Effect ①

Molecular Physics

If asked magnetic moment of an atom, take only contribution of electrons
 $\therefore \mu \propto \frac{1}{m}$

- ✓ Elementary idea about rotational , vibrational and electronic spectra of diatomic molecules : ③
 - Frank Condon Principles
- ✓ Raman Effect & Laser Raman Spectroscopy ①
- ✓ Fluorescence & Phosphorescence : 21 cm line of H₂ ①
- ✓ NMR / EPR ①

$$\vec{\mu}_J = -g_J \frac{e}{2m} \vec{J}$$

$$\Delta E = \mu_B B g_J m_J$$

A & M Physics

- Quantum Analysis is the best study of A & M Physics
- No e⁻ occurs in isolation. We need to study via a sample.

similar atoms & Molecules require samples.

✓ Best way to reveal internal structure of nucleus, atom & molecules is spectrum.

Spectral line can be characterized by γ or ω or λ .

Every field of science has its own notations!!

$$\frac{\gamma}{c} = \bar{\omega} = \frac{1}{\lambda_{\text{vacuum}}}$$

* Called wave number, $\bar{\omega}$

= no. of waves per metre or centimetre

ω is a replacement of frequency which is usually a large number. It remains const. irrespective of medium.

* As long as particle (e⁻ or atom or molecule or nucleus) is in fixed state, no energy released. Bohr's Argument

When it goes to higher energy and it comes down and releases energy

$$\Delta E = h\gamma = hc\bar{\omega} = \left(\frac{hc}{\lambda}\right)$$

• Same specimen can give spectra of e⁻, atoms, molecules & nucleus.

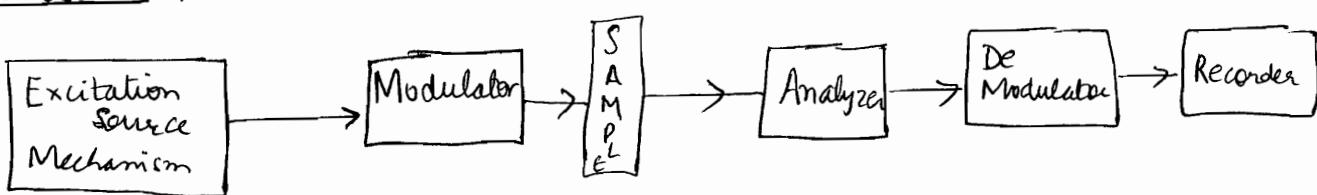
• Excitation Mechanism : that causes particle to go to higher energy.

It has to be chosen in such a way that it is able to

change: Molecular Energy levels
& Atomic Energy levels
& Nucleus Energy levels

It could be suitable radiation or current or atomic collisions.

Typical Spectrometer

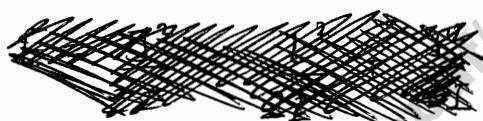
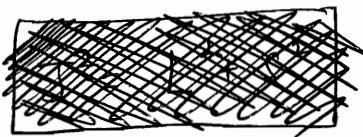


① If white light source, I require modulator to choose wavelength of our choice (filter)

Maximum ΔE : atoms several eV eg. (-13.6 eV)
 $- \left(-\frac{13.6}{4}\right) \text{ eV}$

Then ΔE : molecular

Then ΔE_{\min} : nuclear $\approx \underline{10^{-8} \text{ eV}}$



② Note that there are two types of nuclear energy levels. 1 due to excitation of shell model states ... they correspond to γ ray. While those states that are created due to external magnetic field are

Radio Frequency Regions that of radio frequency rays.

$$\underline{\Delta E_{\text{nucleus}} \approx 10^{-8} \text{ eV}}$$

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

Hence, Radio Frequency spectra of nuclear energy levels
Therefore suitable source is Radio Frequency Oscillator.

example NMR.

$$\underline{\Delta E_{\text{molecular}} \approx 10^{-3} \text{ eV}}$$

3 types of energy: ① Rotational \rightarrow MICROWAVE SPECTRA

eg. Klystron Oscillator: Microwave source

② Vibration 10^{-11} eV \rightarrow Infrared Region

③ Electronic Energy levels \rightarrow several eV
i.e. 10^1 eV

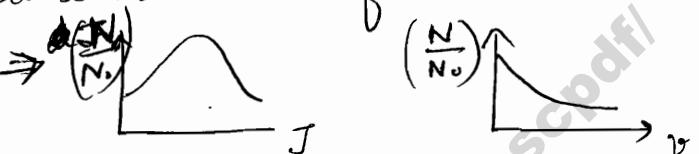
i.e. Visible or UV range.

$\Delta E_{\text{atomic}} \approx \text{many eV}$ ← Balmer ← Paschen, Brackett, Pfund ...
 ← UV, visible and Infrared Spectrum
Lyman ← due to jumping of e^-
 eg. $(13.6 - \frac{13.6}{4}) \text{ eV}$ in H atom

If $T = 300 \text{ K} = 27^\circ \text{C}$

$$\text{Equivalent} = kT = 0.026 \text{ eV}$$

It is sufficient to cause rotation of molecules but not vibration.

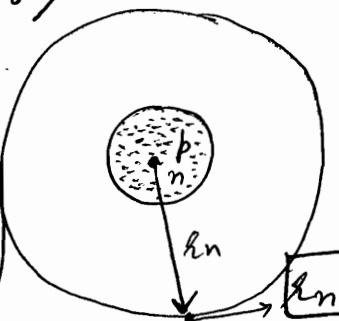


Atomic Models

Thomson Model (Plum Pudding Model)



Rutherford Model
Based on scattering experiment



Bohr's Model (1913) (Angular Momentum Quantization Model)

$$r_n = a n^2$$

$$a = 0.53 \text{ Å}$$

$$E_n = -\left(\frac{13.6}{n^2}\right) \text{ eV}$$

Sommerfeld's Model

Dirac's Quantum Mechanical Model
or

Vector Model of Atom

Bohr's Model

- Bohr removed discrepancies in Rutherford Model by introducing quantization of Angular Momentum, thereby quantizing energy and saying that Energy will remain const. And energy will not be continuously emitted thereby e^- will not collapse in nucleus.

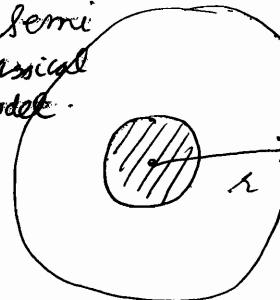
① Bohr quantized Angular Momentum $|\vec{L}| = |\vec{\omega} \times \vec{p}| = n\hbar$

$$E_n = -\left(\frac{13.6}{n^2}\right)$$

② $\Delta E = \left(\frac{hc}{\lambda}\right) \Rightarrow E_f - E_i = \frac{hc}{\lambda}$
 $= 13.6 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

$$\frac{mv^2}{r} = \frac{Zq^2}{4\pi\epsilon_0 r^2} \quad m\hbar v = \frac{Zq^2}{4\pi\epsilon_0} \quad \Rightarrow v = \frac{Zq^2}{n\hbar 4\pi\epsilon_0} \quad r = \frac{n^2 k^2}{Zme^2} 4\pi\epsilon_0$$

mvr = $n\hbar$ Classical Quantization Semi-classical Model



$$k = \left(a_0 \frac{n^2}{Z} \right)$$

$$v = \frac{Z v_0}{n}$$

$$a_0 = 0.53 \text{ \AA}$$

$$v_0 = 2.18 \times 10^6 \text{ m/s}$$

$$E = \frac{p^2}{2m} + V(r)$$

$$= \frac{p^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$= \frac{1}{2} mv^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$= \frac{1}{2} me \frac{Z^2 e^4}{n^2 \hbar^2 (4\pi\epsilon_0)^2} - \frac{e^4 Z^2 m_e}{(4\pi\epsilon_0)^2 n^2 \hbar^2} = -\frac{1}{2} \frac{Z^2 me^4}{n^2 \hbar^2 (4\pi\epsilon_0)^2}$$

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \Leftarrow \frac{1}{137} \quad \text{dimensionless number} : \text{FINENESS CONSTANT.}$$

$$E_n = -\frac{me^4}{2(4\pi\epsilon_0)^2 \hbar^2} \left(\frac{Z^2}{n^2} \right) = -R hc \left(\frac{Z^2}{n^2} \right)$$

$$R = \text{Rydberg Const.} = \frac{(me^4 / 8\epsilon_0^2 c h^3)}{}$$

$$R = 1.09 \times 10^7 \text{ m}^{-1}$$

$$E_n = -13.6 \left(\frac{Z^2}{n^2} \right)$$

Remember,
 $E_n = - (k \cdot E_i)_n$

$$1 < n < \infty$$

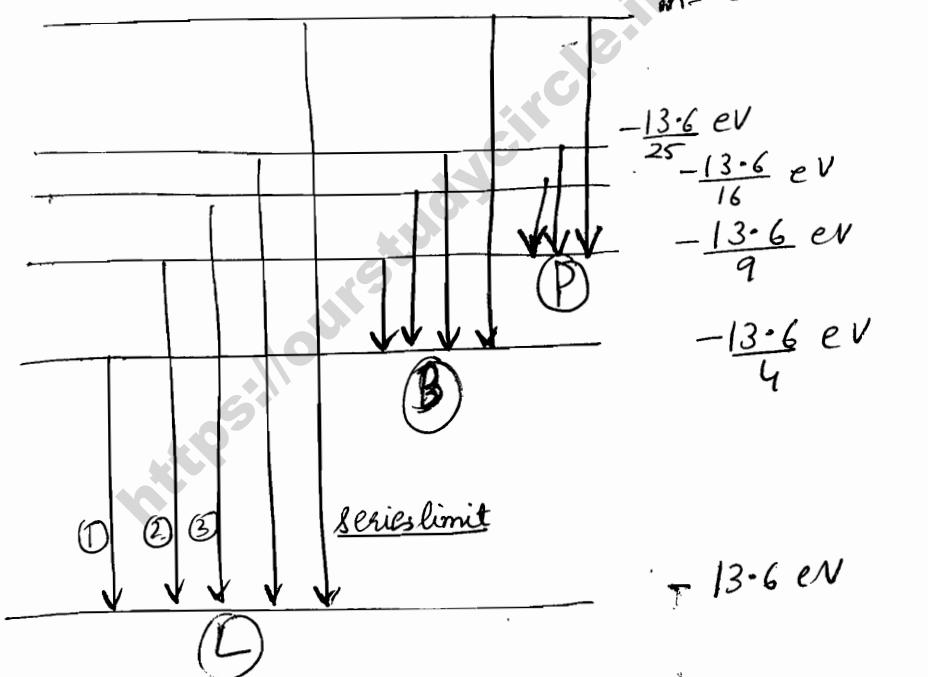
For e^- to move out of atom, $k \cdot E_i > P.E.$

@ $n = \infty$

$$E = 0$$

$$\frac{1}{2} m v^2 = \frac{Ze^2}{4\pi \epsilon_0 R}$$

Atomic
Spectra is
line
spectra



$n = n$ to $n = 1$: Dyman Series

UV Region 912 - 1200 Å

$n = n$ to $n = 2$: Balmaa Series

Visible Region 3647 Å - 6564 Å

$n = n$ to $n = 3$: Paschen Series

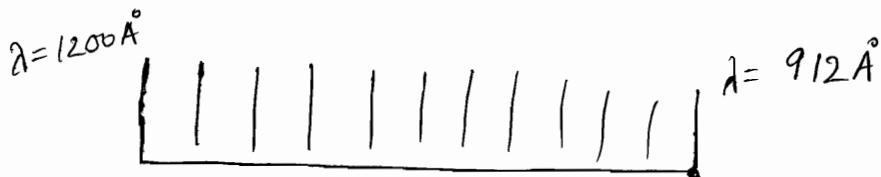
IR

$n = n$ to $n = 4$: Brackett Series

IR

$n = n$ to $n = 5$: Pfund Series

IR



Dyman Series

[U.V.]

$$\bar{\omega} = \frac{1}{\lambda}$$

$$\frac{1}{\lambda} = R \left[\frac{1}{n_2^2} - \frac{1}{n_1^2} \right]$$

lowest Wavelength
i.e.
Highest Wavenumber

$$\frac{1}{\lambda_{\min}} = R \left[\frac{1}{1^2} - \frac{1}{\infty} \right] = R \Rightarrow \lambda = \frac{1}{R} = \frac{1}{1.09 \times 10^7}$$

$$\approx 912 \text{ Å}$$

$$\frac{1}{\lambda_{\max}} = R \left[\frac{1}{1^2} - \frac{1}{2^2} \right] = \frac{3R}{4} \Rightarrow \lambda_{\max} = \frac{4}{3(R)} \approx \frac{1200 \text{ Å}}{1}$$

note that we are always interested
in this series $\therefore \alpha$ (n=3 to n=2) β (n=4 to n=2) refer to this series

Balmer Series $\frac{1}{\lambda_{\min}} = R \left[\frac{1}{2^2} - \frac{1}{\infty} \right] = \frac{R}{4}$

[Visible Region] $\Rightarrow \lambda_{\min} = \frac{4}{R} \approx \frac{4000 \text{ Å}}{1}$

$$\frac{1}{\lambda_{\max}} = R \left[\frac{1}{2^2} - \frac{1}{3^2} \right] = \frac{5R}{36}$$

$$\Rightarrow \lambda_{\max} \approx \frac{36}{5R} \approx \frac{7000 \text{ Å}}{1}$$

Visible Spectrum

If I see from very sensitive spectrometer, I can see few lines in between these lines also, called fine structure.

~~Note that Quantum Mechanics also give these lines.~~

→ there can be dependence upon other quantum numbers (l, m_l, m_s) too.

Bohr's Model Drawbacks

- ① Not valid for more than 1 e- atoms. (couplings)
 - ② It does not explain fine structure of lines.
No logic or reason given for quantization of angular momentum.
 - ③ ~~Bohr's model fails to predict intensity of lines.~~
 - ④ Whenever atom is kept in external field, it does not tell the behaviour : Zeeman Effect (Magnetic Field)
Stark Effect (Electric Field)
 - ⑤ Precise orbits do not exist. Quantum Mechanical Probabilities.
- * Note that if I take Hamiltonian as $\left(\frac{p^2}{2m} + V_k\right)$, I will get same Energy values as Bohr Model. Unless I change Hamiltonian, I won't get fine structure by Quantum Mechanics. That change is SPIN.
- (Remember, in s-coupling we add the term $\propto \frac{\vec{L} \cdot \vec{S}}{R^3}$ in Hamiltonian)

- ⑥ Electron Spin introduced in 1925 by Goudsmit & Uhlenbeck.

~~(1) To correct Gyromagnetic Ratio~~

~~Magnetic Moment~~
~~Angular Momentum~~ = $\frac{\mu}{L} = -\frac{e}{2m}$

$$\vec{\mu}_e = -\frac{e}{2m} \vec{L} \quad \underbrace{\vec{\mu}_s = -\frac{e}{2m} 2\vec{S}}$$

it needed to be introduced

- (2) To ~~explain~~ fine structure of atomic spectra
- (3) To explain Zeeman Effect
- (4) To explain Stern-Gerlach Experiment.

$$\text{Now } \vec{\mu}_e = -\frac{e}{2m} \vec{L} = -\frac{e}{2m} g_e \vec{L} \quad g_e = 1$$

$$\begin{aligned} \text{Quantum Mechanically } \vec{\mu}_s &= -\frac{e}{2m} \vec{2s} \\ &= -\frac{e}{2m} g_s \vec{s} \quad g_s = 2 \end{aligned}$$

s orbital $l=0 \Rightarrow L=0 \Rightarrow \mu_e = 0$

$$|\vec{\mu}| = |\vec{\mu}_s| = \sqrt{s(s+1)} \hbar = \frac{\sqrt{3}}{2} \hbar \quad \vec{\mu}_s = -\frac{e}{2m} \vec{2s}$$

but if $s=0 \Rightarrow \mu_s = 0 \}$ fully filled orbitals


p orbital $l=1 \Rightarrow L=\sqrt{2}$

$$\vec{J} = \vec{L} + \vec{S} : LS \text{ coupling}$$

$$\vec{\mu}_J = \frac{e}{2m} g_J \vec{J} : g_J: \text{Landé's "g" splitting Factor}$$

This is called Vector Model of Atoms

for Multi-Electron Atom : LS Coupling

for Single-Electron Atom : Spin-Orbit Coupling

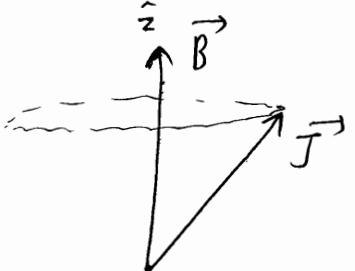
If I keep the atom in Magnetic Field (\vec{B}'),

if $\vec{B}_{\text{external}} \Rightarrow$ (Zeeman Effect) / (Paschen Beck Effect)
(weak \vec{B}') (strong \vec{B}')

if $\vec{B}_{\text{internal}} \Rightarrow$ LS Coupling or Spin Orbit Coupling
(^{multi}~~e-~~-atom) (~~single~~^{single}~~e-~~-atom)

$$\vec{\tau} = \vec{\mu}_J \times \vec{B} \quad \left(\begin{array}{l} \vec{\mu}_J \propto \vec{J} \\ \Rightarrow \vec{\tau} \perp \vec{J} \\ \Rightarrow \text{Precession} \end{array} \right)$$

Torque will try to align $\vec{\mu}_J$ along \vec{B}' . Hence $\vec{\mu}_J$ will precess i.e. \vec{J} will precess in direction of \vec{B}' .



Remember from space quantization, that in whatever direction I apply \vec{B} , \vec{J} will align at specific angles to that direction s.t.

$$J = \sqrt{j(j+1)} \hbar \quad J_z = m_j \hbar$$

Since $m_j < j \Rightarrow \vec{J}$ cannot be \parallel to \vec{B}

When \vec{J} is precessing, J_z will be const., $J_z = m_j \hbar$

$$j \leq m_j \leq j$$

$2j+1$ Orientations

$$\boxed{\frac{d\vec{J}}{dt} = -\frac{e}{2m} g_J (\vec{J} \times \vec{B})} \quad \text{Larmor Precession}$$

$$\boxed{E = -\vec{\mu}_J \cdot \vec{B}}$$

Potential Energy of Orientation of Dipole

$$= +\frac{e}{2m} g_J \vec{J} \cdot \vec{B}$$

$$= +\frac{e}{2m} g_J B J_z$$

$$\boxed{E = +\frac{e\hbar}{2m} B \cdot g_J m_j}$$

Stark-Gerlach Experiment

It is "VIVID CONFIRMATION OF VECTOR MODEL OF AN ATOM"

Vector Model : $\vec{J} = \vec{L} + \vec{S}$

(*) Total angular momentum of an atom results from the combination of spin and orbital angular momenta of its electrons. Since ang. momentum is a vector quantity, we can represent the total angular momentum as addition of orbital and spin angular momentum vectors.

In Bohr Model, only $L = n \ h$

$$E = -\frac{13.6}{n^2}$$

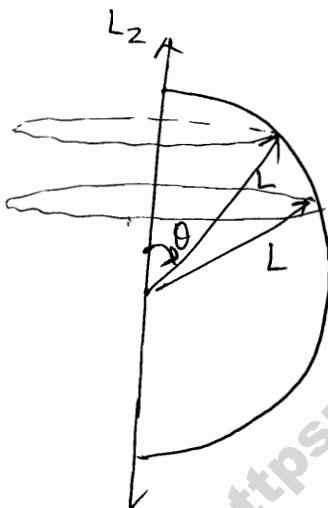
Coming out due to quantization of \vec{L}

It is demonstrating

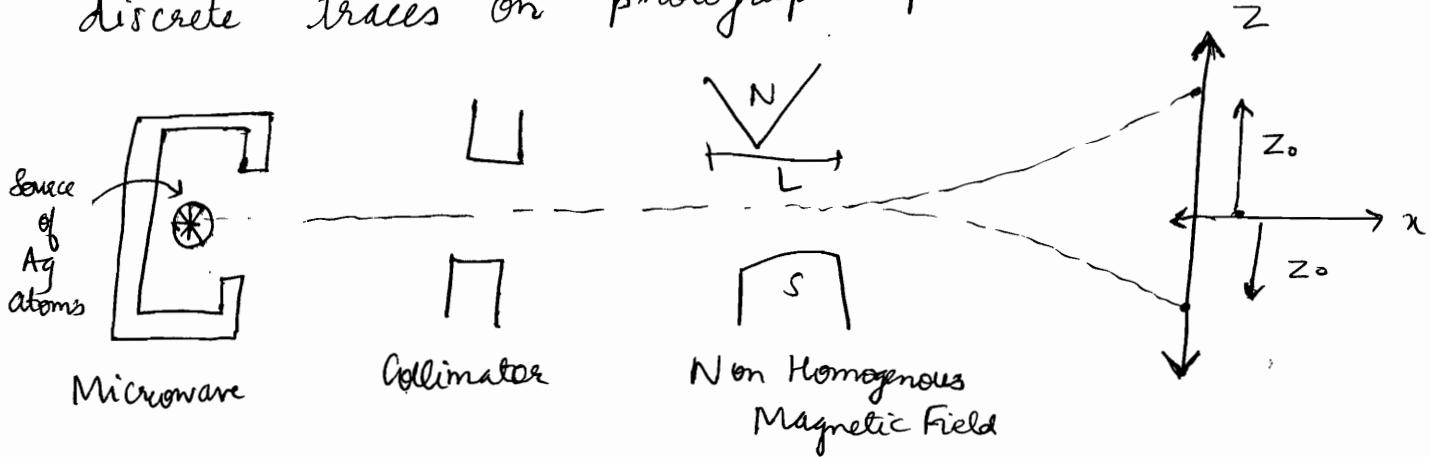
- ① Orbital Motion or Space Quantization
- ② Spin Motion governed by

$$S^2 = s(s+1) \ h^2$$

$$S_z = m_s \ h \quad -s < m_s < s$$



"Beam of neutral silver (Ag) Atoms is passed through non-homogeneous magnetic field giving rise to 2 discrete traces on photographic plate"



A & M PHYSICS (2)

Ag ($Z=47$) $5s^1$: e^- are responsible for ΔE .

Note that only valence e^- are responsible for jumps.

For fully filled orbitals, $L=0$ and $S=0$ i.e. $J=0$

$$\left. \begin{array}{l} nS^2 \\ np^6 \\ nd^{10} \end{array} \right\} \begin{array}{l} L=0 \\ S=0 \end{array}$$

Note that energy level is defined by \vec{J} . Hence they contribute nothing to ΔE .

In spectroscopy, valence electrons are called Optically Active Electrons.

For Ag, $L=0$ $\vec{J} = \vec{L} + \vec{S} = \vec{S}$
 (s orbital) $S_z = m_s \hbar$

$$\vec{\mu}_J = -\frac{e}{2m} \cdot g_J \vec{J}$$

$$\vec{\mu}_S = -\frac{e}{2m} 2\vec{S}$$

✓ Whenever it is kept in field, Torque acts giving rise to Precession.

$$E = -\vec{\mu}_s \cdot \vec{B} = -(\mu_s)_z B$$

(if $\vec{B} = B \hat{z}$)

$$(\vec{\mu}_s)_z = -\frac{e}{2m} g_m \vec{s}_z$$

$$(\mu_s)_z = -\frac{e\hbar}{2m} g_s m_s$$

$$\frac{e\hbar}{2m_e} = \mu_B : \text{Bohr Magneton}$$

$$\mu_B = 9.27 \times 10^{-24} \text{ Joule/Tesla}$$

$$(s_z = m_s \hbar)$$

★ The quantity $\left(\frac{e\hbar}{2m}\right)$ forms a natural unit for the measurement of atomic magnetic dipole moments and is called Bohr Magneton, denoted by μ_B .

$$\frac{e\hbar}{2m_p} : \text{Nuclear Bohr Magneton}$$

✓ $(\mu_s)_z$ can take no. of value that m_s can have.
Hence Stern-Gerlach Experiment also gives quantization of magnetic moment.

✓ It should not be a charged particle. Otherwise $F = q(\vec{v} \times \vec{B})$ will act and circular path will be obtained, hence no trace on plate. Hence, we took Ag neutral particles.
We want only force in z direction.

Experiment will not succeed if \vec{B} is Homogeneous, because otherwise no net force will act on dipole moment.

$$\vec{F} = (\vec{\mu} \cdot \vec{\nabla}) \vec{B}$$

$\vec{F} = 0$ for homogeneous field

$$\vec{F} = \vec{\nabla}(\vec{\mu} \cdot \vec{B})$$

$$= \frac{\partial}{\partial z} (\mu_z B_z) = \mu_z \left(\frac{\partial B_z}{\partial z} \right)$$

\vec{F} is non homogeneous

$$\vec{B} = 0\hat{i} + 0\hat{j} + B_z \hat{k} = B_z \hat{k}$$

$$\text{and } \left(\frac{\partial B_z}{\partial z}\right) \neq 0 ; \quad \frac{\partial B_z}{\partial x} = 0 = \frac{\partial B_z}{\partial y}$$

$F_z = \mu_B \left(\frac{\partial B_z}{\partial z} \right)$

remember
its
 μ_B

$$= \mu_B g_s m_s \left(\frac{\partial B_z}{\partial z} \right)$$

$$\text{distance } x = L$$

$$\text{velocity } x = v_x \text{ (const.)}$$

$$t = \left(\frac{L}{v_x} \right)$$

$$v_{z,i} = 0$$

$$a_z = \left(\frac{F_z}{m} \right) \Rightarrow z = \frac{1}{2} a_z t^2 = \frac{1}{2} a_z \left(\frac{L}{v_x} \right)^2$$

$$= \frac{1}{2} \frac{\mu_B \left(\frac{\partial B_z}{\partial z} \right)}{m} g_s m_s \frac{L^2}{v_x^2}$$

$\frac{1}{2} m v_x^2$: k.E. that can be considered by temp. of oven

Normally, it is $\frac{3}{2} kT$

$$\left[\begin{array}{l} \text{at } 300 \text{ K: } \frac{3}{2} kT \\ > 300 \text{ K: } \frac{4}{2} kT \end{array} \right]$$

$$\Rightarrow z = \frac{\mu_B \left(\frac{\partial B_z}{\partial z} \right) L^2}{3kT} \frac{g_s m_s}{2}$$

$$Z = \left(\frac{\mu_B \left(\frac{\partial B_z}{\partial z} \right) L^2}{3kT} \right) m_s$$

$j=2$

○ Cadmium } fully
Mercury } filled
 orbits

Now we will get m_s no. of traces.

N_{m_s} can be $2s+1 = 2$ i.e. $\pm \left(\frac{1}{2}\right)$

$\Rightarrow S=0, L=0$
No deviation in
Stom Gerlach

Hence 2 traces.

Also 2 traces $\Rightarrow 2s+1=2 \Rightarrow S=\frac{1}{2}$ fixed

$$\Rightarrow Z = \pm \frac{1}{2} \cdot \left(\frac{\mu_B \left(\frac{\partial B_z}{\partial z} \right) L^2}{3kT} \right) = \pm Z_0$$

(⁴ Quantum numbers) (^j dependent) (^{B applied} $\Rightarrow m_j$ dependent) ^(2s+1) L_j
State, level, sub level, Spectral Term

State : Complete description $\psi(n, l, m_e, m_s)$

We require all the 4 set of quantum numbers.

Energy level : Energy level defined by \vec{j} ($= \vec{L} + \vec{s}$)

more the j ,

more the energy

hence in general

If \vec{j} exists $\Rightarrow \mu_j$ exists

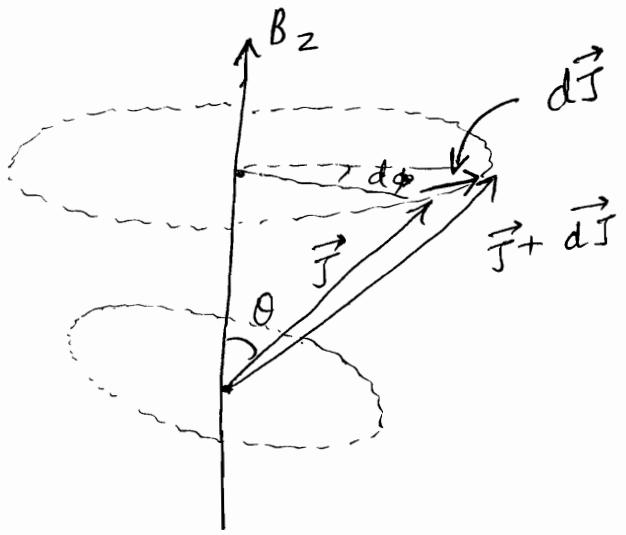
Ref to P-77 and J8

of Rajkumar

$E_s < E_p < E_d$ for same n If \vec{B} exists $\Rightarrow \vec{j}$ will precess about \vec{B}

It's called LaMer Precession

→ 2 levels on after \vec{j} line ; 2 sublevels (of different levels of course) in \vec{j} component (defined by m_j)



$$d\vec{J} \perp \vec{J}$$

$$\omega_p = \left(\frac{d\phi}{dt} \right) = \left(\frac{dJ}{J \sin \theta} \right)$$

EXTERNAL MAGNETIC FIELD

$$I = \frac{dJ}{dt} = \vec{\mu}_J \times \vec{B} = \mu_J B \sin \theta$$

$$\Rightarrow \omega_p = \frac{\mu_J B \sin \theta}{J \sin \theta} = \frac{e}{2m} B g_J$$

$$\left(\frac{\mu_J}{J} = \frac{e}{2m} g_J \right)$$

$$\Rightarrow \boxed{\omega_p = \frac{e}{2m} g_J B}$$

$\Rightarrow \omega_p$ is independent of m_J

 all have same ω_p

$$E = -\vec{\mu} \cdot \vec{B} = \frac{e}{2m} g_J \vec{J} \cdot \vec{B}$$

$$\boxed{E = \mu_B B g_J m_J}$$

$$= \frac{e}{2m} g_J m_J \vec{B} \cdot \vec{J} \quad j < m_J < j$$

$$= \cancel{\mu_B g_J m_J B} \Rightarrow N_{mj} = (2j+1)$$

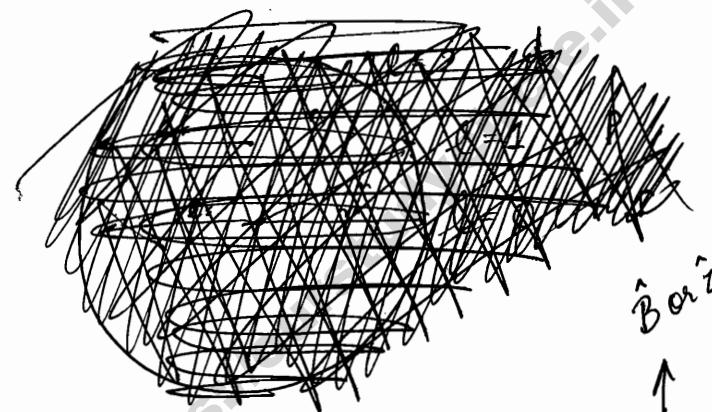
$$\gamma_p = \frac{e}{4\pi m} B g_J$$

m_j : Magnetic Moment Quantum No.

→ Each energy level will be split into $(2j+1)$ energy sublevels.

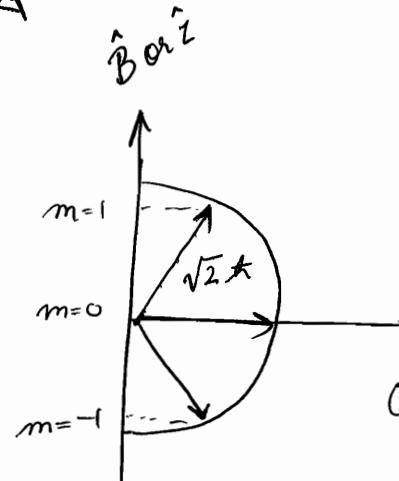
★ $(2j+1)$ gives different orientation of j i.e. no. of values of m_j i.e. number of deflections in Stern Gerlach

l	0	1	2	3	4	5	6
Orbital	s	p	d	f	g	...	



Zooming $l=1$

from top view



Counting only valence electrons

γ = Multiplicity = $(2s+1)$ for single e^- atom

Many electron atoms : $2s+1$ ($L>s$)

$2L+1$ ($s>L$)

① $\gamma = 2s+1$ always
② multiplicity =

$$L = \boxed{2(s \text{ दोषावलि}) + 1} = \text{no. of energy levels}$$

e.g. Na^+

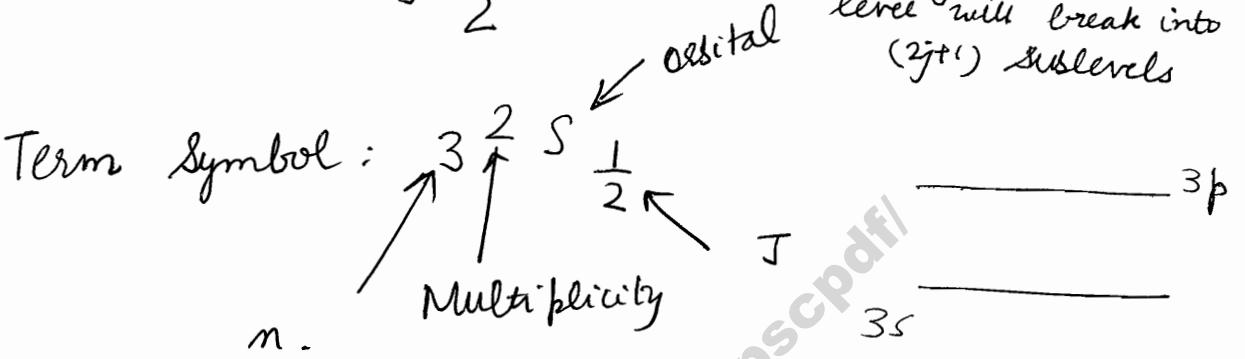
$$\frac{1s^2 \ 2s^2 \ 2p^6}{X} \quad L=0$$

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

$$J = \frac{1}{2}$$

- ★ 1 term symbol corresponds to 1 energy level i.e. 1 particular value of J .

- ★ When subjected to B_{ext} , each J i.e. each level will break into $(2J+1)$ sublevels



For excited Na atom,

$$l=1 \quad (\text{p})$$

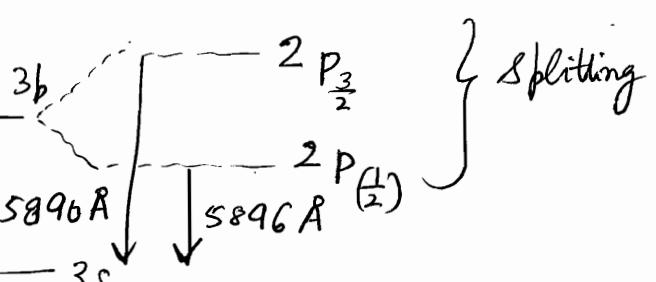
$$S = \frac{1}{2}$$

$$j = l \pm s = \frac{1}{2}, \frac{3}{2}$$

hence

Note that we have taken $3p$ to be of more energy than $3s$. Why? The explanation lies in Dirac Quantum Model.

$$\Delta E = -\frac{5.8 \times Z^4}{n^3} \left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right]$$



D_1 and D_2 lines

This is called Fine Structure caused due to spin

Energy level "j" : transition between 2 energy levels : line
 (Note that sodium transitions are 2 lines)

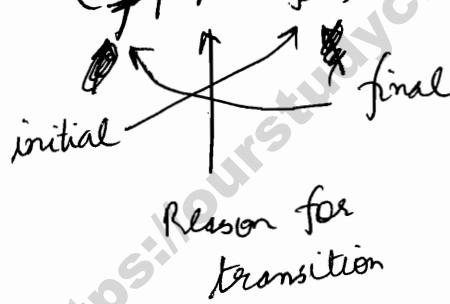
Energy sublevel : Component : transition b/w 2 sublevels
 (Components are those that in Zeeman effect on Sodium Transitions)
 (of course, not 2 sublevels of same level)

Spectral Term γ_{Lj} : Multiplets : transition b/w 2 spectral levels.

But what are allowed transition?

It is governed by Selection Rule $\Delta j = \pm 1$

$$P(\text{transition}) = \langle f | A | i \rangle \neq 0$$



} Laporte's rule

$$\text{e.g. } \langle i | \mu_z | f \rangle \neq 0$$

$$\text{For allowed transition } \int \psi_i^* \mu_z \psi_f d\tau > 0$$

$$\text{we get, } \Delta m_j = \pm 1, 0 \quad \text{for Zeeman Effect}$$

When $2e^-$ are said to be equivalent?

$2p^1 3p^1$: non equivalent

$2p^1 2p^2$: Equivalent

Equivalent means :- n and l quantum numbers are same.

IT IS APPLICABLE AND OBSERVABLE IN ALL ATOMS.... IT IS MORE DOMINANT IN HEAVIER ATOMS WHERE \vec{L} and \vec{S} ARE INDIVIDUALLY

Spin Orbit Coupling

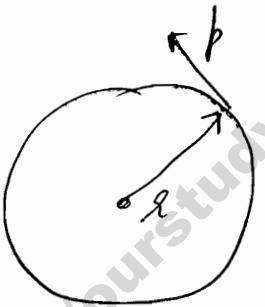
NON EXISTENT
ONLY \vec{J} electron

FOR INDIVIDUAL ELECTRONS AND
IS OBSERVABLE. THIS COUPLING IS

Spin e^- produces its own $\vec{\mu}_s$

NOT STRONG IN

LIGHT ATOMS WHERE \vec{L} 's and \vec{S} 's INDIVIDUALLY COUPLE AND THEN COMBINED \vec{L} AND \vec{S} INTERACT...



Orbiting $e^- \Leftrightarrow$ Current loop \Rightarrow creates its own magnetic field

* For current loop,

$$B = \left(\frac{\mu_0 I}{2\pi} \right)$$

$$B = \frac{\mu_0}{2\pi} \left(\frac{e \omega}{2\pi} \right) = \frac{\mu_0 e (m r^2) \omega}{2\pi \cdot 2\pi \cdot m r^2}$$

imp.
step

$$= \frac{\mu_0 e L}{4\pi m r^3} = \left(\frac{e}{m} \right) \left(\frac{\mu_0}{4\pi} \right) \frac{L}{r^3}$$

$$\boxed{\vec{B}_{int} = \frac{e}{m} \frac{\mu_0}{4\pi} \frac{\vec{L}}{r^3}}$$

In e^- frame of reference, nucleus is rotating with ω . Hence it will experience force due to field created by nucleus.

$$\vec{B}_{\text{int}} = 0 \text{ only if } \vec{L} = 0$$

$$\vec{T} = \vec{\mu}_s \times \vec{B}$$

$$= \mu_s B \sin \theta$$

$$d\omega = T d\theta = -\vec{\mu}_s \cdot \vec{B} = \frac{e}{2m} \cdot 2\vec{s} \cdot \vec{B}$$

$$E = -\vec{\mu}_s \cdot \vec{B}$$

$$= 2 \frac{e}{2m} \vec{s} \cdot \vec{B}$$

$$= \frac{e}{2m} 2\vec{s}_z B$$

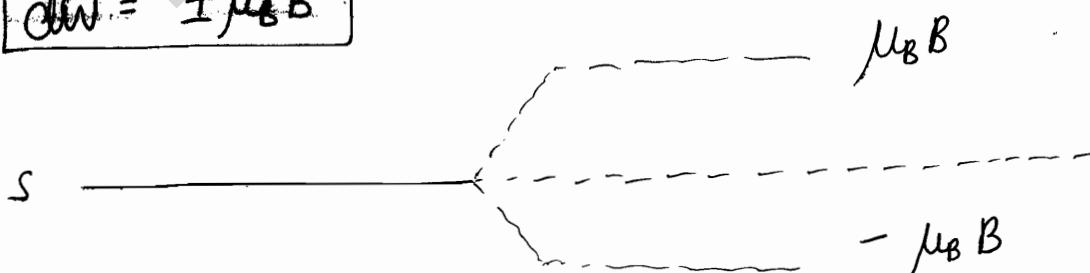
$$= \frac{e\hbar}{2m} 2m_s B$$

$$m_s = \pm \frac{1}{2}$$

$$d\omega = \pm \left(\frac{e\hbar}{2m} \right) B = \pm \mu_B B$$

✓ $d\omega = \pm \mu_B B$

INTERNAL MAGNETIC FIELD



It will result into fine structure doubling.

This analysis for single valence e^- .

- ① Single e^- atom's $\vec{\mu}_s$ interacting with \vec{B}_{int} to lift the energy levels.

It's a weak interaction.

Refer last
Page

$$E = \left(\frac{e}{m}\right)^2 \vec{s} \cdot \frac{\mu_0}{4\pi} \frac{\vec{L}}{r^3}$$

✓ $E_{l,s} = \left(\frac{\mu_0}{4\pi}\right) \left(\frac{e}{m}\right)^2 \frac{1}{r^3} (\vec{L} \cdot \vec{s}) = \vec{\mu}_s \cdot \vec{B}$

$$\Rightarrow E = \alpha \frac{1}{r^3} \vec{L} \cdot \vec{s}$$

Hence it's called Spin Orbit Coupling.

- ⑥ Now $E_{l,s}$ is the correction factor in Hamiltonian.
It will now give fine structure, Quantum
Mechanically.

$$H' = \frac{p^2}{2m} + V(r) + \boxed{\frac{\alpha(\vec{L} \cdot \vec{s})}{r^3}}$$

$$H' = H + \frac{\alpha(\vec{L} \cdot \vec{s})}{r^3}$$

$$\text{from, } H\Psi = E\Psi$$
$$E = -\frac{B \cdot 6}{n^2}$$

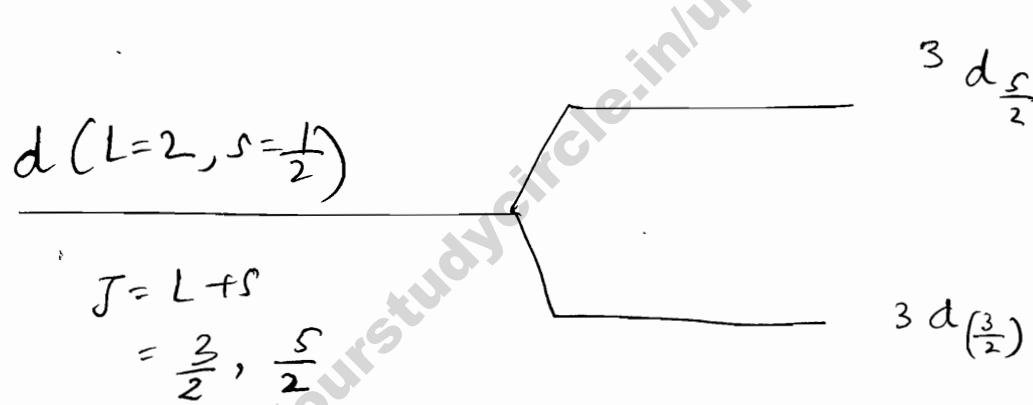
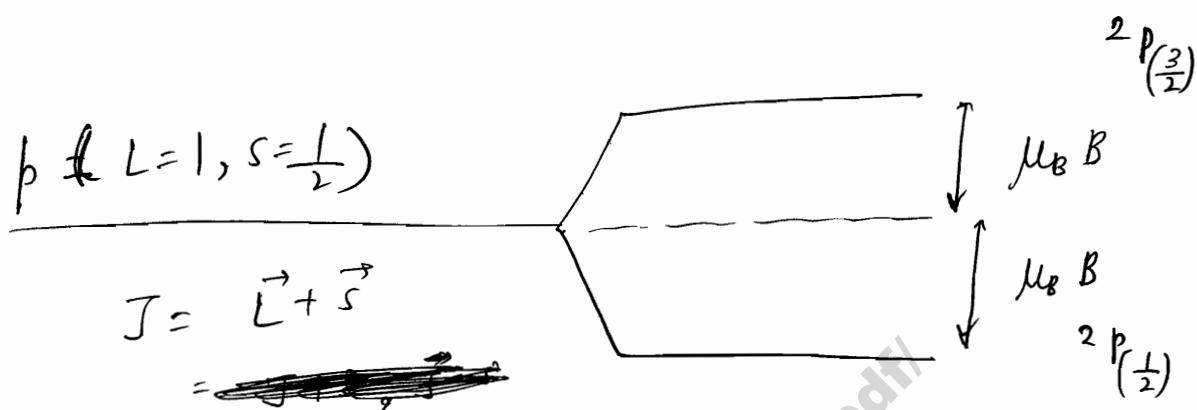
$$\left\langle \frac{1}{r^3} (\vec{L} \cdot \vec{s}) \right\rangle$$

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

$$J^2 = L^2 + S^2 + 2\vec{L} \cdot \vec{S}$$

$$\vec{L} \cdot \vec{S} = \frac{J^2 - L^2 - S^2}{2} = \frac{j(j+1) - l(l+1) - s(s+1)}{2} \frac{\hbar^2}{\hbar}$$

$$E_{LS} = \left(\frac{\mu_0}{4\pi}\right) \left(\frac{e}{m}\right)^2 \left(\frac{\hbar^2}{2}\right) \frac{1}{r^3} \quad [j(j+1) - l(l+1) - s(s+1)]$$



$$= \alpha [j(j+1) - l(l+1) - s(s+1)] \langle \frac{1}{r^3} \rangle$$

eg.
H atom $\langle n, l, m | \frac{1}{r^3} | n, l, m \rangle$

★ Perfect Example for Spin Orbit Coupling are d₁ and d₂ lines of sodium lamp.

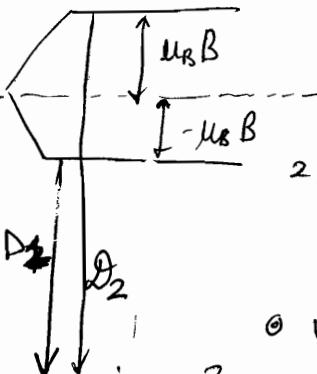
Sodium lamp

① Note that we achieve at $E_2 > E_1$ after getting results of modified hamiltonian

$E_1 \quad 3s$

$E_2 \quad 3p$

${}^2P_{\frac{3}{2}}$ $[E_2 + \mu_B B]$



② dotted b'cos not observed

${}^2P_{\frac{1}{2}}$ $[E_2 - \mu_B B]$

③ vertical energy drift line/component
right side लिखते हैं
और draw करते हैं !!

④ For spin Orbit Coupling

$$\left\{ \begin{array}{l} \Delta l = \pm 1 \\ \Delta j = 0, \pm 1 \\ \Delta s = 0 \end{array} \right.$$

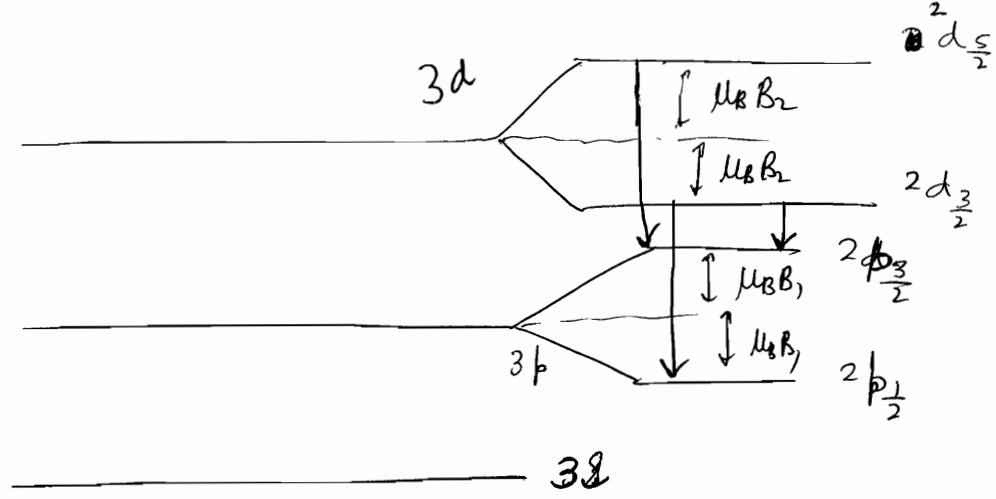
Selection rules

$$\lambda_1 = \frac{hc}{\lambda_1} = (E_2 - \mu_B B) - E_1 = (E_2 - E_1) - \mu_B B$$

$$\lambda_2 : \frac{hc}{\lambda_2} = (E_2 - E_1) + \mu_B B$$

$$hc \left[\frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right] = 2 \mu_B B$$

Bire can be calculated which is felt by p electrons
No coupling in s electron.



B_1 and B_2 are not equal in general.

3 spectral lines for
 $d \rightarrow p$ transitions

$$\left. \begin{array}{l} \Delta l = \pm 1 \\ \Delta j = 0, \pm 1 \\ \Delta s = 0 \end{array} \right\}$$

Fine Structure of H atom

Dirac's Quantum Mechanical Model

~~① Spin Orbit Coupling~~

$$H^{\text{extra}} = \frac{\mu_0}{4\pi} \left(\frac{e}{m}\right)^2 \frac{\hbar^2}{2} [j(j+1) - L(L+1) - s(s+1)]$$

$$= Z^2 R^2 \frac{\hbar^2}{n^3 l(l+1)} = \frac{5.84 \text{ Ry}}{n^3 l(l+1)}$$

~~② Relativistic correction in Hamiltonian.~~

$$\begin{aligned} H &= E - m_e c^2 + V \\ &= c^2 [m - m_0] + V \\ &= m_0 c^2 \left[\left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}} - 1 \right] + V \\ &= m_0 c^2 \left[1 + \frac{v^2}{2c^2} - \frac{3}{8} \frac{v^4}{c^4} + \dots \right] A + V \\ &= \frac{1}{2} m_0 v^2 \left(-\frac{3}{8} \frac{v^2 m_0}{c^2} \right) + V \end{aligned}$$

$$\text{Relativistic Correction} = -\frac{3}{8 m_e^3 c^2} \beta^4$$

$$\langle H' \rangle = -\frac{3}{8 m_e^3 c^2} \langle \beta^4 \rangle$$

Solution of $H\psi = E\psi$ gives Bohr's n^{th} level

The departure from these values is given by the above 2 corrections. It comes out to be:

$$\Delta E = -\frac{Z^4 \alpha^2 R_\infty}{n^3} \left[\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right]$$

$$\Delta E \approx -5.84 Z^4 \left[\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right] \text{ cm}^{-1}$$

Dirac's Quantum Mechanical Model

① Also refer HARTREE'S MODEL P-127 This is responsible for $E_d > E_p > E_s$!!

Eq. $n=3$ ----- $n=3$ Bohr Energy
and s ignored

$\Rightarrow l=0, 1, 2$ ----- $3d$

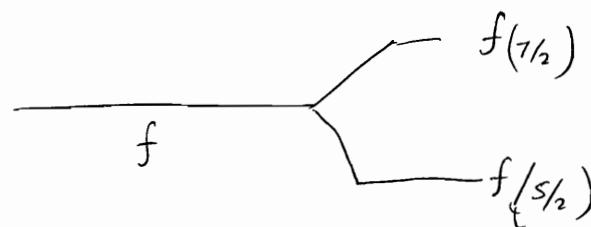
$\Delta E = -\frac{9}{4} A, = \frac{1}{4} A, = \frac{1}{4} A$
 $3s$ $3p$ $3d$

Hence Energy depends on DIRAC QUANTUM n value; then on a finer level it depends on j values \uparrow ; then on a further finer level E depends on l values (Lamb effect)... finally it further depends on m_j (Zeeman)

A & M Physics (3)

22/02/2012

- s^1 values have no spin orbit coupling



- Spin Orbit Coupling only for single e^- atoms.

- Spin Orbit Coupling Rules of Selection :

$$\left\{ \begin{array}{l} \Delta l = \pm 1 \\ \Delta j = 0, \pm 1 \\ \Delta s = 0 \end{array} \right\} \quad \left(\begin{array}{l} j=0 \\ j=0 \end{array} \right) \text{ is not allowed}$$

$$\begin{aligned} \Delta T &= -\frac{R_\infty \alpha^2 Z^4}{n^3} \left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right] \\ &= -\frac{5 \cdot 84}{n^3} Z^4 \left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right] \end{aligned}$$

Departure from
Bohr's n^{th} level

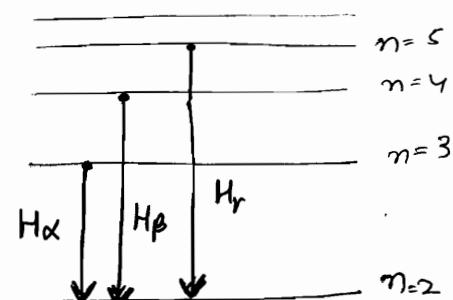
This is Dirac's Quantum Mechanical Model to explain fine spectrum of lines.

H_α , H_β and H_γ lines come in the **BALMER series** of H spectrum

$H_\alpha : n=3 \rightarrow n=2$

$H_\beta : n=4 \rightarrow n=2$

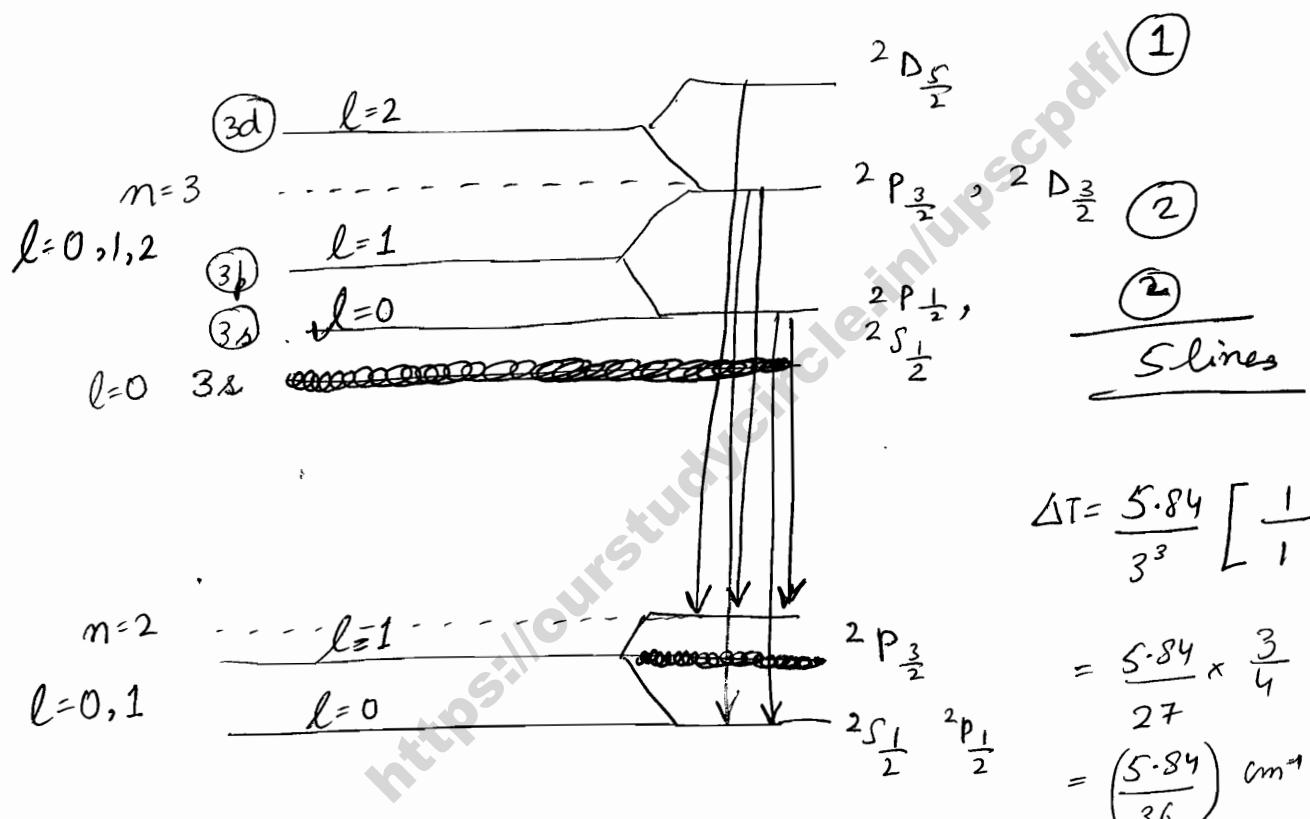
$H_\gamma : n=5 \rightarrow n=2$



$$\frac{1}{\lambda_{H\alpha}} = R \left[\frac{1}{2^2} - \frac{1}{3^2} \right] \Rightarrow \lambda_{H\alpha} = \left(\frac{36}{5R} \right)$$

But when I look at H_α using high resolution spectroscope, I can see 7 lines, not one.

Similarly H_β shows 12 lines that are not explained by Bohr's Model.



$$\begin{aligned}\Delta T &= \frac{5.84}{3^3} \left[\frac{1}{1} - \frac{8}{5} \right] \\ &= \frac{5.84}{27} \times \frac{3}{4} \\ &= \left(\frac{5.84}{36} \right) \text{ cm}^{-1}\end{aligned}$$

According to Dirac's Quantum Mechanical, we can explain **5** lines as ΔT only depends on j and n .

Hence, $2S\frac{1}{2}$ & $2P\frac{1}{2}$ have same ΔT .

Hence a contradiction??

This was explained by Lamb & Rutherford.

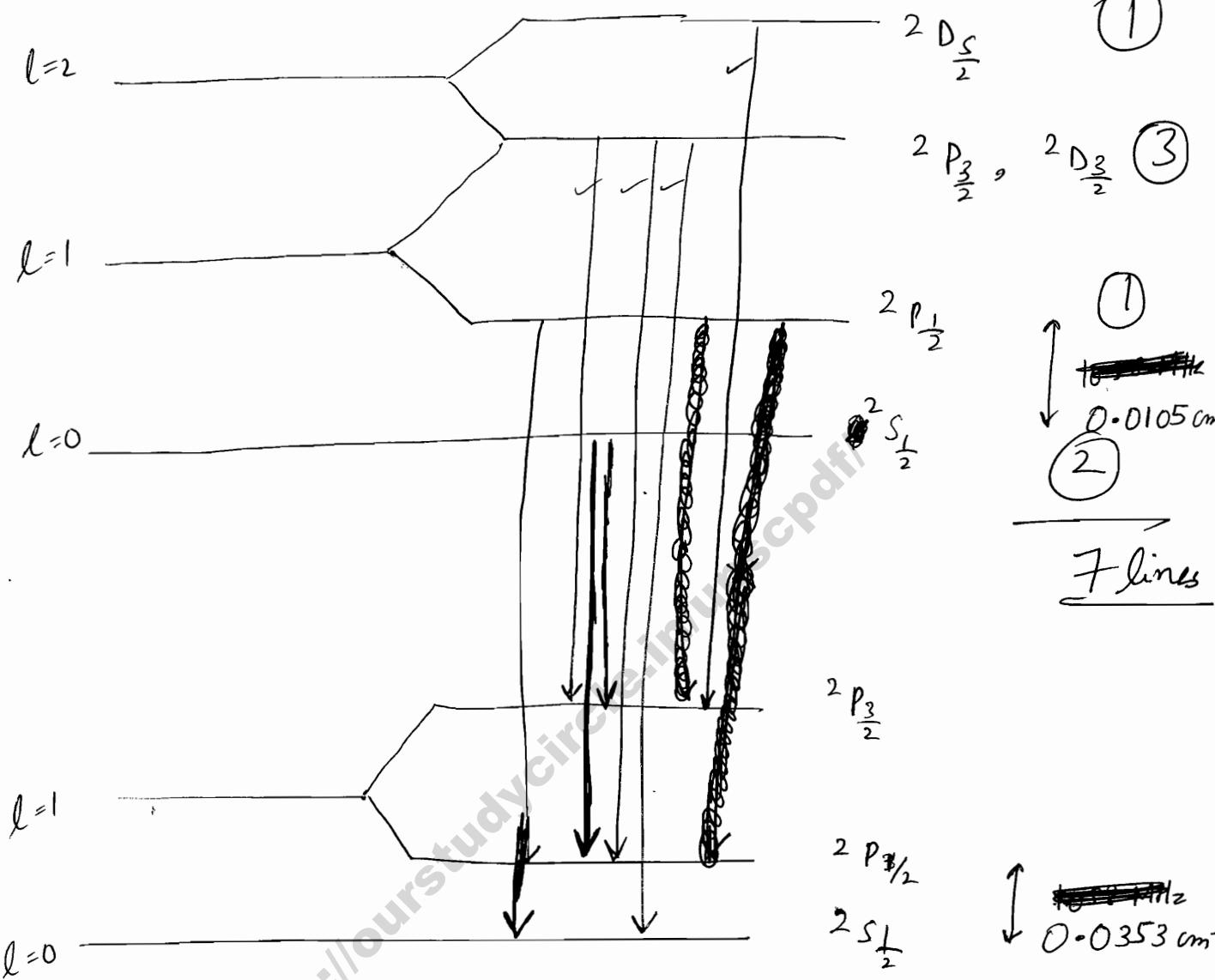
It is called LAMB SHIFT.

✓ It says $2S\frac{1}{2}$ and $2P\frac{1}{2}$ are non-degenerate for low l levels.

It does not change energy levels of $2P\frac{3}{2}$ and $2D\frac{3}{2}$

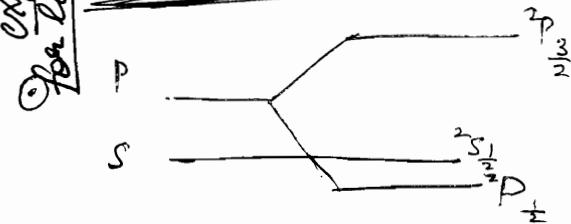
Now the diagram becomes

① Note that $\Delta l \neq 0$
it should be ± 1



① Lamb shift is observed in H like atoms i.e. single e- atoms.

For drawing spectra, EM radiation falls on atom.
It interacts with e- in vacuum, and exerts force. Due to this force, interaction of e- with nucleus is weakened, resulting into removal of degeneracy of lower l values.

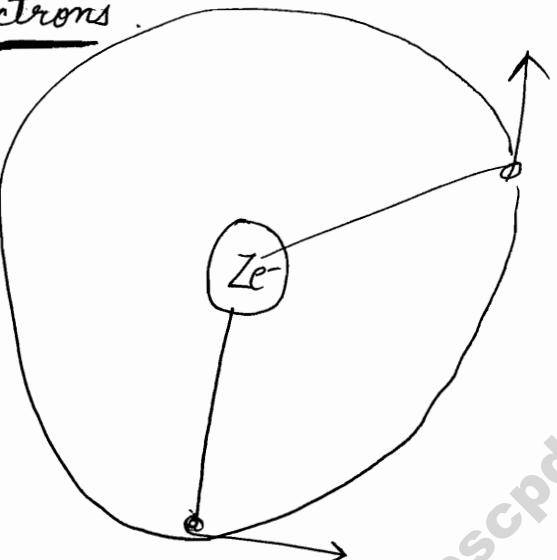


★ Note that in lamb shift, the level of $^2P_{\frac{3}{2}}$ energy is actually lower than $^2S_{\frac{1}{2}}$ energy.

LS and JJ Coupling (for many e⁻ atoms)

Phenomenon of many e⁻ atoms. Many e⁻ means many valency electrons.

Note that upto now, we were focusing on H-like atoms e.g. the formula for S-O interaction was derived for single electron atoms.



① $\vec{L}_{\text{net}} = \vec{L}_1 + \vec{L}_2$

It's called orbital-orbital interaction: electrostatic interaction

$$H = \frac{\vec{p}_1^2}{2m} + \frac{\vec{p}_2^2}{2m} + V(r_1, r_2) : \text{Unperturbed Hamiltonian}$$

$|\vec{L}_{\text{max}}| = |\vec{L}_1| + |\vec{L}_2|$: lowest energy (due to d_{max})
 All \vec{l} in same direction $\Rightarrow N+N+N \Rightarrow$ repulsion \Rightarrow low energy as $E \propto \frac{1}{d}$

$|\vec{L}_{\text{min}}| = |\vec{L}_1| - |\vec{L}_2|$: highest energy (due to d_{min})
 $\vec{l} \uparrow$ and other $\vec{l} \downarrow \Rightarrow N+S \Rightarrow$ attraction \Rightarrow more energy

② $\vec{S}_{\text{spin}} = \vec{s}_1 + \vec{s}_2$ Its called spin-spin interaction

$$S_{\text{min}} = s_1 - s_2 = 0 \quad \text{Max. Energy}$$

$$S_{\text{max}} = s_1 + s_2 \quad \text{Min. Energy} \rightarrow \text{These 3 are perturbations in } H$$

③ Spin-Orbit Interaction * Hence more 'l' or more 's' implies lesser energy. \therefore Order is ex. $\frac{1}{2} \leftarrow \frac{1}{2}$

Lighter Atom: C $1s^2 2s^2 2p^2$: Spin Orbit Coupling low Interaction

Heavier Atoms: skin Orbit ~~Coupling~~ high Interaction

L.S. coupling : also called Russel-Saunders Coupling

J.J. Coupling

① For lighter atom,
where spin-orbit
interaction is lowest.

$$\vec{S} = \vec{S}_1 + \vec{S}_2$$

$$|S_1 - S_2| \ll s < |S_1 + S_2|$$

$$\vec{L} = \vec{l}_1 + \vec{l}_2$$

$$|t_1 - \zeta| \leq l \leq |L_1 + \zeta|$$

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

$$F = \alpha [\overrightarrow{L} \cdot \overrightarrow{S}] \quad (\text{LS coupling})$$

$$|L-S| \leq J \leq |L+S|$$

Spin Orbit Coupling dominates over others, in heavier atoms.

$$\vec{h}_1 + \vec{s}_1 = \vec{J}_1$$

$$\vec{J}_1 + \vec{J}_2 = \vec{J}_2$$

$$\vec{r}_1 + \vec{r}_2 = \vec{r}$$

$$|\vec{J}_1 - \vec{J}_2| < |\vec{J}| < \|\vec{J} + \vec{J}_2\|$$

Individual e^- 's angular momenta couple and form whole angular momentum of atom. It's called ~~$\sum J_J$~~ J coupling.

$S = \frac{1}{2}$: Fermion

$2p$ $3p$: Terms due to

LS Coupling

$$2p: \quad l_1=1 \quad \quad s_1=\frac{1}{2}$$

$$3 \nmid: \ell_2 = 1 \quad s_2 = \frac{1}{2}$$

Triplet lies below singlet ~~s=0~~ s=1

$$S=0, \quad \begin{matrix} 1 \\ \downarrow \\ 3 \end{matrix}$$

$$\sigma=1, \quad \begin{matrix} \downarrow \\ \text{Singlet} \end{matrix}, \quad \begin{matrix} \downarrow \\ \text{Triplet} \end{matrix}$$

Boson

Note that S was never 0 in single e⁻ atoms.

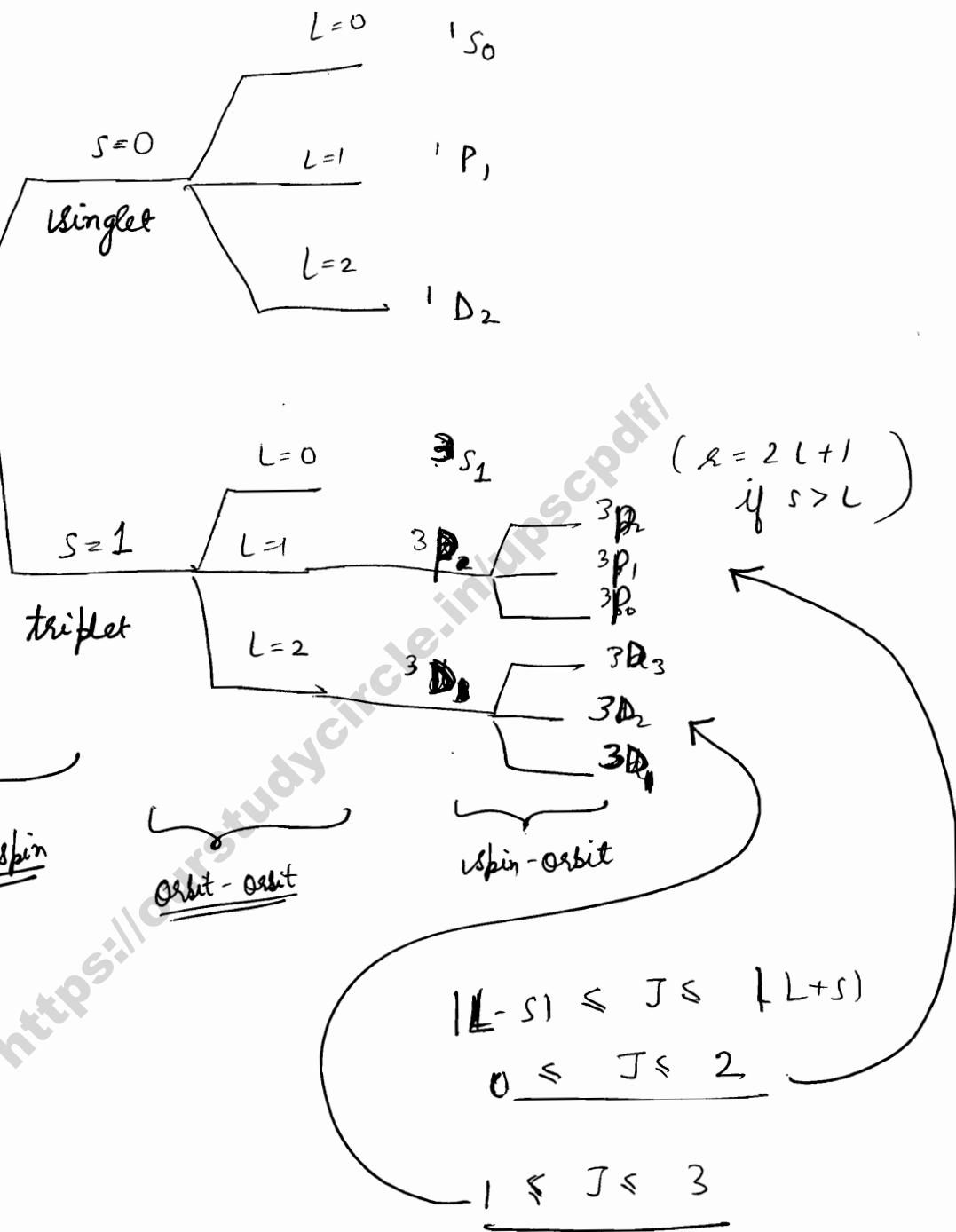
$$L = l_1 + l_2$$

$$= 0, 1, 2$$

$$|l_1 - l_2| \leq L \leq (l_1 + l_2)$$

$$0 \leq L \leq 2$$

★ Note that total number of possible states of $(2p, 3p)$ are $6 \times 6 = 36$. Apply Zeeman Effect and count... final states will be $3^6 = 729$ all will be non-degenerate
For LS coupling, every state has degeneracy $= (2j+1)$.



* In final Spin Orbit Coupling, order is according to j

★ Note that here ' $L=1$ ' or ' $L=2$ ' has no meaning w.r.t. subshell l . It just means |addition of m_l 's|

★ Note that spin-orbit interaction studied for He was a special case of general LS coupling.

① $1s^2 \underbrace{2s^2 2p^6}_{\text{Completed subshells}} 3s^2 3p^2$

b.d

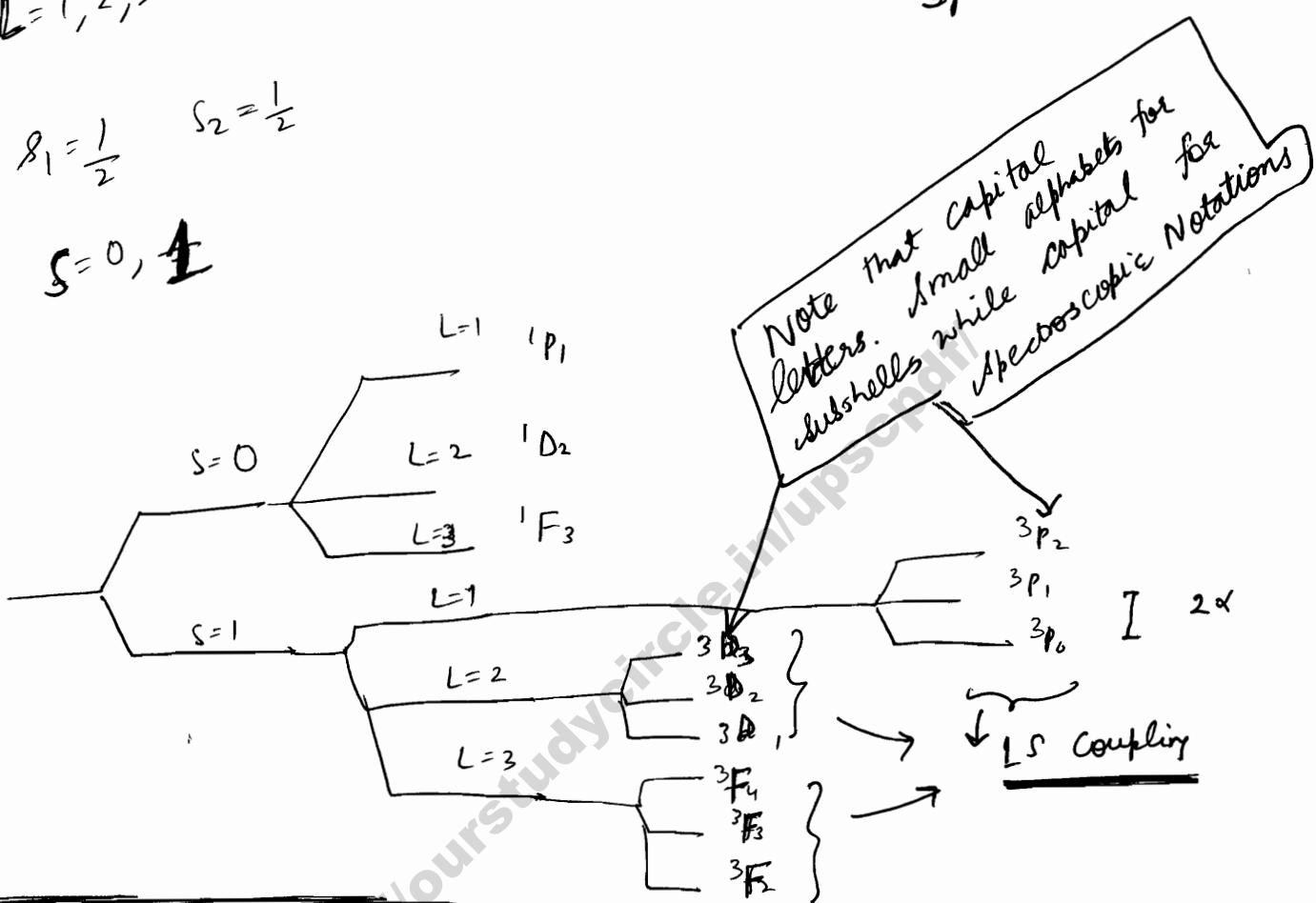
$$l_1 = 1 \quad l_2 = 2$$

$$L = 1, 2, 3$$

$$S_1 = \frac{1}{2} \quad S_2 = \frac{1}{2}$$

$$S = 0, \pm 1$$

Completed subshells
No contribution to \vec{l} or \vec{s}
Only Contribution from $3p^2$ electrons.



LANDÉ'S INTERVAL RULE

$$E = \alpha L \cdot S$$

$$= \alpha [J(J+1) - L(L+1) - S(S+1)]$$

The relative spacing of the fine structure levels within a multiplet is governed by Landé Interval Rule.

$$\begin{aligned} E_{(J+1)} - E_{(J)} &= \alpha [(J+1)(J+2) - J(J+1)] \\ &= 2\alpha [J+1] \end{aligned}$$

i.e.

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

★ Energy interval or spacing between consecutive levels J and $J+1$ of a fine-structure multiplet is proportional to $(J+1)$, that is, to the larger of the 2 J values involved.

L-S Coupling selection rules:

$$\Delta L = 0, \pm 1$$

$$\Delta J = 0, \pm 1$$

$$\Delta S = 0$$



proportional to $(J+1)$, that is, to the larger of the 2 J values involved.

Spectral terms of equivalent electrons due to LS coupling

b^2 : n and l are same for both
 m_l and m_s will be different to follow Pauli's exclusion principle.

$$\vec{s} = s_1 + s_2 = 0, 1$$

$s=0$: m_s values for both e^- are different

$$m_1 = \left(\frac{+1}{2}\right) \quad m_2 = \left(-\frac{1}{2}\right)$$

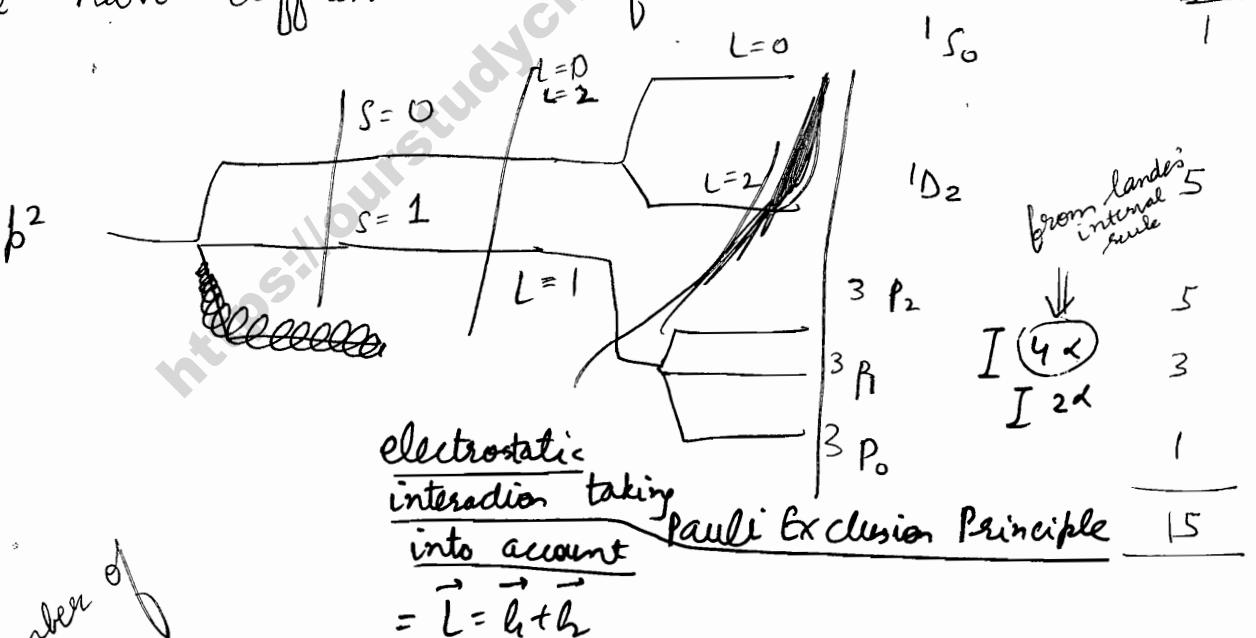
$s=1$: m_s values same

$$L = l_1 + l_2 = 0, 1, 2$$

Along with $s=1$, only that values of L will go that will have different values of m_L .

Multiplet terms of
 $b^2 \leftrightarrow b^4$
 $d^4 \leftrightarrow d^6$
 $(nl)^2 \leftrightarrow (ne)^{n-2}$

n : maximum no. of electron in l subshell

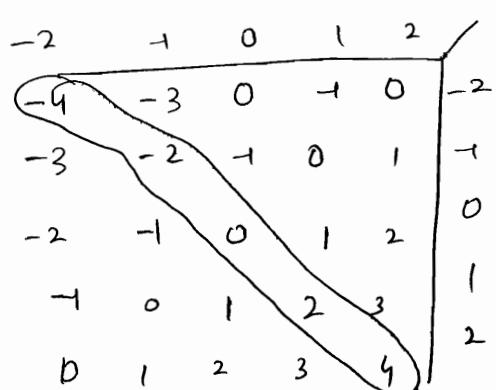
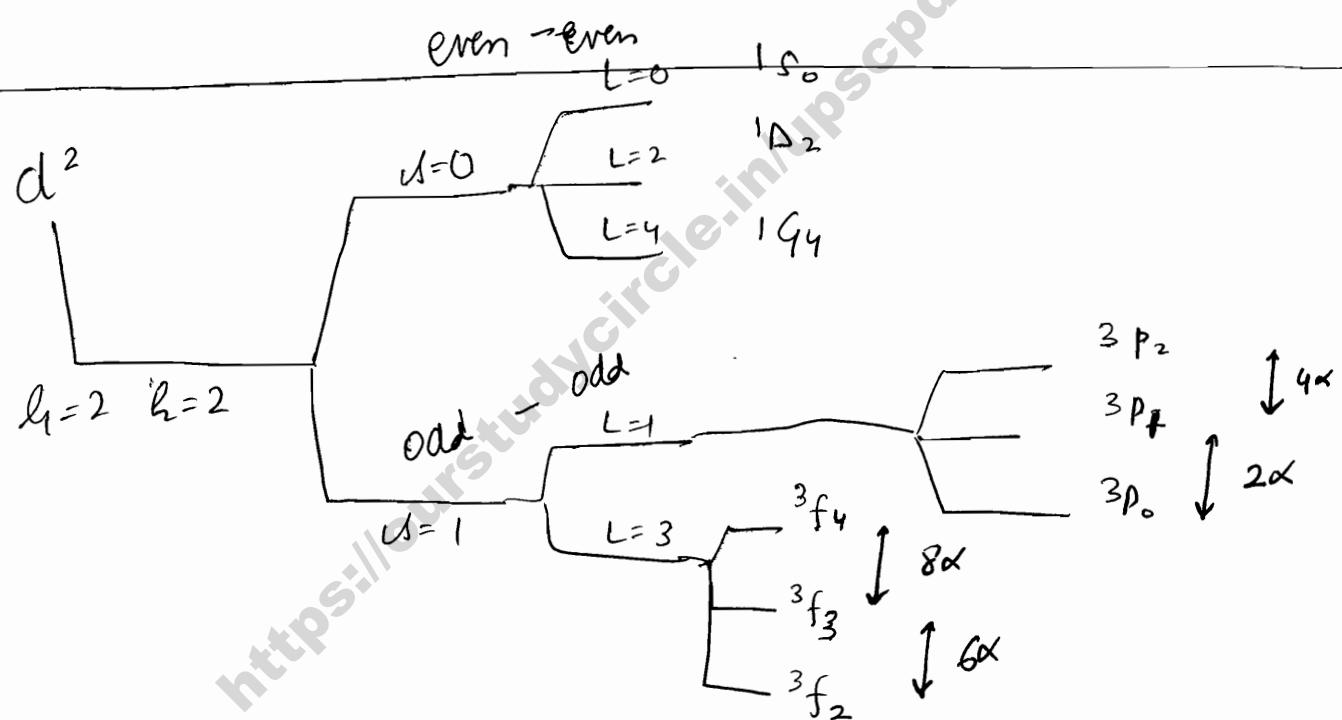
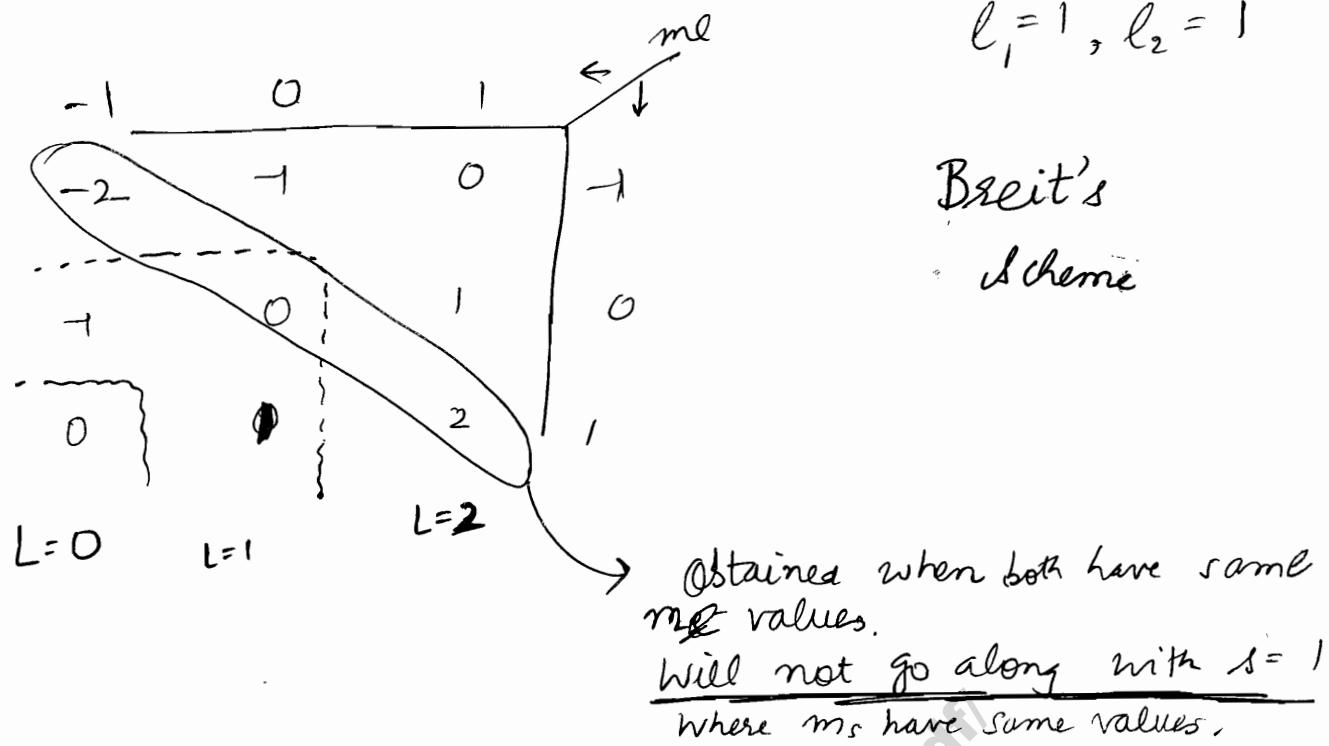


$$\vec{J} = \vec{L} + \vec{s}$$

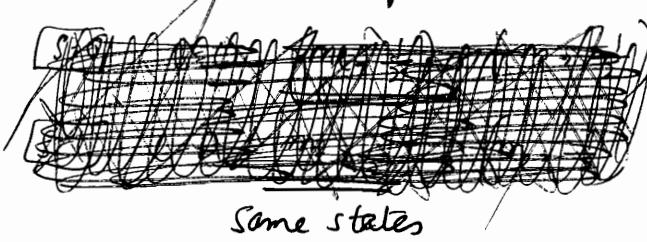
LS coupling

Total number of possibilities are $n^2 m^2$.
 For $1s^2$, 1^0
 For $2p^6$, 6^0
 For $2e^-$, 6^0
 For $2e^-$, 6^0
 For $2e^-$, 6^0
 For $2e^-$, 6^0

(can be seen from $(2e^-)^6$)



★ Note that in p_0 or $2p\ 3p$ LS coupling, we could associate all l values with every S . But here we can not. If we try to associate $l=1$ and 3 with $s=0$, in the above example, e^- with same quantum states will result.



A & M Physics (4)

J-J coupling

★ For heavier atoms, for which the spin-orbit (magnetic) interaction term in Hamiltonian predominates over the residual electrostatic interaction and the spin-spin correlation.

~~J-L coupling occurs~~. $\vec{J}_1 = \vec{l}_1 + \vec{s}_1$

It occurs for heavier elements
when spin-orbit coupling dominates
other types of interaction

e.g. $4p\ 5d$

$$n_1=4 \quad l_1=1 \quad s_1=\frac{1}{2} \quad \Rightarrow \quad J_1 = \frac{1}{2}, \frac{3}{2}$$

$|L-S| \rightarrow |L+S|$

\uparrow
 J variation

$$n_2=5 \quad l_2=2 \quad s_2=\frac{1}{2} \quad \Rightarrow \quad J_2 = \frac{3}{2}, \frac{5}{2}$$

★ We cannot write finally common integral J terms as even 'same J ' terms are distinct $\boxed{J : (\frac{1}{2}, \frac{3}{2})}$

Combinations

$$(\frac{1}{2}, \frac{5}{2})$$

$$(\frac{3}{2}, \frac{3}{2})$$

$$(\frac{3}{2}, \frac{5}{2})$$

★ Each of the four levels is further splitted by $J=1, 2$ residual electrostatic interaction and spin-spin correlation into a no. of integral J levels.

$$J=0, 1, 2, 3$$

$$J=1, 2, 3, 4$$

Selection rule for J-J coupling:

$$\textcircled{1} \quad \Delta J = 0, \pm 1$$

$$J=0 \leftrightarrow J=0$$

that is....

No rule for $\Delta S, \Delta L$ as they are no longer good quantum numbers

$$|J_1 - J_2| \leq J \leq (J_1 + J_2)$$

★ Pure J-J coupling occurs relatively seldom. In fact, there is gradual shift from L-S coupling for lighter atoms towards J-J coupling for heavier atoms. show J-J coupling.

After Carbon, atoms typically

Zeeman Effect

Behaviour of atom in external weak/ intermediate magnetic field.

$$E = -\vec{\mu} \cdot \vec{B} = \omega_p \cdot J_z$$

If Field is external \Rightarrow Zeeman Effect
(Internal ~~at~~ spin-orbit interaction)

$$\omega_p = \frac{e}{2m} g B$$

[Angular Velocity of LARMER PRECESSION]

$$\Rightarrow E = \frac{e}{2m} g B m_j \downarrow$$

$$E = \mu_B g B m_j$$

Note that we have taken vector model i.e. combined L and S and taken J .

Note that if field is strong, it's called Paschen Block Effect.

Hence Perturbation $\Delta E = \mu_B B (g m_j)$

Selection Rule comes out to be:

$$\Delta m_j = 0, \pm 1$$

π component

σ components

linearly polarized

For complete answer, we have to mention selection rule.

have sublevels

* Note that spectroscopic notation represented levels. Now, in Zeeman effect, we have sublevels. One energy level is split into $(2J+1)$ sublevels. Transition b/w them will lead to different components.

→ There are 4 types of Zeeman Effect:

Transverse Zeeman Effect :

↑
Perpendicular
→
→

Spectra is viewed perpendicular to direction of applied magnetic field.

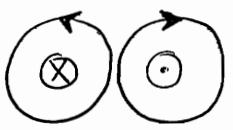
It will give plane polarized π and σ components

$$\Delta m = 0, \pm 1$$

Longitudinal Zeeman Effect :

↑
Parallel

Spectra is viewed parallel to direction of applied magnetic field.



It will give circularly polarized components.

RCP and LCP

$$\Delta m_j = \pm 1$$

Normal Zeeman Effect

Non Spin Effect. i.e. occurs in atoms where $S=0$ i.e. cannot occur in single e- atoms. Atoms should have even electrons. (necessary but not sufficient condition)

In 1896, Peter Zeeman observed it in Zn and Cd.

It could be transverse or longitudinal depending upon angle of viewing. It is rare.

Anomalous Zeeman Effect : Could be both but typically

transverse. S is non zero.

It is more common and most general case. We will explain this in detail.

Quantum Mechanical Explanation

$$\text{if } \vec{L} \Rightarrow \mu_L = -\frac{e}{2m} \vec{L}$$

$$\text{if } \vec{S} \Rightarrow \mu_S = -\frac{e}{2m} 2\vec{S}$$

$$\begin{aligned} \vec{\mu} &= \vec{\mu}_L + \vec{\mu}_S \\ &= -\frac{e}{2m} (\vec{L} + 2\vec{S}) \end{aligned}$$

$$T = \vec{\mu} \times \vec{B} = -\frac{e}{2m} [(\vec{L} \times \vec{B}) + (2\vec{S} \times \vec{B})]$$

Both precess about \vec{B}

* We know \vec{L} and \vec{S} couple to form \vec{j} and \vec{j} precesses about \vec{B} . But in strong field, this coupling breaks down and the 2 components \vec{L} & \vec{S} individually precess about \vec{B} !!

$$= -\frac{e}{2m} [(\vec{L} \times \vec{B}) + (2\vec{S} \times \vec{B})]$$

Both will individually precess about \vec{B}



$$W = -\vec{\mu} \cdot \vec{B} = \frac{e}{2m} (\vec{L} \cdot \vec{B} + 2\vec{S} \cdot \vec{B})$$

$$= \frac{e\hbar B}{2m} (m_L + 2m_S) = \mu_B B (m_L + 2m_S)$$

This is Paschen Beck Effect

But Zeeman Effect has :

$$\vec{\mu} = -\frac{e}{2m} (\vec{L} + \vec{S} + \vec{s})$$

$$= -\frac{e}{2m} (\vec{J} + \vec{s})$$

We are interesting in $\vec{\mu}_J$ because in weak field, $\vec{\mu}_L$ and $\vec{\mu}_S$'s are individually non-existent, and therefore, their combination i.e. \vec{J} causing $\vec{\mu}_J$ exists.

[L-S coupling : a weak field effect]

★ Note that $\vec{\mu}$ is not parallel to \vec{J} but we are interested in $\vec{\mu}_J$ i.e. component of $\vec{\mu}$ along \vec{J} ...

[In strong field, they will individual process]

In strong field, Coupling will break down and \vec{L} and $2\vec{S}$ will individually process

$\vec{J} = \vec{L} + \vec{S}$: Vector model of atom

This model is applied in Zeeman Effect i.e. weak field.

$$\vec{\mu}_J = (\vec{\mu} \cdot \hat{\vec{J}}) \hat{\vec{J}}$$

$$\vec{T} = \vec{\mu}_J \times \vec{B} = \mu_J B \sin\theta$$

$$d\omega = T d\theta = \mu_J B \sin\theta d\theta$$

$$E = -\vec{\mu}_J \cdot \vec{B} = -(\mu_J)_z B = \mu_B B g m_j$$

$$\vec{\mu}_J = (\vec{\mu} \cdot \hat{J}) \hat{J} = -\frac{e}{2m} \left[\frac{(\vec{J} + \vec{S}) \cdot \vec{J}}{|\vec{J}|^2} \right] \vec{J}$$

$$= -\frac{e}{2m} \left[\frac{|\vec{J}|^2 + (\vec{S} \cdot \vec{J})}{|\vec{J}|^2} \right] \vec{J}$$

$$= -\frac{e}{2m} \left[1 + \frac{(\vec{S} \cdot \vec{J})}{|\vec{J}|^2} \right] \vec{J}$$

Note that $\vec{\mu}$ is not antiparallel to \vec{J} , but we are interested in only antiparallel component of $\vec{\mu}$ i.e $\vec{\mu}_J$ b'coz other components avg. to 0

$$\begin{cases} \vec{L} = \vec{J} - \vec{S} \\ \vec{L} \cdot \vec{L} = (\vec{J} - \vec{S}) \cdot (\vec{J} - \vec{S}) \\ \Rightarrow \vec{S} \cdot \vec{J} = \frac{J^2 + S^2 - L^2}{2} \end{cases}$$

due to L-S coupling

Now all are quantized

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

$$S^2 = s(s+1) \hbar^2$$

$$L^2 = l(l+1) \hbar^2$$

refer to
derivation

on
p- 205, 206

$$= -\frac{e}{2m} \left[1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right] \vec{J}$$

$$\vec{\mu}_J = -\frac{e}{2m} g_J \vec{J}$$

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

The importance of the g factor is that it directly gives the relative separation of Zeeman levels for different terms.

$$\Rightarrow \vec{\mu}_L = -\frac{e}{2m} g_L \vec{L}$$

$$\vec{\mu}_S = -\frac{e}{2m} g_S \vec{S}$$

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

$$\Rightarrow \vec{\mu}_J = -\frac{e}{2m} g_J \vec{J}$$

$$g_J = 1 + \left[\frac{J(J+1) + s(s+1) - L(L+1)}{2J(J+1)} \right]$$

$$4D_1 \xrightarrow{\frac{1}{2}} \Rightarrow g = 0$$

for purely orbital motion, $s=0$ & $j=l$

$$\Rightarrow g_J = 1 + \frac{0}{l(l+1)} = 1$$

for purely spin motion, $l=0$ & $j=s$

$$g_J = 1 + \frac{2s(s+1)}{2s(s+1)} = 2$$

If \vec{J} precesses $\Rightarrow \vec{\mu}_J$ will precess as $\vec{\mu}_J$ is antiparallel to \vec{J} .

\vec{J} precesses about $\vec{B} \Rightarrow \vec{\mu}_J$ precessing about \vec{B} and

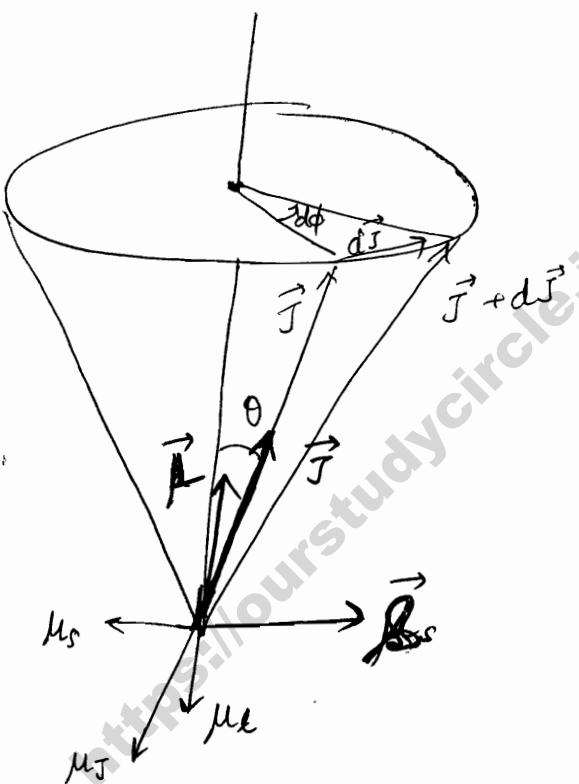
$$J_z = mj\hbar$$

$$E = \omega_p J_z$$

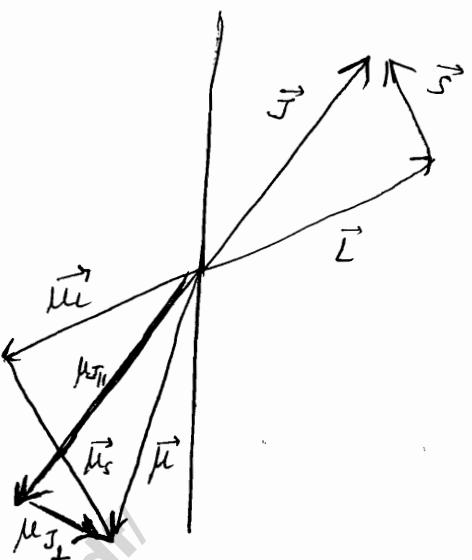
$$= \frac{e}{2m} g_B B J_z$$

$$= \left(\frac{e\hbar}{2m} \right) g_B B m_j$$

$$E = \mu_B B (g_B m_j)$$



We should take $\Delta E = \vec{\mu} \cdot \vec{B}$
and not $\Delta E = \vec{\mu}_J \cdot \vec{B}$
But we have taken so. Why?



$\vec{\mu} \parallel -\vec{J}$ because

$$\vec{\mu} = \frac{e}{2m} [\vec{L} + 2\vec{S}]$$

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

But, \vec{L} , \vec{S} , $\vec{\mu}_J$, $\vec{\mu}_S$ and
therefore $\vec{\mu}$ all precess
about \vec{J} .
(\vec{J} in turn precesses about \vec{B})

$$\Rightarrow \vec{\mu} = \vec{\mu}_{J_{||}} + \vec{\mu}_{J_{\perp}}$$

The $\vec{\mu}_{J_{\perp}}$ averages to zero
due to the precession motion.

$$\Rightarrow \Delta E = \vec{\mu}_{J_{||}} \cdot \vec{B}$$

$$E = -\vec{\mu}_J \cdot \vec{B} = \frac{e}{2m} g_J B J_z$$

$$= \frac{e\hbar}{2m} g_J B m_j$$

$$E = \mu_B B (g_J m_j)$$

Normal Zeeman Effect

$$E = \mu_B B \quad g = m_J$$

Normal
Zeeman
Effect

$$\Delta E = \mu_B B \quad \Delta m_J$$

(if $s=0$)
i.e. $g_J = g_e = 1$

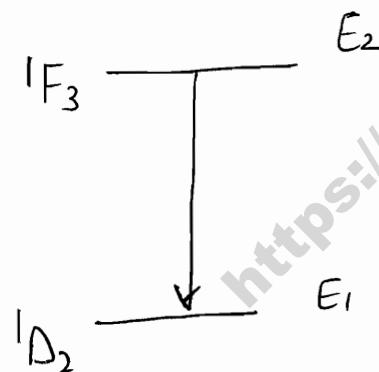
$$\Delta m_J = 0, \pm 1$$

Transverse Normal Zeeman Effect : $\pi, 2\sigma$
3 Components

Longitudinal Normal Zeeman Effect: 2 circularly polarized components

Anomalous Zeeman Effect: 1 line is split into several components.

Q) Draw Zeeman pattern of $^1F_3 \rightarrow ^1D_2$



Now in presence of B , it will split into $(2J+1)$ sublevels.

$$(2s+1) = 1 \Rightarrow s=0$$

Hence Normal Zeeman Pattern

$$\Rightarrow J=l=3 \quad \text{for } ^1F_3$$

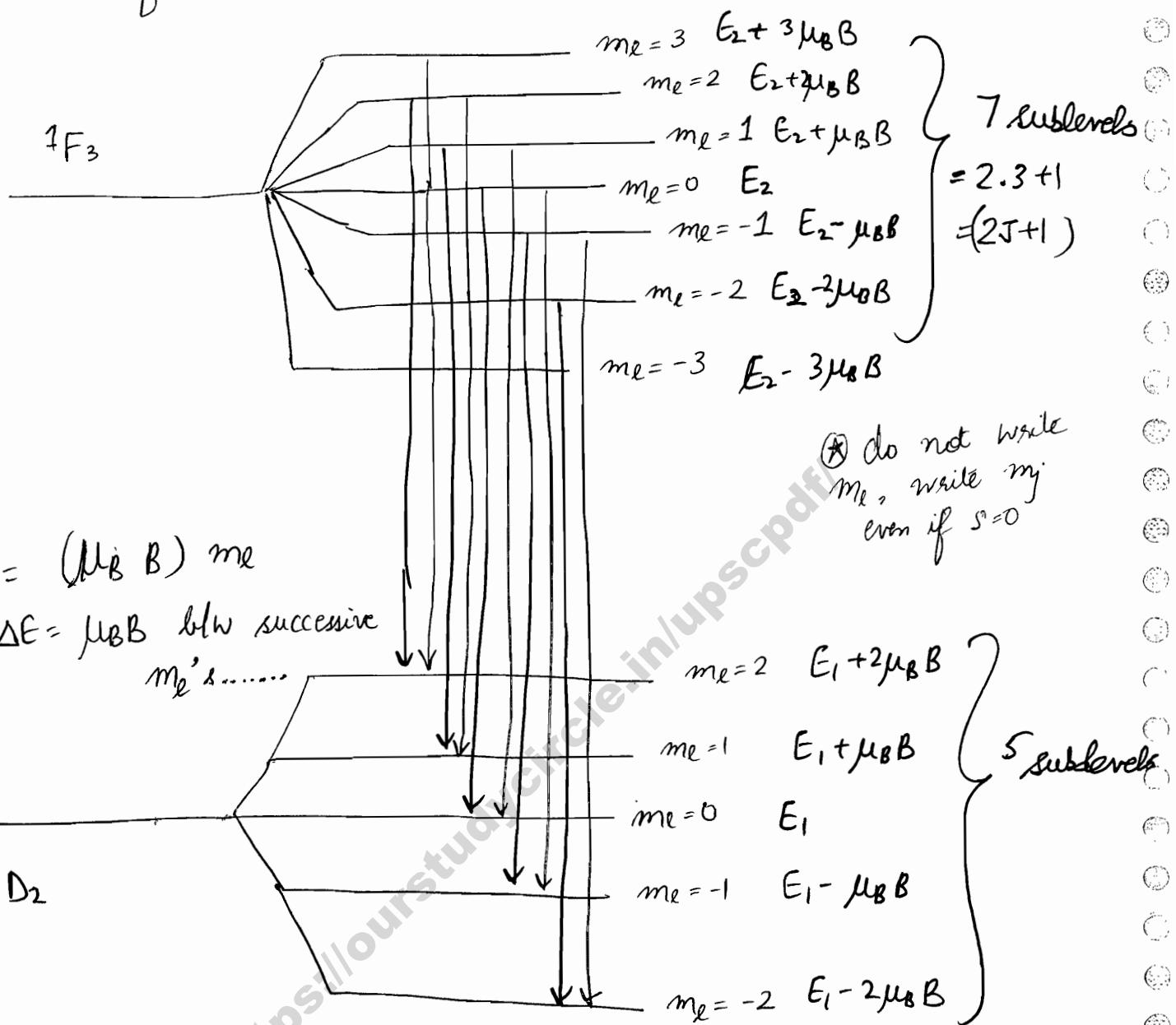
$$J=l=2 \quad \text{for } ^1D_2$$

★ π Component : \vec{E} parallel to External Magnetic Field II

σ Component : \vec{E} perpendicular to External Magnetic field □

★ Intensity ratio are derived from Correspondence principle.
i.e. σ Components together have same intensity as π Component.

Energy level will split into $(2J+1)$ levels in presence of external field.

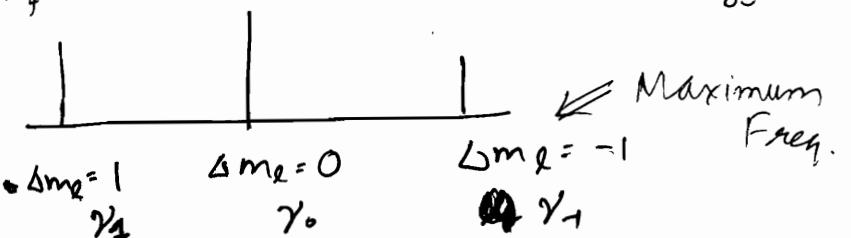


(*) Note that
is allowed!!

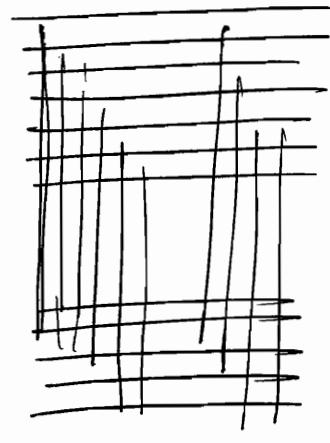
$\Delta m_e = 0, \pm 1$

For all red lines, $\Delta E = (E_2 - E_1)$, hence only 1 line in spectrogram. It corresponds to $\Delta m_e = 0$

Green : $m_f - m_i = -1$: It has maximum energy.



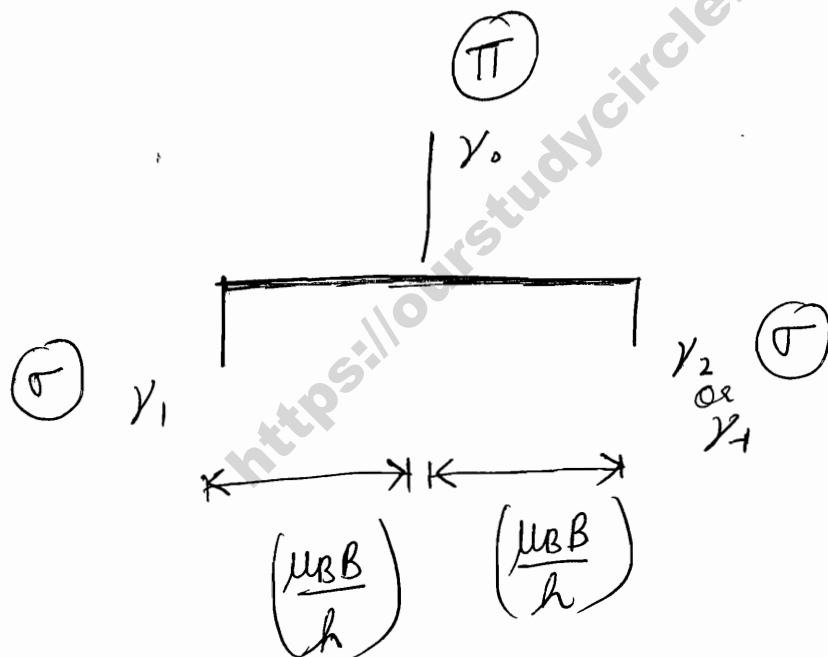
⑥ In exam ~~draw~~ draw more energy lines on right and less energy lines on left.



$$\gamma_0 = \frac{\Delta E}{\hbar} = \left(\frac{E_2 - G}{\hbar} \right)$$

$$\gamma_{-1} = \frac{\Delta E}{\hbar} = \frac{E_2 - G}{\hbar} + \frac{\mu_B B}{\hbar}$$

$$\gamma_1 = \frac{\Delta E}{\hbar} = \frac{E_2 - G}{\hbar} - \frac{\mu_B B}{\hbar}$$



⑥ Π represented above horizontal line while

σ are represented below this line.....

In longitudinal, γ_0 will be missing

$$\text{Zeeman Shift} = \frac{\mu_B B}{\hbar} = \left(\frac{eB}{4\pi m} \right)$$

① Note that irrespective of no. of transitions, there are 3 components in Zeeman Effect, where $S=0$.

We can calculate B from this Zeeman Shift.

Anomalous Zeeman Pattern

① Zeeman Effect of Sodium lines D_1 and D_2

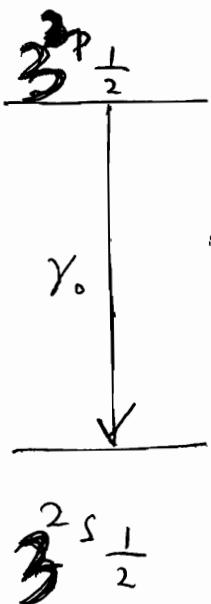
D_1 : 4 components

D_2 : 6 components

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

$$^2P_{\frac{3}{2}} \rightarrow ^2S_{\frac{1}{2}}$$

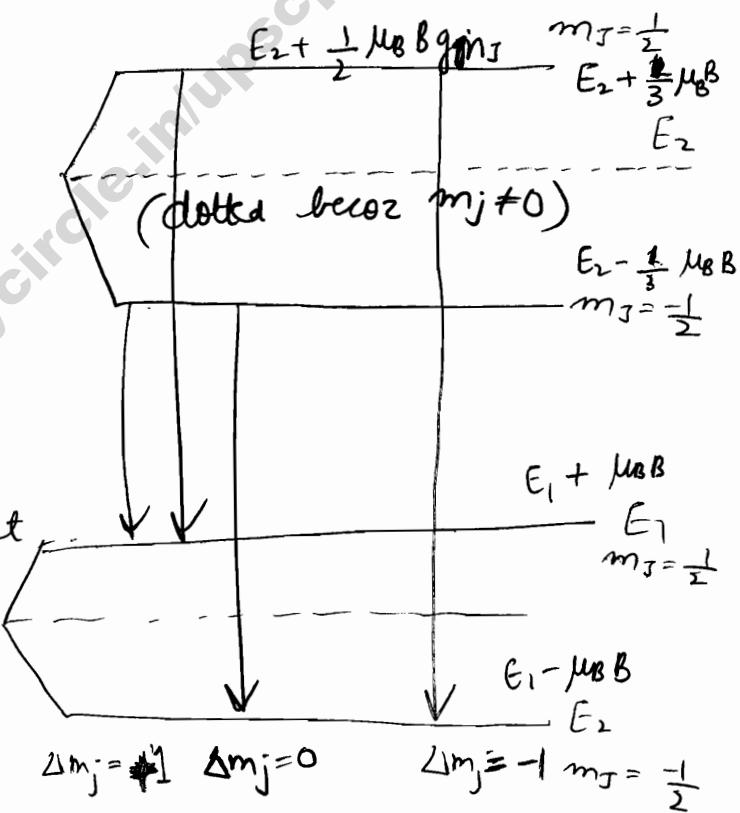
D_1 line



Now \vec{B} is applied

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

\Rightarrow Anomalous Zeeman Effect



Now note that $E = -\mu_B B(g m_J)$

We have to take g into account for both levels

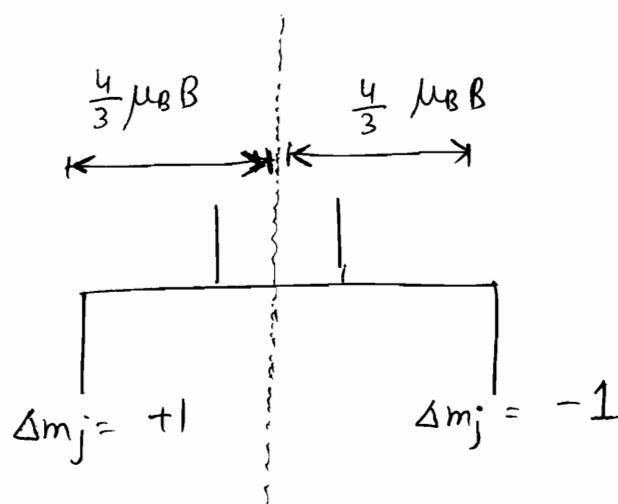
Hence 2 different components for $\Delta m_J = 0$

$$g(^2S_{\frac{1}{2}}) = 2$$

$$g(^2P_{\frac{1}{2}}) = 1 + \left(\frac{\frac{1}{2} \cdot \frac{3}{2} + \frac{1}{2} \cdot \frac{3}{2} - 1 \cdot 2}{2 \cdot \frac{1}{2} \cdot \frac{3}{2}} \right) \\ = 1 + \frac{\frac{3}{4} + \frac{3}{4} - 2}{\frac{3}{2}} = 1 - \frac{1}{3} = \frac{2}{3}$$

$$\gamma_1 = \gamma_0 - \frac{4}{3} \mu_B B$$

D₁: ESR line
D₂: EFT line



Reference line
Corresponding to D₁ line.

★ $\gamma_1 = \gamma_0 - \frac{4}{3} \frac{\mu_B B}{h}$ Δm = +1

$$\gamma_2 = \gamma_0 - \frac{2}{3} \left(\frac{\mu_B B}{h} \right) \quad \} \quad \Delta m = 0$$

$$\gamma_3 = \gamma_0 + \frac{2}{3} \left(\frac{\mu_B B}{h} \right)$$

$$\gamma_4 = \gamma_0 + \frac{4}{3} \left(\frac{\mu_B B}{h} \right) \quad \} \quad \Delta m = -1$$

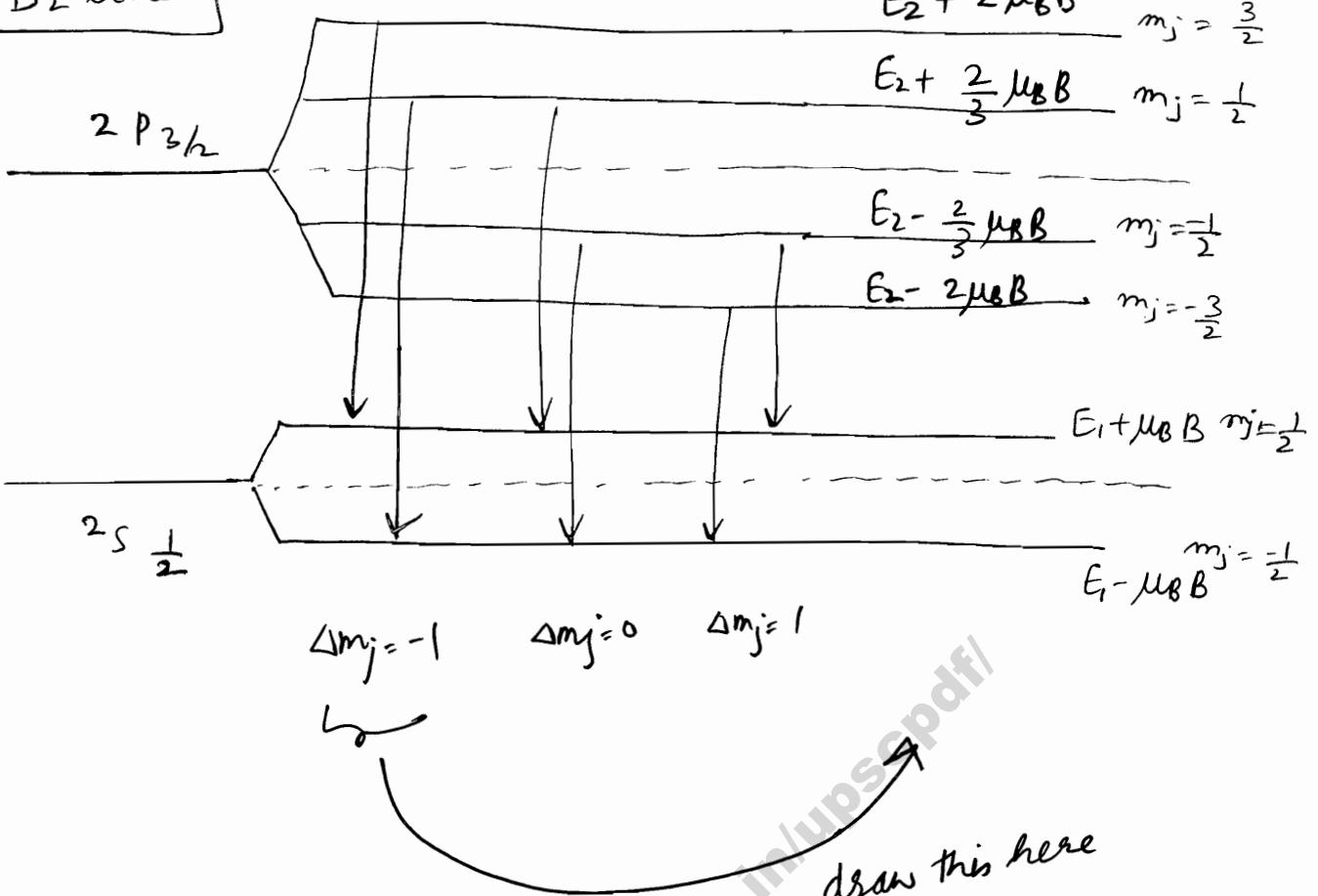
Selection rule for Zeeman:

$$\Delta m = 0, \pm 1$$

$$M_j = 0 \leftrightarrow M_j = 0 \text{ if } \Delta J = 0$$

e.g. ${}^3P_1 \rightarrow {}^3S_1$ transition

D₂ line



$$\begin{aligned}
 g(\text{ }^2\text{P}_{\frac{3}{2}}) &= 1 + \frac{\frac{3}{2} \cdot \frac{5}{2} + \frac{1}{2} \cdot \frac{3}{2} - 1 \cdot 2}{2 \cdot \frac{15}{4}} \\
 &= 1 + \frac{\frac{15}{4} + \frac{3}{4} - \frac{8}{4}}{\frac{15}{4}} = 1 + \frac{\frac{10}{4}}{\frac{15}{4}} = 1 + \frac{2}{3} = \left(\frac{4}{3}\right)
 \end{aligned}$$

★ Note that selection rules do not absolutely prohibit transitions that violate the rule, but only make such transitions very unlikely.

★ Spin has no classical analogue. It's a purely quantum concept and any spatial motion is accounted as part of orbital angular momentum. If e⁻ is considered as a charged body rotating about its own axis, then such magnitude of momentum (angular) would demand the equatorial velocity of spinning electron to be much greater than c. i.e. $v_{eq} \gg c$ which is not possible.

★ Spectroscopy is that branch of Physics which deals with the observation and interpretation of radiation emitted and absorbed by atoms and molecules, thereby, throwing light on their structure.

★ Rydberg - Ritz Combination Principle says that the wave number of spectral lines can be expressed by the difference of spectroscopic terms in such a way that other differences of these terms also give the wave numbers of lines in the same spectrum.

★ Allowed transitions are governed by Laporte's rule which says that in an electric dipole transition, the parity of the state of the atom must change.

Proof Transition Rate for x -component of dipole moment = $\langle \psi_f | A_{xi} | \psi_i \rangle$

$$= \int_{-\infty}^{\infty} \psi_f^* \left(\sum_j e_j x_j \right) \psi_i dx$$

Let's say ψ_i : even

Now if $\sum_j e_j x_j$ is odd function

\Rightarrow if ψ_f is even \Rightarrow integrand = 0

$\Rightarrow \psi_f$ is odd

and vice versa.

Hence Parity will undergo change.

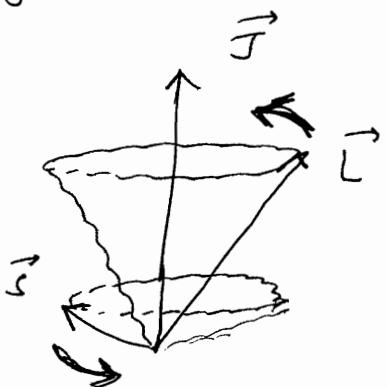
★ \vec{L} can never be aligned exactly parallel to \vec{B} as $|m_L|$ is always less than $\sqrt{l(l+1)}$

★ It has been concluded from experimental data that the gyromagnetic ratio for electron spin is twice the corresponding ratio for orbital angular momentum i.e. $\frac{\mu_s}{s} = 2 \left(\frac{\mu_e}{l} \right) \Rightarrow g_s = 2 g_e \left(\because \frac{-e}{2m} \text{ is same } g \text{ factor} \right)$

★ Spin Orbit Interaction

Angular Momenta of atomic electron, \vec{L} and \vec{s} interact magnetically, which is known as spin orbit interaction.

They exert torques on each other. These internal torques do not change the magnitudes of the vectors \vec{L} and \vec{s} but cause them to precess about their result \vec{J} . If atom is in free space and no external torque acts, then total angular momentum \vec{J} remains conserved.



$$J^2 = L^2 + s^2 + 2(\vec{L} \cdot \vec{s})$$

Spin Orbit Interaction, together with relativistic correction, explains the Hydrogen Fine structure.

[Lamb Shift Phenomenon is also observed in fine structure]

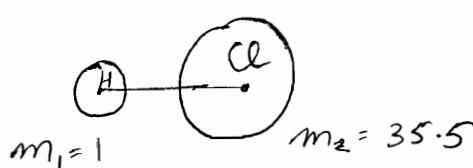
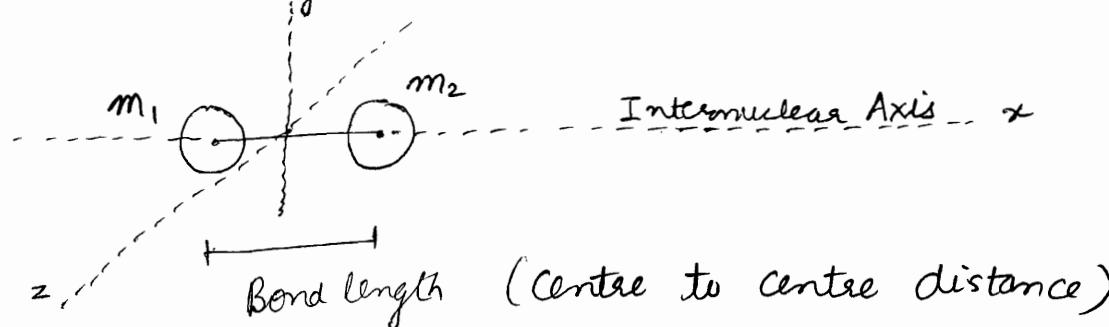
- ★ Energy levels expressed in wave numbers are called terms.
- ★ The "state" of an atom is the condition of motion of all the electrons. It is specified by listing four quantum numbers of each electron.
- ★ Energy level : A collection of states having the same energy, in the absence of external magnetic or electric field constitutes an 'energy level'.
- ★ Energy Sublevel : An external field splits any energy level into several sublevels, each characterized by one or more magnetic quantum numbers.
- ★ Multiplet is a collection of spectral lines or transitions between two terms, eg 6 components comprise D2 multiplet of Na ${}^2P_{3/2} \rightarrow {}^2S_{1/2}$

Molecular Physics (1)

24/02/2012

ROTATIONAL SPECTRA

- We study diatomic molecules and generalize the results.



$$\bar{\omega} = [I_e' + G(v) + F(v, J)] - [I_e'' + G''(v) + F''(v, J)]$$

Remember the notations...

Thank God, [its] Friday

Symmetric : $I_{yy} = I_{zz}$

Asymmetric Molecules : $I_{yy} \neq I_{zz}$

Spherical Top : $I_{xx} = I_{yy} = I_{zz}$

Rigid rotator molecules : 'r' (Bond length) is fixed i.e. no stretching along internuclear axis.

At first at a particular vibrational mode it's rotation about internuclear axis is fix

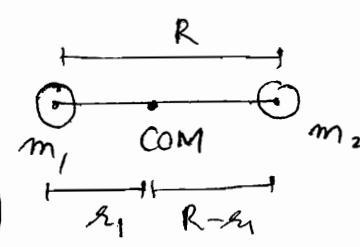
about internuclear axis is negligible. Rotation is possible only along line passing through Centre of Mass, and \perp to internuclear axis.

→ Locating COM,

Now we know,

$$m_1 s_1 = m_2 (R - s_1)$$

$$s_1 = \left(\frac{m_2 R}{m_1 + m_2} \right) \Rightarrow R - s_1 = \left(\frac{m_1 R}{m_1 + m_2} \right)$$



① For rigid rotator,

$$I_{CM} = m_1 s_i^2 + m_2 (R - s_i)^2 = \frac{m_1 m_2 R^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2 R^2}{(m_1 + m_2)^2}$$

~~$m_1 + m_2$~~ ~~s_i^2~~ ~~R^2~~ ~~m_1^2~~

$$= \frac{m_1 m_2 R^2}{(m_1 + m_2)}$$

$$= \left(\frac{m_1 m_2}{m_1 + m_2} \right) R^2$$

$I_{CM} = \mu R^2$

R: Bond length

$$J_{CM} = \mu s^2 \omega = I_{CM} \omega$$

$$E = \frac{J^2}{2I} = \frac{(I_{CM} \omega)^2}{2 I_{CM}} = \frac{1}{2} I_{CM} \omega^2$$

② No matter due to what reason, J is created, it will quantum mechanically take values corresponding to $\sqrt{j(j+1)} \ h$ ($j = 0, 1, 2, \dots$)

$$\Rightarrow E_j = \frac{J^2}{2I_{CM}} = \left[j(j+1) \frac{\hbar^2}{2 I_{CM}} \right] = \left(\frac{\hbar^2}{8\pi^2 I_{CM}} \right) j(j+1)$$

Zero Point Energy = 0

Note that J can take $(0, 1, 2, 3, \dots)$ values
Energy in Wave numbers or cm^{-1}
We usually define Numbers i.e.

$F(J) = \frac{E(J)}{h c} = \frac{\hbar}{8\pi^2 I_{CM} c} j(j+1) = \underline{\underline{B j(j+1)}}$

"Born - Oppenheimer" Approximation has been used, to solve J values quantum mechanically for rigid rotator molecule.

Now $F(J)$ can have values $0, 2B, 6B, 12B, 20B, \dots$
hence discrete energy spectrum.

Now due to what property of molecule rotation occur ??

Note every molecule rotates. H_2, N_2, O_2 molecules i.e.

(Homonuclear)
similar atoms diatomic molecules do not give rotational
or vibrational spectra or rotational-vibration spectra.

Only Heteronuclear Molecules possess rotation.

Heteronuclear Molecules possess dipole moment. e.g. HCl
 HBr
 CO

Presence of permanent dipole moment is reason for rotation.

When it interacts with incident source, it interacts with \vec{E} and torque $= (\vec{\mu} \times \vec{E})$ acts.

For rigid rotator molecule, selection rules of permanent dipole moment, give:

→ This is known by the study of matrix elements of dipole transition

Rigid Rotator Molecular —: $\Delta J = \pm 1$
Non Rigid Rotator —: $\Delta J = \pm 1$ (Same)

For

(Non Rigid Rotation)



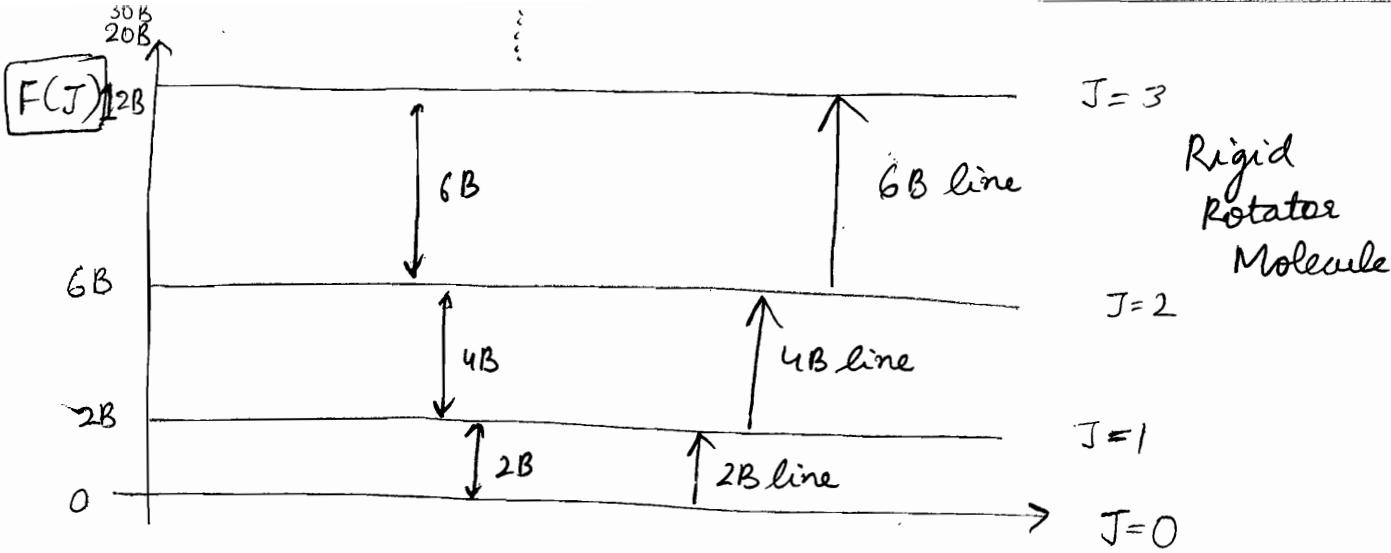
$$\frac{J_{yy}^2}{2I_{yy}} + \frac{J_{zz}^2}{I_{zz}} \Rightarrow E = j(j+1)B - D[j(j+1)]^2$$

Centrifugal distortion coefficient [CDC]
↑
only this term in rigid rotator

Order of $B \approx 10 \text{ cm}^{-1}$

Order of $D \approx \frac{1}{1000} \text{ cm}^{-1}$

→ Centrifugal distortion effect for non rigid rotator is appreciable only at higher values of J .



→ Rotational levels are increasing gaps

$$\text{Order of } B \approx 0.001 \text{ eV}$$

Rotational spectra are typically observed in absorption not in emission spectra. In emission spectra, it will come if initially, there is sufficient population in excited level.

① Remember more $|J|$ means more energy

$$\Delta J = +1, -1 \text{ (emission)} \\ (\text{absorption})$$

Depending upon energy of klystron oscillator, the various jumps can occur. [Microwave source]

All frequencies of klystron oscillator are not easily available.

$\therefore \Delta J = \pm 1 \Rightarrow$
Similar to wave interval
rule

$$2B \quad 4B \quad 6B \quad 8B \dots$$

$$\Delta E \propto j(j+1) - (j-1)j = j(2) = 2j$$

$$\Rightarrow \Delta E = 2jB$$

$$\Rightarrow \Delta(\text{spectral line}) = 2B$$

$$\rightarrow \bar{\omega}$$

uniform gaps in rotational spectra of diatomic rigid rotator molecules.

→ If gap is not uniform \Rightarrow ~~Non rigid rotator~~ molecules ~~not~~
~~Non rigid rotator~~

If uniform gap \Rightarrow rigid rotator (nature of molecule)

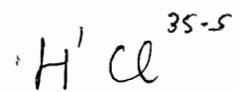
$$\Rightarrow B = \frac{h}{8\pi^2 c I_{cm}}$$

$$\Rightarrow I_{cm} = \frac{h}{8\pi^2 c B} \quad (\text{Moment of Inertia})$$

$$\Rightarrow \mu r^2 = I_{cm}$$

$$\Rightarrow r = \sqrt{\frac{I_{cm}}{\mu}} \quad (\text{Bond length})$$

Hence 3 things were calculated from seeing gap.



$$\mu = \frac{1 \times 35.5}{36.5}$$



$$\mu = 2 \times \frac{35.5}{37.5}$$

If $\mu \uparrow \Rightarrow B \downarrow$

\Rightarrow from shift in B , we can obtain information about isotope. This is called isotope effect.

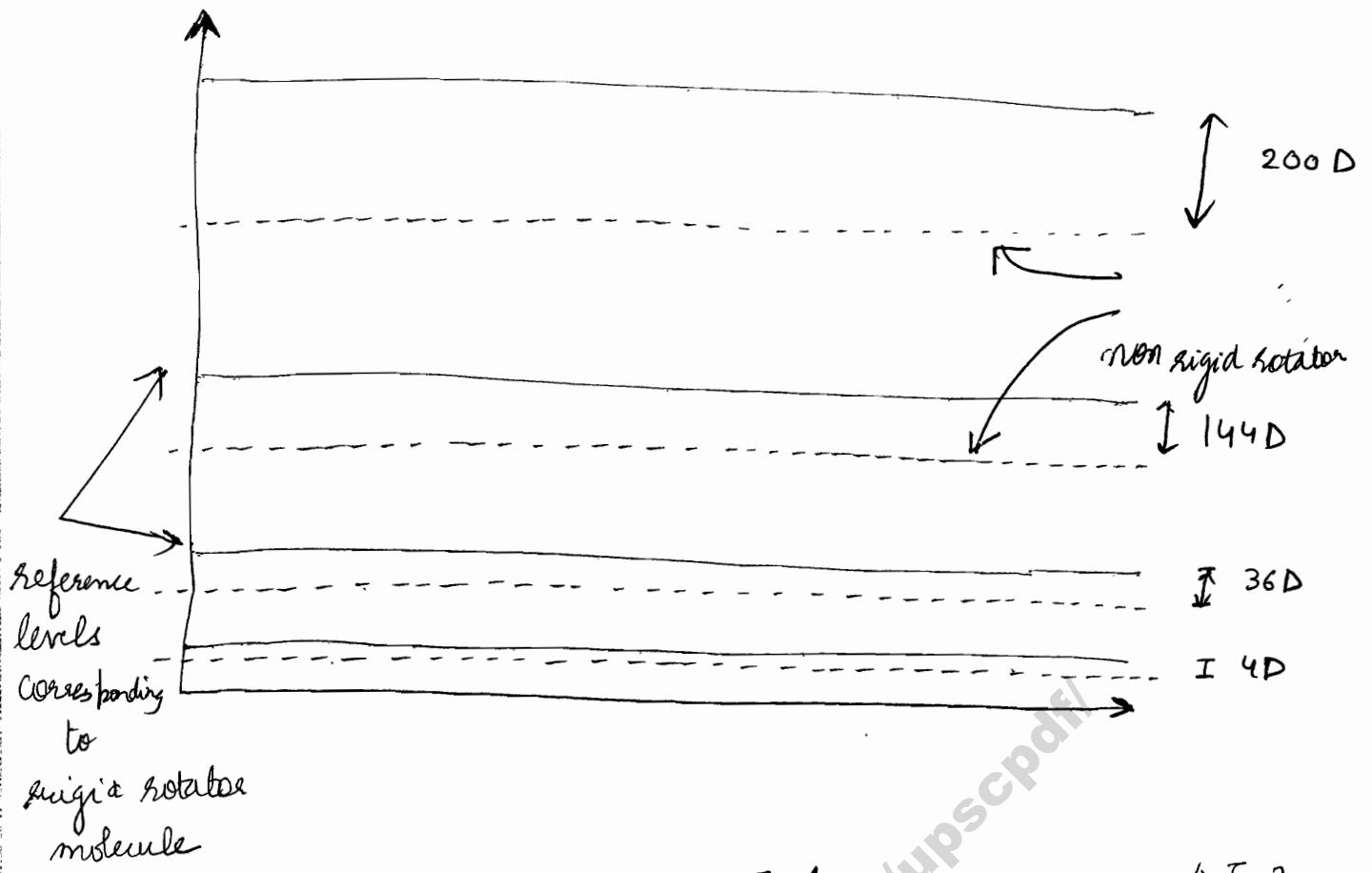
\Rightarrow 4th information we get is Isotope Effect from gap.

For ~~Non Rigid Rotator~~ (Non Rigid Rotator)

$$F(J) = BJ(J+1) - D(J)^2(J+1)^2$$

$$F(0) = 0 ; F(1) = 2B - 4D ; F(2) = 6B - 36D ;$$

$$F(3) = 12B - 144D ; F(4) = 20B - 400D$$



$$F(0) = 0$$

$$F(1) = 2B - 4D$$

$$F(2) = 6B - 36D$$

$$F(3) = 12B - 144D$$

$$F(4) = 20B - 400D$$

$$\Delta J=1$$

$$2B - 4D$$

$$4B - 32D$$

$$6B - 108D$$

$$8B - 256D$$

$$\Delta J=2$$

$$6B - 36D$$

$$10B - 140D$$

$$14B - 364D$$

gap is non
uniform

non rigid rotator molecule

If 3 lines are given \Rightarrow $2B - 4D$: known
 $4B - 32D$: known

x_1
 x_2
 x_3

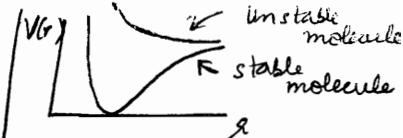
(Q8) CO : $J=0 \rightarrow J=1$

$$F(J) = BJ(J+1)$$

$$F(0) = 0$$

$$F(1) = 2B$$

$$2BC = 2^* \text{ Hz}$$



For the curve that has no minima, it corresponds to unstable molecules in which there is repulsion between the 2 nuclei at all separations.

VIBRATIONAL SPECTRA

In non homogeneous Electric Field, permanent dipole moment experiences

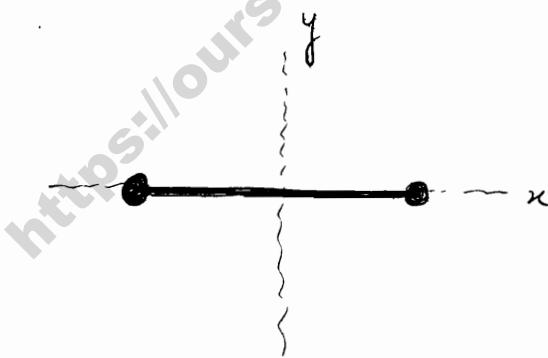
$$\vec{F} = (\vec{p} \cdot \vec{\nabla}) \vec{E}$$

\Rightarrow Oscillatory Force due to oscillating \vec{E} .

\Rightarrow vibration

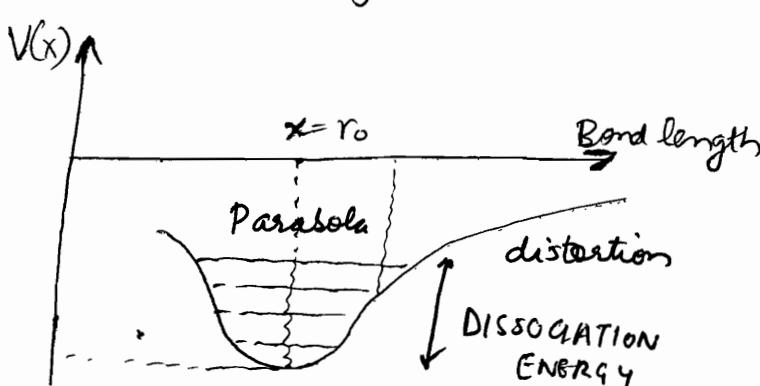
Molecule behaves like simple Harmonic Oscillator.

~~For rigid rotator molecule, no vibration along internuclear axis. Only vibrational moment along direction perpendicular to internuclear axis passing through CCR.~~



$$F_y = -ky \quad V = \frac{1}{2}ky^2 \quad (\text{Parabolic Potential})$$

But molecules may not be simple harmonic oscillator

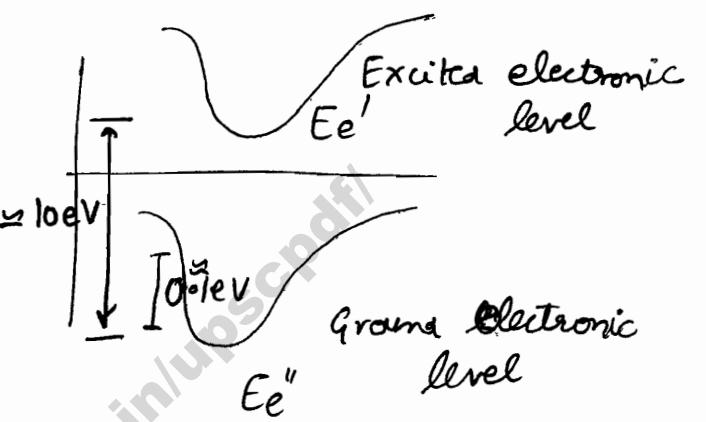


Potential for diatomic molecule
Combination of Parabolic Aberratic curves.

$$V(x) = Fx^2 - gx^3 \quad ; \quad x = (r - r_0)$$

Dissociation Energy: Amount of energy required to dissociate the bonds.

Note that we are not changing electronic levels. The parabolic curve drawn is for a particular electronic configuration.



Ee'' : double prime for ground state electron } Assume the primes like floors of Basement
 Ee' : single prime for excited electron }

In vibrational spectra, we are not interested in excitation of electronic levels. We are not providing that much energy.

Harmonic Oscillator

In lower levels, $V(x) = Fx^2$

At higher levels : $V(x) = -gx^3$ [ignoring it for simpler analysis]

$$V = \frac{1}{2} kx^2 \quad \text{Quantum solution}$$

$$E(v) = \left(\sqrt{\frac{v}{2}} + \frac{1}{2}\right) \hbar \bar{\omega}$$

$$\bar{\omega} = \frac{1}{2\pi c} \sqrt{\frac{k}{m}}$$

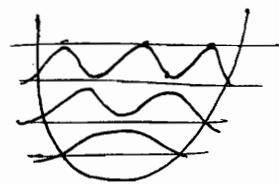
write
 $\hbar \omega = \bar{\omega} h c$
 $\Rightarrow \bar{\omega} = \frac{1}{2\pi c} \sqrt{\frac{k}{m}}$

Quantum Number $v = 0, 1, 2, 3, \dots$

$$\bar{\omega} = \left(\frac{2}{c}\right)$$

$$G(\nu) = \frac{E(\nu)}{hc} = \left(\nu + \frac{1}{2}\right) \bar{\omega}$$

$$\boxed{\Delta\nu = \pm 1}$$



$$\frac{1}{2}h\nu \quad \frac{3}{2}h\nu \quad \frac{5}{2}h\nu$$

If only ± 1 allowed, \Rightarrow only single line $= h\nu$ is obtained.

But this is not obtained, b'cos exact curve is having distortions too eg. $Fx^2 - gx^3$

Harmonic Oscillation

- Q) $f(x)$: Continuous in some interval.
Expand it about x_0 .

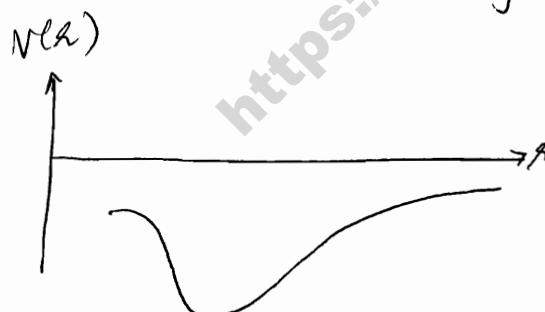


$$f(x) = f(x_0) + (x-x_0)f'(x_0) + \frac{(x-x_0)^2}{2!} f''(x_0) + \dots$$

Taylor Series

$$+ \frac{(x-x_0)^3}{3!} f'''(x_0)$$

Using Taylor Series,



$$V(x) = V(x_0) + (x-x_0)V'(x_0) + (x-x_0)^2 V''(x_0) + \dots$$

$$\Rightarrow V(x) - V(x_0) = 0 \quad \text{if } \cancel{V'(x_0) = 0} \quad V'(x_0) = 0$$

\Rightarrow Force = 0

EQUILIBRIUM

$$V''(x_0) > 0$$

\Rightarrow Put $(x-x_0)$ = displacement from equilibrium as x .

Now $V''(x_0) > 0$: Minima

$$V'''(x_0) < 0$$

Every subsequent coefficients are lesser in Taylor series

$$f^n(x) < f^{n-1}(x)$$

Hence lets fix,

$$V(x) = \cancel{f x^2} - g x^3 \leftarrow \underline{\text{Mechanical Anharmonicity}}$$

Eigen Value Problem has solutions,

$$\boxed{E(V) = \left(\nu + \frac{1}{2}\right) \hbar c \bar{\omega} - \left(\nu + \frac{1}{2}\right)^2 \hbar c \bar{\omega} x_e}$$

ω_e : Anharmonicity Const. $\omega_{de} \ll \omega_e$

ω_e : energy state if curve was parabola

$$G(E) = \frac{E(\nu)}{\hbar c} = \left(\nu + \frac{1}{2}\right) \bar{\omega}_e - \left(\nu + \frac{1}{2}\right)^2 \bar{\omega}_e x_e$$

Quantum Number $\nu = 0, 1, 2, \dots$

decreasing
energy levels
due to
mechanical
anharmonicity

~~selection rule of electric dipole moment~~ ~~for transitions~~

$\Delta\nu = \pm 1$: Harmonic Oscillations

$\Delta\nu = \pm 1, \pm 2$: Anharmonic Oscillations ~~of a system~~

electrical
anharmonicity

$\Delta\nu = +1$

$\Delta\nu = +2$

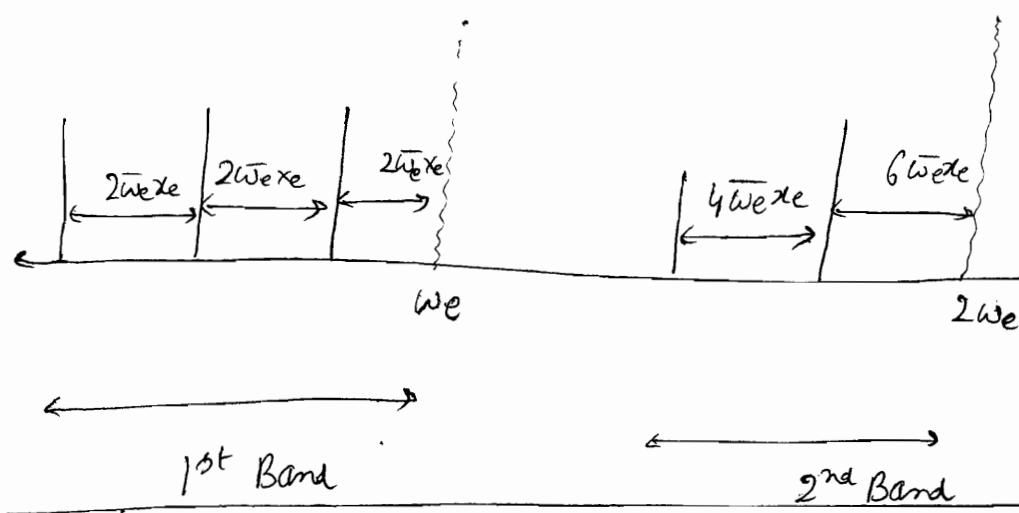
$$G(0) = \frac{1}{2} \bar{\omega}_e - \frac{1}{4} \bar{\omega}_e x_e \quad \begin{cases} \bar{\omega}_e - 2 \bar{\omega}_e x_e \\ 2 \bar{\omega}_e - 6 \bar{\omega}_e x_e \end{cases}$$

$$G(1) = \frac{3}{2} \bar{\omega}_e - \frac{9}{4} \bar{\omega}_e x_e \quad \begin{cases} \bar{\omega}_e - 4 \bar{\omega}_e x_e \\ 2 \bar{\omega}_e - 10 \bar{\omega}_e x_e \end{cases}$$

$$G(2) = \frac{5}{2} \bar{\omega}_e + \frac{25}{4} \bar{\omega}_e x_e \quad \begin{cases} \bar{\omega}_e - 6 \bar{\omega}_e x_e \\ 2 \bar{\omega}_e - 12 \bar{\omega}_e x_e \end{cases}$$

$$G(3) = \frac{7}{2} \bar{\omega}_e - \frac{49}{4} \bar{\omega}_e x_e$$

- Atomic spectra: line spectra
- Molecular spectra : Band spectra



Gross
Structure
of
Vibrational
Rotational

- Classical frequency for a harmonic oscillator is : $\nu_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$. For anharmonic oscillator, this frequency decreases as n (quantum no.) increases.

Vibration spectra occurs in IR region.....

★ Born - Oppenheimer Approximation

Quantum Mechanical Hamiltonian operator for a molecule, containing terms for electronic & nuclear motion is very complex. In order to solve Schrodinger's equation, Born Oppenheimer approximation is used, according to which:

- first, due to slow moving massive nuclei, the wave equation for electronic motion alone is solved, in which nuclear coordinates appear simply as parameter.
- then, the wave equation for motion of nuclei alone is solved in which ~~the~~ eigenvalues of electronic motion occur as part of potential energy function of nuclear motion.
- Complete wave function = $\psi_1 \psi_2$

★ Some characteristics :

- 1 Electronic spectra in emission as well as absorption, while Vibrational Rotational & Rotational in absorption.
- 2 Electronic spectra band has a sharp edge, called Band Head, where intensity is zero at one side and fall off

on other side.

(3) Each vibrational rotational band consists of an intense band called Fundamental Band, which is accompanied by a few weak bands.

(4) Electronic : homonuclear as well as heteronuclear
Vibrational rot, rotational : heteronuclear only.

★ Re : equilibrium

@ $r < r_e$: more nuclear repulsion
@ $r > r_e$: ~~less~~ electronic attraction } $\Rightarrow V$ increases
in both cases

★ Zero Point energy for rotational spectra = 0
for vibrational spectra = $\frac{1}{2} \bar{\omega}$

★ Molecular Spectra

All the spectral lines arising from transitions between rotational levels J' and J'' associated with a given pair of vibrational levels v' and v'' of a given pair of electronic levels form a band.

Thus for a given band, J' and J'' vary from line to line while v' and v'' are constants.

All the Bands which arise from transitions between vibrational levels of a given pair of electronic levels constitute a Band System, the values of v' and v'' varying from Band to Band.

Thus, a single electronic transition gives rise to a band system. Each line in each band of the system arises due to a change in all the three energies $E_e, E_v & E_r$.

$$\bar{\omega} = \bar{\omega}_e + \bar{\omega}_v + \bar{\omega}_r$$

For a given band, $\bar{\omega}_e$ and $\bar{\omega}_v$ are constants, while $\bar{\omega}_r$ changes from line to line. Position in band where $\bar{\omega}_r = 0$ is called Band Origin, its wave number is $(\bar{\omega}_e + \bar{\omega}_v)$.

For a band system similar, $\bar{\omega}_e$ is const. while $\bar{\omega}_v$ vary from band to band. Position in the system where $\bar{\omega}_v = 0$ is called System Origin, its wave number is $\bar{\omega}_e$.

MOLECULAR PHYSICS (2)

25/02/2012

For vibrational motion,

$\Delta v = +1$: Band :- Most intense line is $v=0$ to $v=1$

$$\text{i.e. } \bar{\omega}_r = \bar{\omega}_e (1 - 2 \chi_e)$$

$\Delta v = +2$: Band

Population is governed by Maxwell Boltzmann Statistics.

$$N_1 = N_0 e^{-\frac{(\Delta E)}{kT}}$$

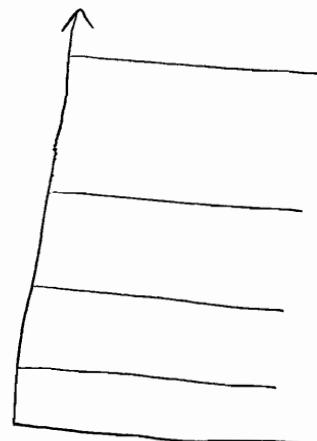
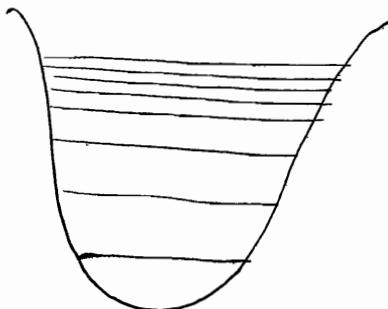
ΔE : Energy b/w

$v=0$ to $v=1$
transition

At room temperature, usually $v''=0$ is seen. But for heavier molecules like I_2 , $\bar{\omega}_e$ is less $\Rightarrow v''=0, 1, 2$ can be seen at room temperature

✓ In certain liquid molecules, where rotation is prohibited due to their molecular structure, only then pure vibration occurs. Otherwise normally, vibration & rotation both occur if energy excitation equivalent to vibrational levels is excited upon the molecules.

We can also say with 0.1 eV gap, many 0.001 eV gap of energy can be included. Hence within 1 vibration energy gap, there can be many rotational energy gaps.



In vibration,

gap ↓

with increase in
quantum number v .

Major difference in spectra of
Rotation & [redacted] Vibration

For rotation, gap ↑ with
increase in quantum number J

Vibration - Rotation Spectra

Molecules having permanent dipole moment interacts with Electric Field and undergoes vibration as well as rotational motion. Combined effect is

$$G(v, J) = G(v) + F(J)$$

$$= \left[\left(v + \frac{1}{2} \right) \bar{\omega}_e - \left(v + \frac{1}{2} \right)^2 \bar{\omega}_e \chi_e \right]$$

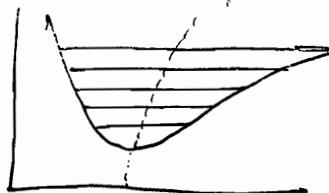
$$+ B J(J+1)$$

B: rotational constant in vibrational level v

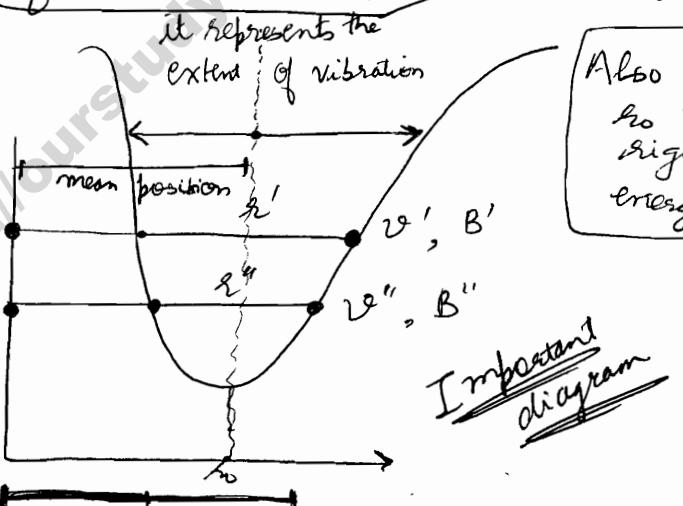
$$= \left(\frac{\hbar}{8\pi^2 c \mu \bar{\omega}^2} \right)$$

Overtones due to
 $\Delta v = 2, 3, \dots$
 Electrical Anharmonicity

- (*) The infrared spectra of a molecule like HCl consists of an intense band, known as fundamental band, accompanied by a no. of weak bands, called overtones at wave numbers approximately double, triple of fundamental band.



$\bar{\omega}_e$ moves towards right
 $\Rightarrow B$ reduces $\bar{\omega}_e$: mean position



internuclear separation, r

In increasing vibrational state, intermolecular distance increases. Although difference is not very significant

Now

$$r' > r''$$

$$B' < B''$$

\Rightarrow

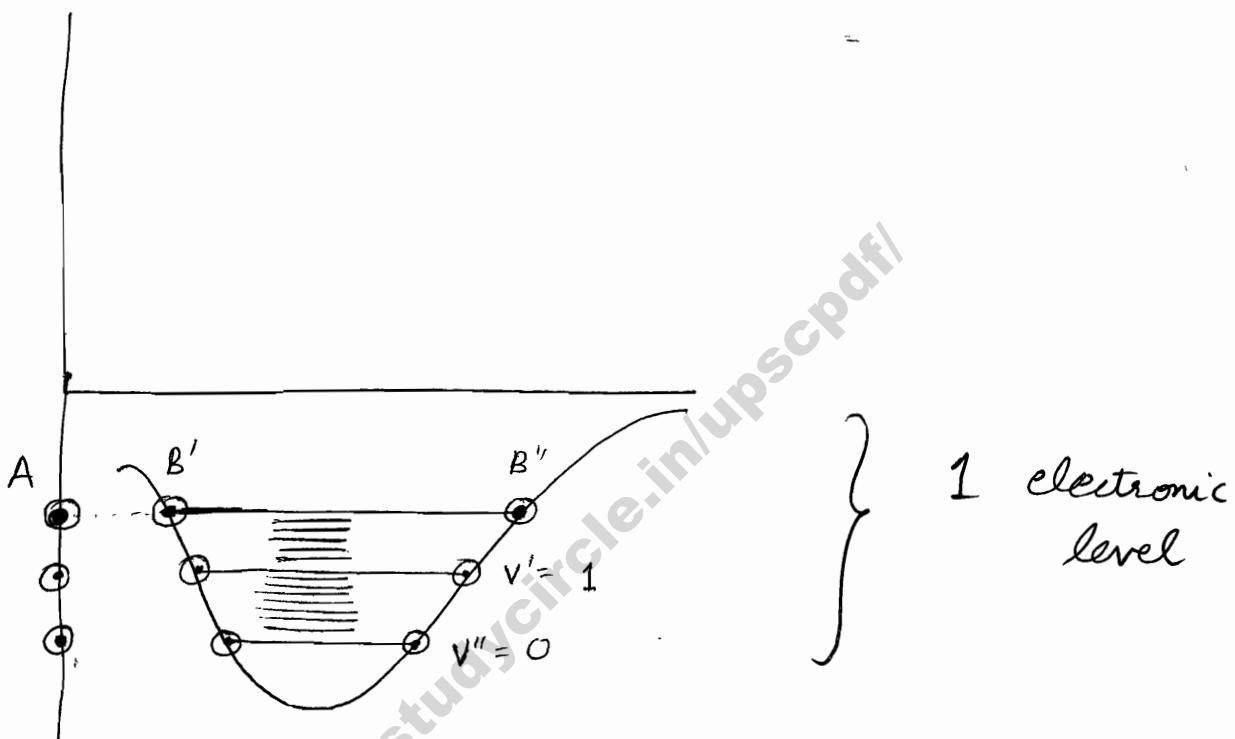
$$B' - B'' < 0$$

$\Rightarrow -B' - B''$ is small negative quantity.

vibrational

Molecule is stretched with every excited molecular state.

Now spectral line will come when $\Delta G(v, J)$ is non zero.



Note that rotational energy starts from zero. i.e. Zero Point Energy = 0.
But in vibrational motion, zero Point Energy $\neq 0$
Many rotational energy are inculcated in this level.

Writing Ground state of Vibrational - Rotational level

$$G(v'', J'') = \left(v'' + \frac{1}{2}\right) \bar{\omega}_e - \left(v'' + \frac{1}{2}\right)^2 \bar{\omega}_e \chi_e + B'' J''(J''+1)$$

$$G(v', J') = \left(v' + \frac{1}{2}\right) \bar{\omega}_e - \left(v' + \frac{1}{2}\right)^2 \bar{\omega}_e \chi_e + B' J'(J'+1)$$

↑

Excited state

- For same electronic level, $\bar{\omega}_e, \chi_e$: same
- For same vibrational level, B is same

$$\bar{\omega}_{v,a} = \Delta G(v, J)$$

$$= G(v', J') - G(v'', J'')$$

$$\bar{\omega}_{v,a} = (v' - v'') \bar{\omega}_e - (v' - v'') (v' + v'' + 1) \bar{\omega}_{ex} + B' J' (J' + 1) - B'' J'' (J'' + 1)$$

Rigid Rotator Diatomic Molecule

$$\Delta v = v' - v'' = 1$$

(absorption)
(-1 for emission)

For Non-Rigid Rotator Molecule

Note that $\Delta J = 0$
is not observed !!

$$\Delta v = \pm 1, \pm 2$$

$$\Delta J = \pm 1$$

For $\Delta v = 1$ ★ We normally study the spectra for normal absorption case $\Delta v = 1$ $v' = 1 \leftarrow v'' = 0$

$$\Rightarrow \bar{\omega}_{v,a} = \bar{\omega}_e - 1 (2v'' + 2) \bar{\omega}_{ex} + B' J' (J' + 1) - B'' J'' (J'' + 1)$$

general for $\Delta v = +1$

Specific Case
 $v'' = 0$ to $v' = 1$: $\bar{\omega}_{v,a}$ = $\bar{\omega}_e - 2\bar{\omega}_{ex} + B' J' (J' + 1) - B'' J'' (J'' + 1)$

Band Vibrational line

Every line of vibrational spectra will show a fine structure and will be a band due to different values of J

Now,

$$\bar{\omega}_{v,\nu} = \underbrace{\bar{\omega}_v - 2\bar{\omega}_e x_e}_{\text{const. for a particular transition}} + B' J' (J'+1) - B'' J'' (J''+1)$$

$\bar{\omega}_v$: const. for a particular transition

ΔG_v will give $\bar{\omega}_v$

The fine lines will come from ΔG_x .

Now, considering $\Delta G(J)$ for

ΔJ :	-2	-1	0	1	2

	{	{	{	{	{
	O	P	Q	R	S

* 2nd Queen
It is !!

$\Delta J = 0$: Q Branch

not observed in diatomic vibrational spectra.
Occurs in electronic spectra.

$\Delta J = 1, -1$: R branch, P branch

$\Delta J = 2, -2$: S branch, O Branch

Hence in vibrational band, only P and R branch are observed to be seen.

R branch

$$\Delta J = +1$$

$$J' - J'' = 1$$

$$J'' = 0, 1, 2, \dots$$

$$\Rightarrow \boxed{\bar{\omega}_{v,\nu}(\text{R branch})} = \bar{\omega}_v + B' (J''+1)(J''+2) - B'' J'' (J''+1)$$
$$= \bar{\omega}_v + (J''+1) [(B' - B'') J'' + (2B' - B'')]$$

Put $J'' = 0$

$$= \bar{\omega}_v + 1 [2B' - B'']$$

Put $\Delta J = -1$ for P branch,

$$J' - J'' = -1$$

P BRANCH

Here $J'' = 1, 2, 3, 4, \dots$

$$\bar{\omega}_{v,\alpha} (\text{P, branch}) = \bar{\omega}_v + B' (J''^2 - J'') - B'' (J''^2 - J'')$$

$$\bar{\omega}_p = \bar{\omega}_v - (B' + B'') J'' + (B' - B'') J''^2$$

$$\bar{\omega}_R = \bar{\omega}_v + (B' - B'') J'' + (B' - B'') J''^2 + 2B''$$

Note that $\bar{\omega}_p$ and $\bar{\omega}_R$ are bands (for different values of J'' , different lines). Mathematically both of them can be combined into a single equation.

Put

$$\bar{\omega}_{v,\alpha} = \bar{\omega}_v + (B' + B'') m + (B' - B'') m^2$$

where m : parameter

If $m = -J''$: J'' starting from +1
we get P branch

If $m = (J'' + 1)$: we get R branch

It's called

For P series, replacing J values (1, 2, 3, 4, ...)

$$\bar{\omega}_{P(1)} = \bar{\omega}_v - 2B''$$

$$\begin{aligned}\bar{\omega}_{P(2)} &= \bar{\omega}_v - 2(B' + B'') + 4(B' - B'') \\ &= \bar{\omega}_v + 2B' - 6B''\end{aligned}$$

$$\begin{aligned}\bar{\omega}_{P(3)} &= \bar{\omega}_v - 3(B' + B'') + 9(B' - B'') \\ &= \bar{\omega}_v + 6B' - 12B''\end{aligned}$$

↓ decreasing

Refer Fig. 11
on P-313

For R values, $m = J'' + 1$ J'' : starts from 0

For R series

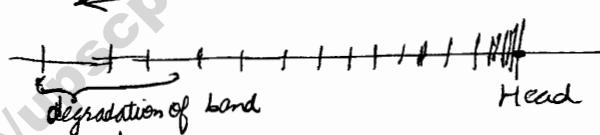
$$\bar{W}_{R(0)} = \bar{W}_v + 2B'$$

$$\begin{aligned}\bar{W}_{R(1)} &= \bar{W}_v + 2(B' + B'') + 4(B' - B'') \\ &= \bar{W}_v + 6B' - 2B''\end{aligned}$$

$$\begin{aligned}\bar{W}_{R(2)} &= \bar{W}_v + 3(B' + B'') + 9(B' - B'') \\ &= \bar{W}_v + 12B' - 6B''\end{aligned}$$

increasing

head formation
tendency toward
high ν side



\bar{W}_{NR} vs m

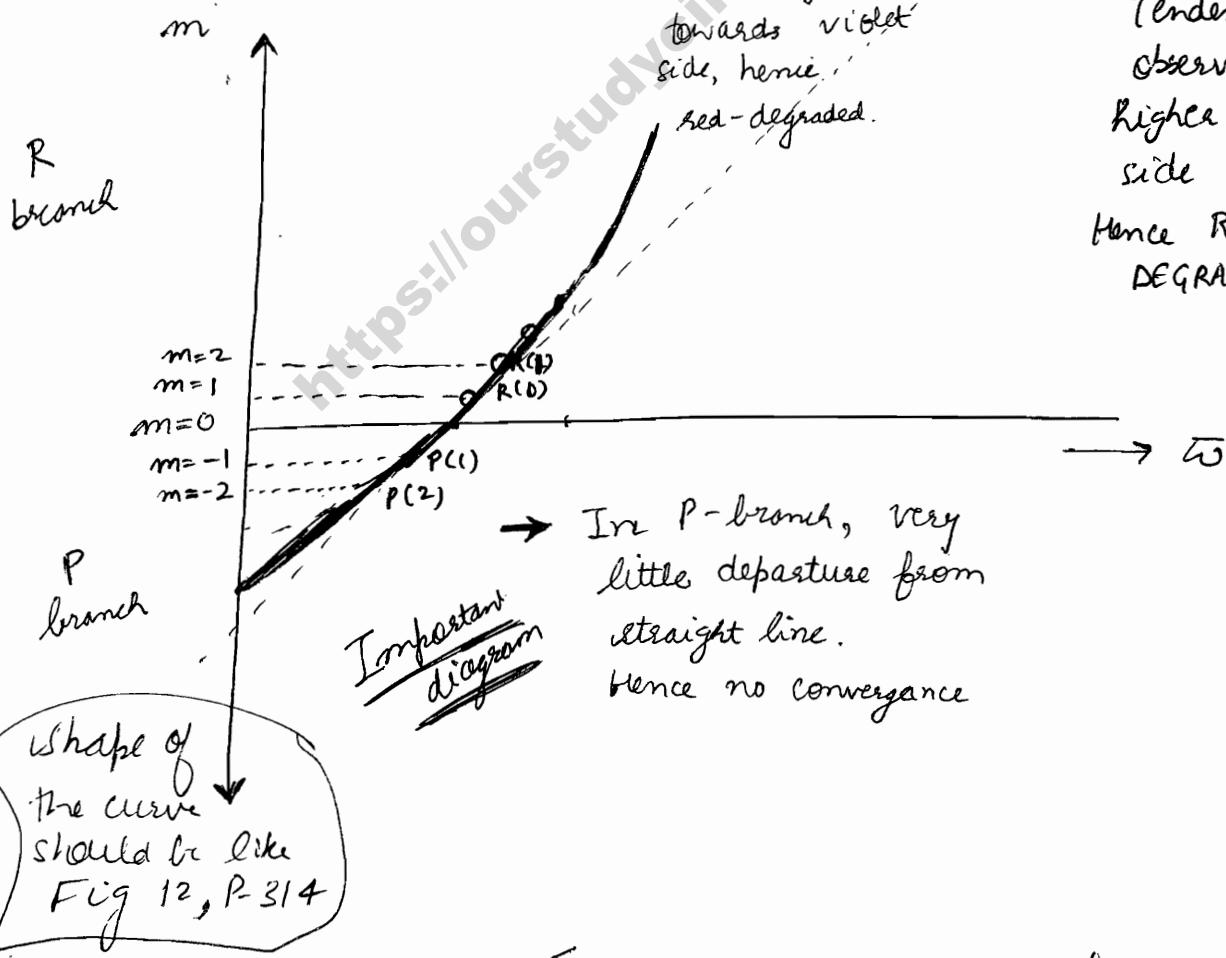
In R-branch, poor convergence.

But convergence is towards violet side, hence red-degraded.

④ Head Formation

Tendency is observed towards higher frequency side i.e. violet side

Hence R GS is DEGRADED.



→ In P-branch, very little departure from straight line.
Hence no convergence

If $B' - B'' > 0 \Rightarrow$ formed in electronic spectra

But $B' - B'' < 0 \Rightarrow$ formed here

For vertex of Parabola

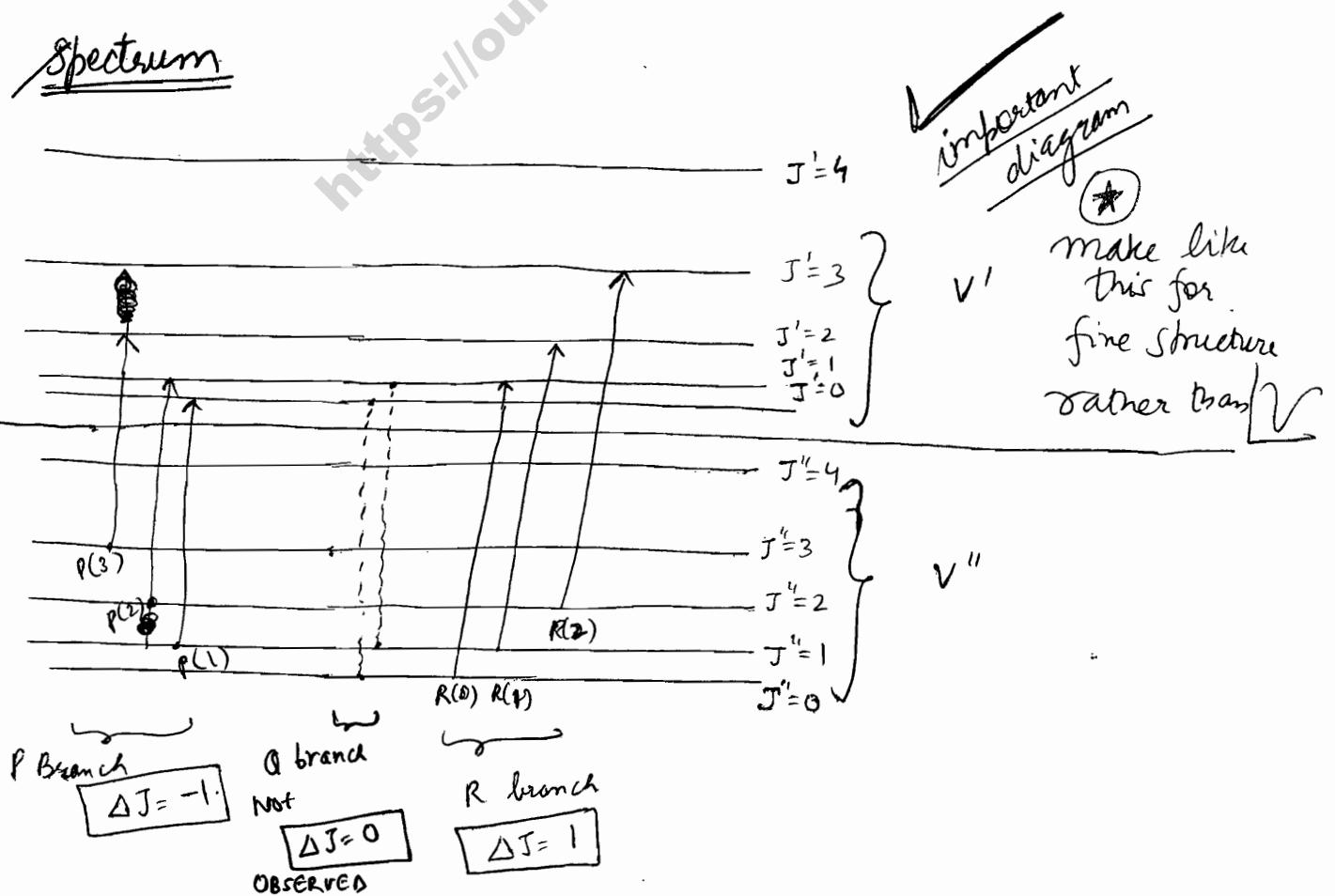
$$\frac{d\omega}{dm} = 0 \Rightarrow (B' + B'') + 2m(B' - B'') = 0$$

$$m = -\frac{(B' + B'')}{2(B' - B'')}$$

- [Vibration Rotation spectra shows poor tendency of head formation towards higher wave number side violet side] (but tendency is)
- [Only bands degraded to only 1 side are formed, i.e. Red degraded only]

Reason for both is $\alpha' > \alpha''$ but difference is small
 $B' < B''$
 $\Rightarrow (B' - B'')$ is small negative quantity

Spectrum



Given 3 lines of infrared spectrum, we can have info about:

- Types of Branch
- I_{cm}
- Isotopic Effect

⑧

$$\lambda_v = 14.7 \mu\text{m}$$

$$\frac{1}{\lambda} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \checkmark$$

$\Rightarrow \mu$: calculated \checkmark

$$J=0 \rightarrow J=1: \text{Rotational} \quad \Delta E = 2B * C = \frac{2h}{8\pi^2 I}$$

$$\nu = \frac{1}{4\pi^2 I}$$

★ Practical difficulty to get emission spectra. Bcoz in order to observe it, we need sufficient of particles in higher energy state. Its difficult to raise them to such low level. Krystan Oscillator not very good.

$$20.68 (J+1)$$

$$E(J+1) - E(J) = B(J+1)(J+2) - B J(J+1)$$

$$= 2B (J+1)$$

$$2B = 20.68$$

$$B = \frac{h}{8\pi^2 c I_{cm}}$$

Hence I_{cm} Obtained.

$$k_1 : k_2 : k_3 = \mu_1 \omega_1^2 : \mu_2 \omega_2^2 : \mu_3 \omega_3^2$$

$$H = \left(\frac{J^2}{2I} \right) = \left[\frac{J_{xx}^2}{2I_{xx}} + \frac{J_{yy}^2}{2I_{yy}} + \frac{J_{zz}^2}{2I_{zz}} \right]$$

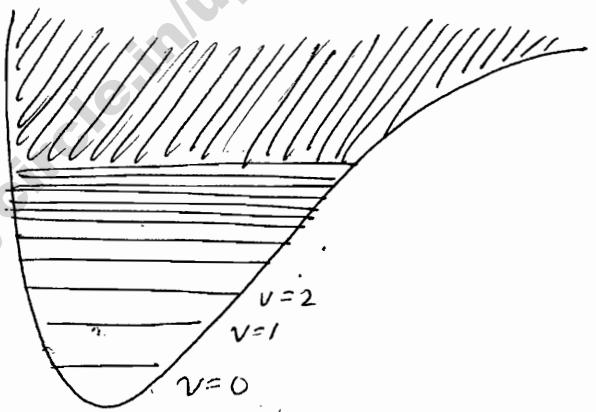
★ Spacings between vibrational levels are considerably larger than the spacings between rotational levels of a molecule, infact larger than kT at room temperature.

Hence most of the molecules in a sample exist in $v=0$ state, with ~~in~~ only their zero point energies. Exceptions are heavy molecules like I_2 that have small $\omega_e \Rightarrow$ they can exist @ $v=0, v=1, v=2$ at room temperature! $v=1$ or $v=0$ ~~at~~ but still appreciable amount ~~at~~.

★ Energy levels of anharmonic oscillator are not equidistant, but their separation decreases slowly with increasing v .

When molecule receives energy more than corresponding to the uppermost vibrational level, it dissociates into atoms and excess energy appears as unquantized kinetic energy of these atoms. Hence a continuum joins the uppermost level.

It is similar to unquantized state beyond series limit in H atom spectrum which follow hyperbolic path (as shown).



★ There are about 50 rotational levels associated with a single vibrational levels for HCl molecule.

★ B_v can be assumed to be $B_v = B_e - \alpha(v + \frac{1}{2})$
where $B_e = \left(\frac{\hbar}{8\pi^2 \mu r_e^2 c} \right)$
Corresponding to \checkmark

MOLECULAR PHYSICS (3)

27/02/2012

For vibrational-rotational motion,

$$\bar{\omega}_{\text{PAR}} = \bar{\omega}_v + (B' - B'') m + (B' - B'') m^2$$

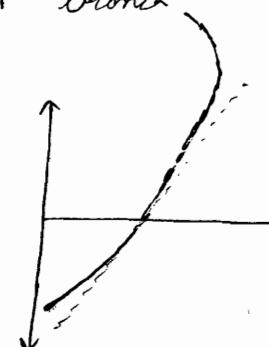
$$m = \pm 1, \pm 2, \pm 3, \dots$$

Positive : R branch

Negative : P branch

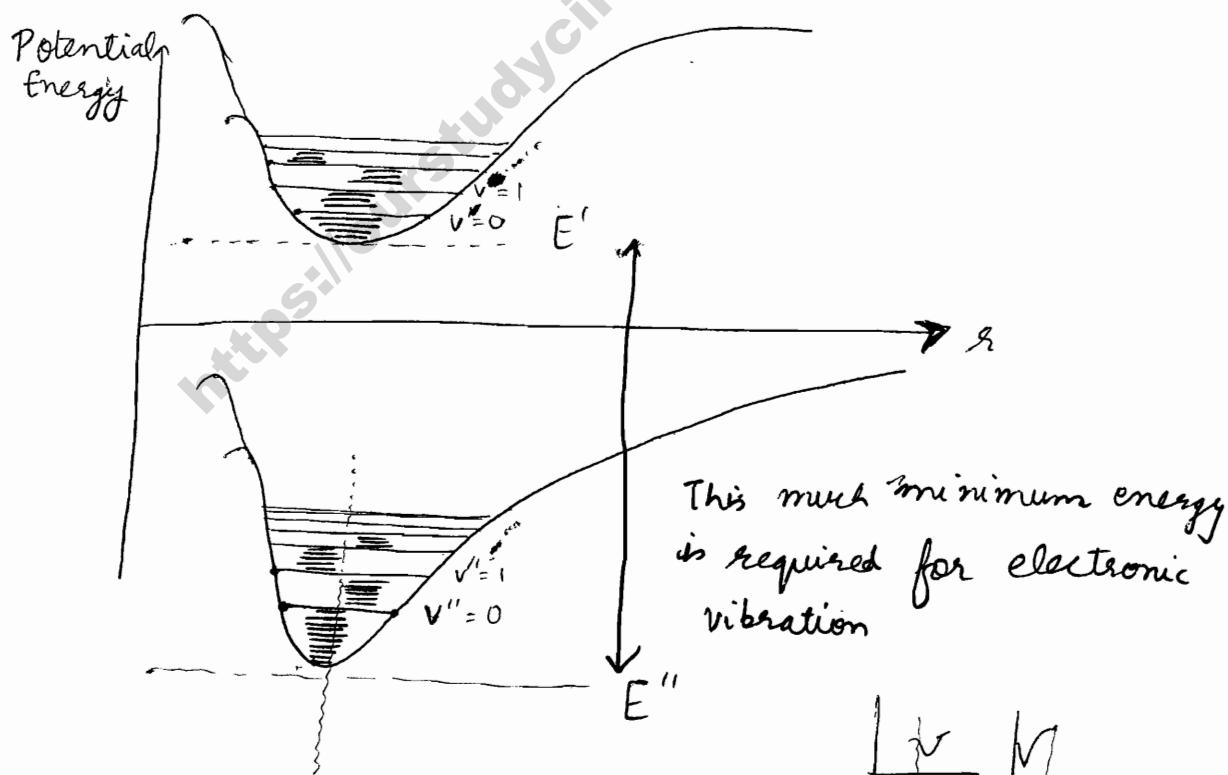
→ The spectrum formation has

- poor tendency for head formation
- red-degraded character



Electronic Spectra

No condition like possession of dipole moment do all molecules give electronic spectra. It is of order of several eV.



In electronic motion, bond length may also be compressed.

There are 4 allowed transitions depending upon m values.
Corresponding to Lz about internuclear axis.

<u>Selection Rules</u>	S	P	D	F	(first letters of corresponding Greek Alphabet)
Δm_e	0	1	2	3	Greek Alphabet
Transition	Σ	Π	Δ	Φ	

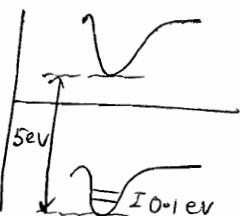
In ' Σ ' transition, $\Delta m_e = 0$. It is 0 for rigid rotator molecules. [Electronic spectra can be obtained in emission

- * also unlike vibrational or rotational level] [Its always easy to have absorption spectra because population is higher in lower levels]

Again note that for rigid rotator molecule, only $\Delta m_e = 0$ is allowed.

$$E = E_e + E_v + E_J$$

e.g. if $\rightarrow 5\text{ eV}$ provided
 E_e changes \Rightarrow new E_e as well as E_v changes to new E_v , new J level
 E_e as well as E_v as well as rotational E is changed \Rightarrow New E , new v , new J .



★ (Note that quantum numbers are so small s.t. such energy level continuum is possible)

$$\Rightarrow \bar{\omega} = \frac{\Delta E(e)}{hc} + \frac{\Delta E(v)}{hc} + \frac{\Delta E(J)}{hc}$$

$$= \Delta \epsilon(e) + \Delta G(v) + \Delta F(J)$$

$$\bar{\omega} = \bar{\omega}_e + \Delta G(v) + \Delta F(J)$$

(note that it is different from we done earlier)

Whenever energy is given in order of ev (typically from white source), electronic levels of molecule change due to change of electronic level of individual atoms.

In electronic spectra, $\Delta\nu$ is unrestricted. When $\Delta\nu$ is unrestricted & ΔJ not considered, it is called coarse structure. When ΔJ is considered, it is called fine structure.

Note that intensity of transitions are governed by Population rules defined by Maxwell Boltzmann statistics.

Gross / Coarse Structure of Electronic Band Spectrum (2 diagrams)

$$\bar{\omega} = \bar{\omega}_e + G(v') - G(v'')$$

In Gross structure, we neglected ΔJ for time being.

$\Delta\nu = \text{Unrestricted}$ (Restriction is only the no. of v levels in single electronic level) $\approx 0, \pm 1, \pm 2, \pm 3, \dots$

$$G(v) = \left(v + \frac{1}{2}\right) \bar{\omega}_v - \left(v + \frac{1}{2}\right)^2 \bar{\omega}_v x_v$$

$$\bar{\omega}_v = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\text{We know } \omega = \sqrt{\frac{k}{m}} \Rightarrow \bar{\omega} = \frac{1}{\lambda} = \frac{1}{ct} = \frac{\nu}{c} = \frac{2\pi\nu}{2\pi c}$$

$$= \frac{\omega}{2\pi c} = \frac{1}{2\pi c \sqrt{\frac{k}{m}}}$$

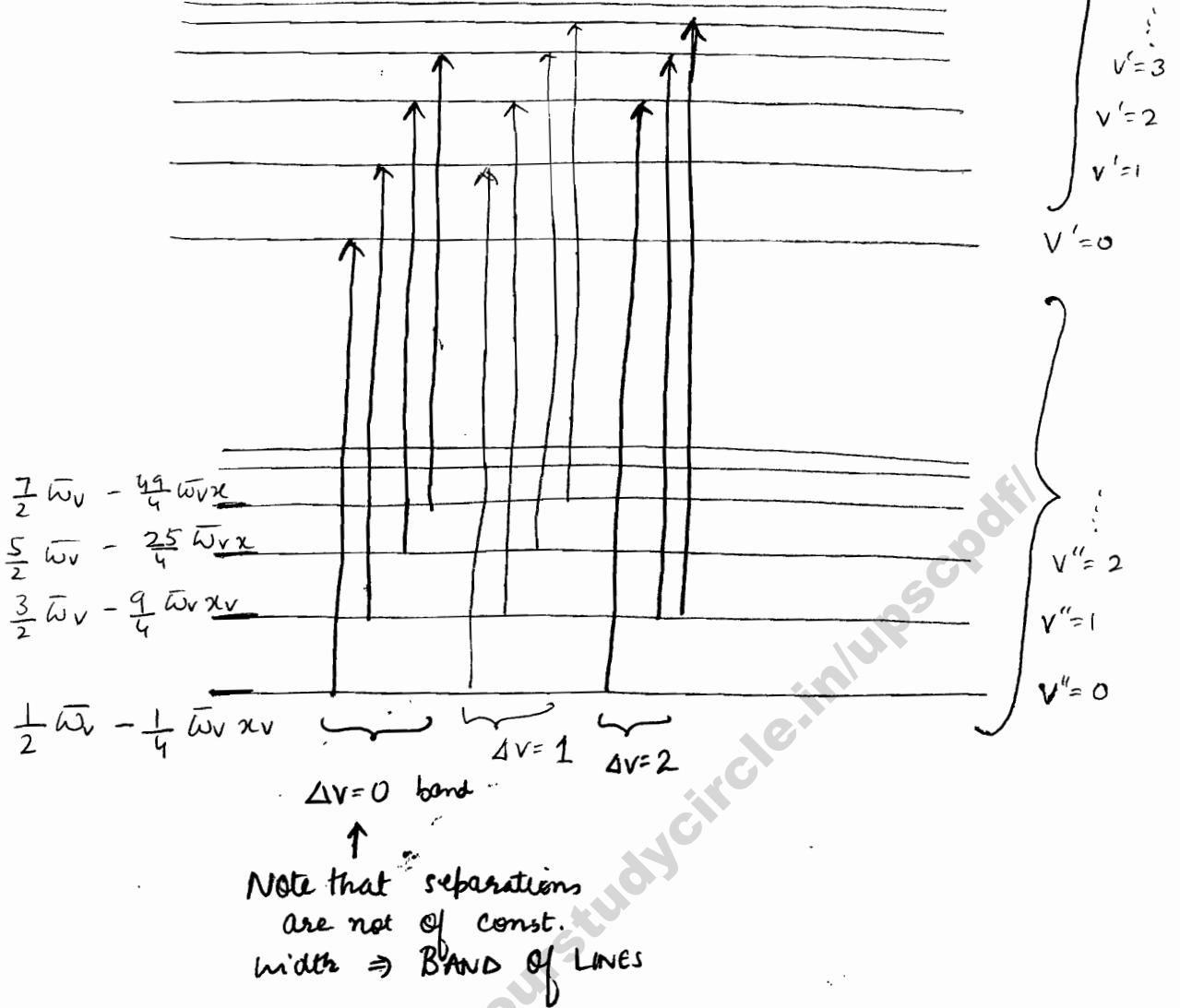
$$\text{In Ground state, } G(v'') = \left(v'' + \frac{1}{2}\right) \bar{\omega}_v - \left(v'' + \frac{1}{2}\right)^2 \bar{\omega}_v x_v$$

$$\text{In Excited state, } G(v') = \left(v' + \frac{1}{2}\right) \bar{\omega}_v - \left(v' + \frac{1}{2}\right)^2 \bar{\omega}_v x_v$$

- Electronic energy is the energy which the molecule possesses if nuclei were fixed, & consists of
 - k.E. & P.E. of extranuclear electrons
 - P.E. of repulsion between nuclei

Absorption Spectra

Gross Spectrum



Similarly, we can draw from $\Delta v = -1, -2, \dots$

Note that it is Absorption spectra. We can draw Emission spectra just by drawing opposite lines given that enough population is there in excited state.

$$\begin{aligned}
 \bar{\omega}_{e,v} &= T(e')^+ G(v) - T(e'')^- G(v'') \\
 &= [T(e') - T(e'')] + [G(v) - G(v'')] \\
 &= \bar{\omega}_e + \left(v' + \frac{1}{2}\right) \bar{\omega}_v - \left(v' + \frac{1}{2}\right)^2 \bar{\omega}_v x_v \\
 &\quad - \left(v'' + \frac{1}{2}\right) \bar{\omega}_v' + \left(v'' + \frac{1}{2}\right)^2 \bar{\omega}_v' x_v
 \end{aligned}$$

~~Clearly, we can do this.~~

Note that $\bar{\omega}_v' \neq \bar{\omega}_v$
(different electronic levels have different curves and different ω_e, ω_v parameters)

$\Delta v = 0$
 $\Delta v = 1$
 $\Delta v = 2$

All are bands having distinct wave number for all lines. These bands are called PROGRESSIONS.

Progression are Bond systems

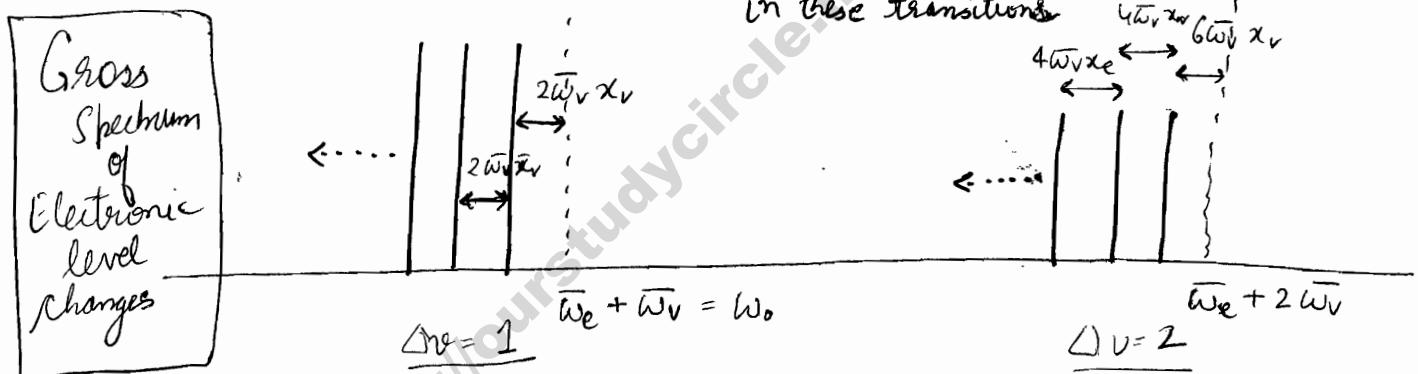
e.g. $\Delta v = 1$ Band or Progression

$$\begin{aligned} v=0 \rightarrow v=1 &\Rightarrow \omega = \bar{\omega}_e + \frac{3}{2} \bar{\omega}_v - \frac{9}{4} \bar{\omega}_v x_v - \frac{1}{2} \bar{\omega}_v' + \frac{1}{4} \bar{\omega}_v' x_v \\ &= \bar{\omega}_e + \bar{\omega}_v - 2 \bar{\omega}_v x_v \\ v=1 \rightarrow v=2 &\Rightarrow \omega = \bar{\omega}_e + \bar{\omega}_v - 4 \bar{\omega}_v x_v \\ v=2 \rightarrow v=3 &\Rightarrow \omega = \bar{\omega}_e + \bar{\omega}_v - 6 \bar{\omega}_v x_v \end{aligned}$$

all take
 $v''=0$
 $v'=1, 2, 3$
 Progression
 for $v''=0$

let us say $(\bar{\omega}_e + \bar{\omega}_v) = \text{reference level } \omega_0$

→ Note that subsequent height of lines decrease due to lower population in these transitions



$\Delta v = 2$ Band or Progression

$$v=0 \rightarrow v=2 \Rightarrow \omega = \bar{\omega}_e + 2 \bar{\omega}_v - 6 \bar{\omega}_v x_v$$

$$v=1 \rightarrow v=3 \Rightarrow \omega = \bar{\omega}_e + 2 \bar{\omega}_v - 10 \bar{\omega}_v x_v$$

Note that $\bar{\omega}' \neq \bar{\omega}''$

Now note that every line of every band will show further fine structure due to different rotational levels.

$$\Delta E = \Delta E_e + \Delta G(v) + \Delta F(J)$$

$$= \bar{\omega}_e + \bar{\omega}_v + \Delta F(J)$$

$$= \omega_0 + \Delta F(J)$$

$$= \omega_0 + B' J' (J'+1) - B'' J'' (J''+1)$$

Selection Rule

$\Delta J = \pm 1$ for rigid rotator molecule

$\Delta J = 0, \pm 1$ for symmetric molecule

$\Delta J = \pm 2, \pm 1$ exceptional cases in certain molecules that are heavy & non rigid rotator.

These transitions are called Branches. Branches are Bands
Here the analysis is same.

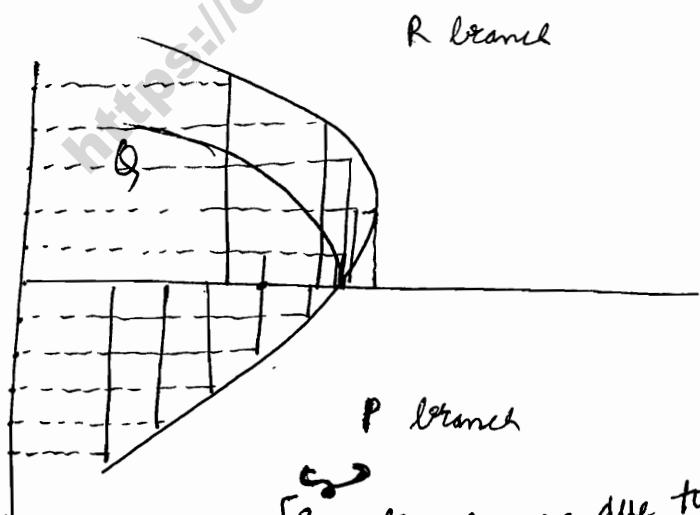
$\Delta J = +1$: R branch

$\Delta J = -1$: P branch

Note that here $\gamma' > \gamma''$ (Possible Case)
 $\Rightarrow (B' - B'') < 0$: Negative Quantity [Not small]

Hence good FORTRET PARABOLA. is formed.

$$\omega = \bar{\omega}_0 + \frac{(B' + B'')}{m} m + (B' - B'') m^2$$

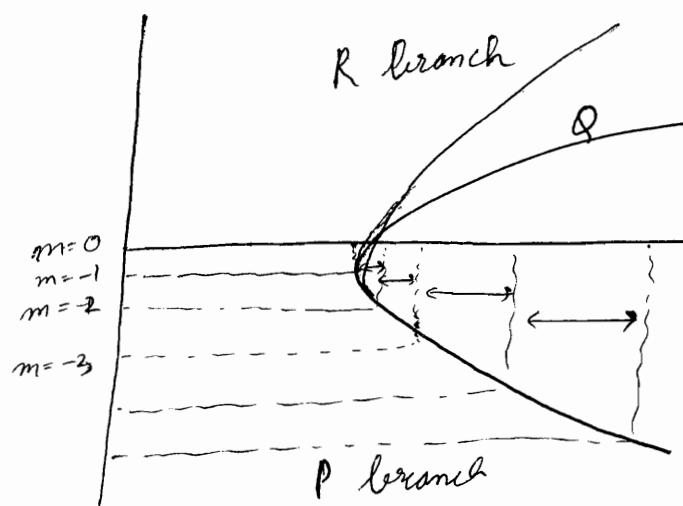


★ [here lines converge due to shape of]
Parabolic curve

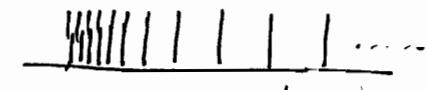
- ① Good tendency for head formation.
- ② Red degraded
- ③ Convergence towards higher wave number side

Also $\tau' < \tau''$ (Possible)

$\Rightarrow B' - B'' > 0$: Positive Quantity



Convergence towards lower wave number side.....



① Violet degraded
Parabola

✓ Vertex in P branch

✓ Convergence is towards lower wave number or red side, hence violet degraded.

Similarly, we can do for Q, S as well as S branches.

$$\bar{\omega} = \bar{\omega}_0 + B' J'(J'+1) - B'' J''(J''+1)$$

$$\bar{\omega} = \bar{\omega}_0 + (B' - B'') J'(J'+1)$$

[Q branch]

in
(symmetric Molecules)

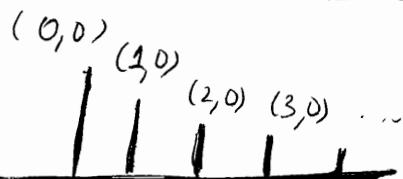
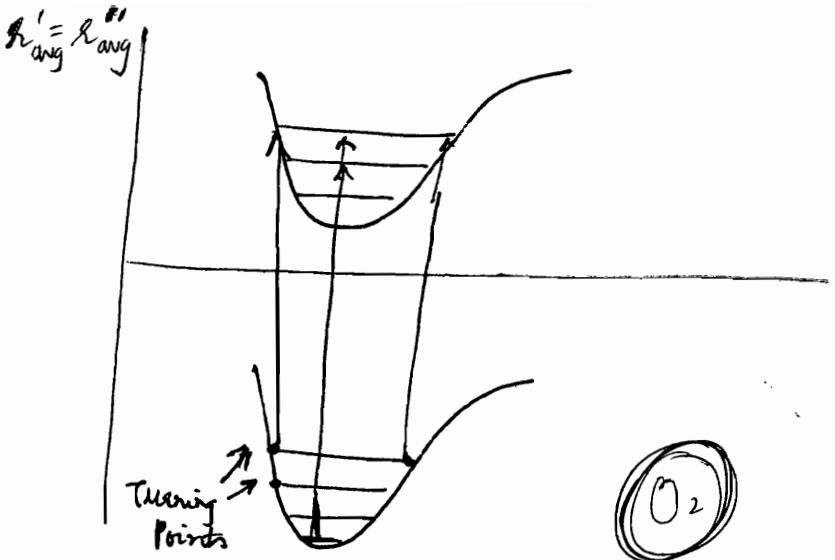
[Again $(B' - B'')$ can be negative]
or positive

FRANK-CONDON PRINCIPLE

'Most favoured transitions' or 'Most Probable Transitions' in electronic spectra are given by this principle.

It is the secondary criteria. Primary criteria is the Population according to Maxwell Boltzmann Curve.

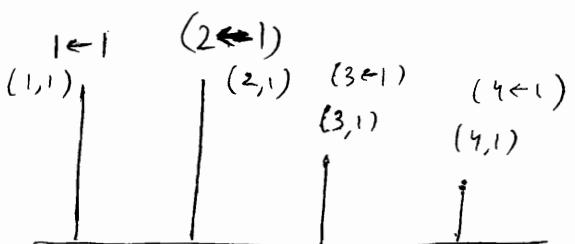
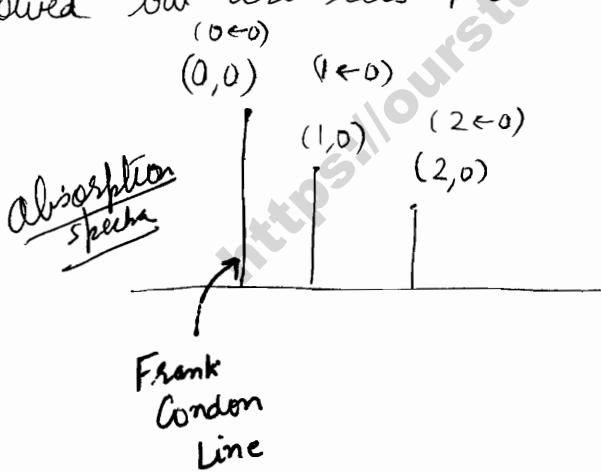
① All transitions must be represented by vertical lines.



→ During transitions, internuclear distances are const. Electrons are so small and shift that in their time of transition, heavy nuclei remain at the same positions.

② For ground state transitions, must occur from middle of level. Any other transitions occur from turning points ($\nabla^2 V$) is more at ends for higher state. → more prob. of transition.

→ Note that transitions according to F.C. Principle are most probable and most intense. Other transitions are of course allowed but are less probable.



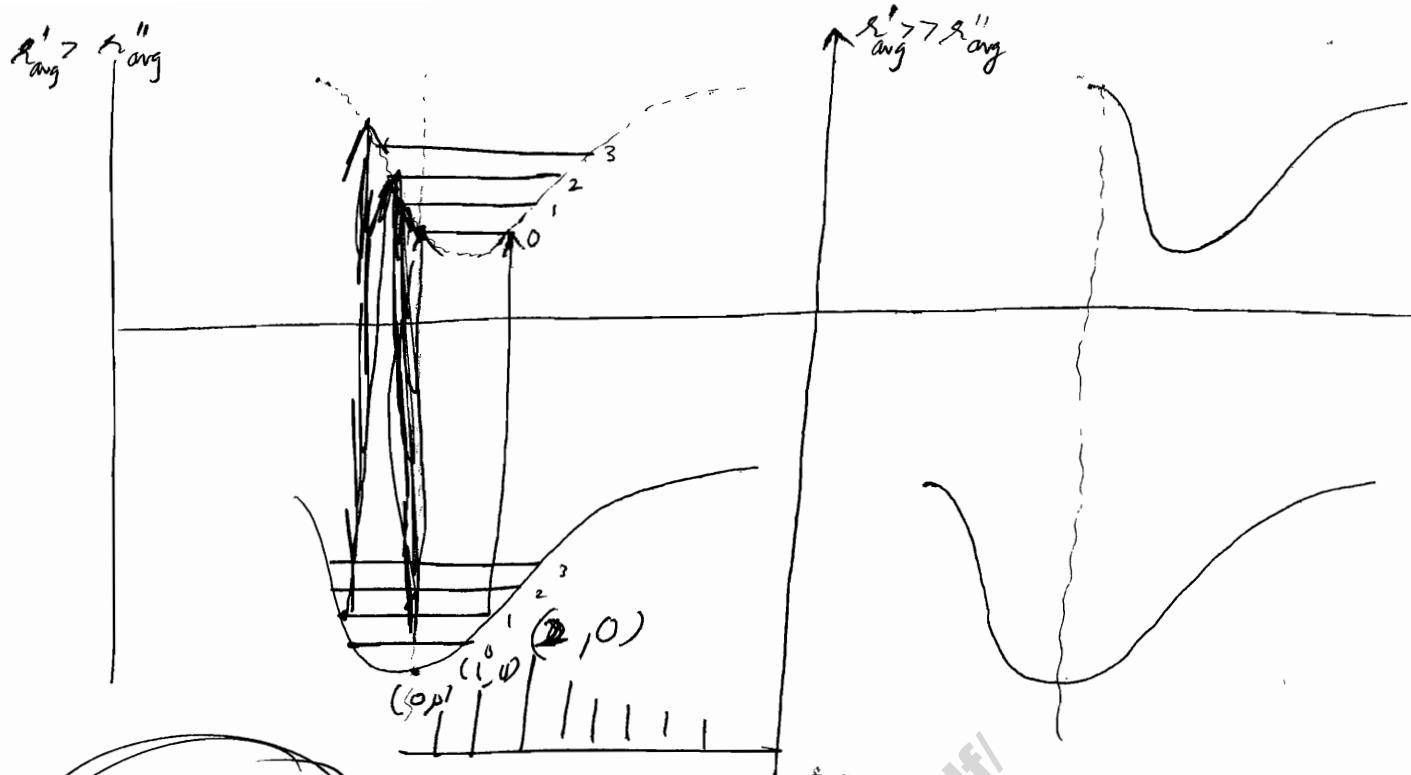
→ Note how the transitions are represented (x, y)

$x \uparrow$ higher energy state
 $y \downarrow$ lower energy state

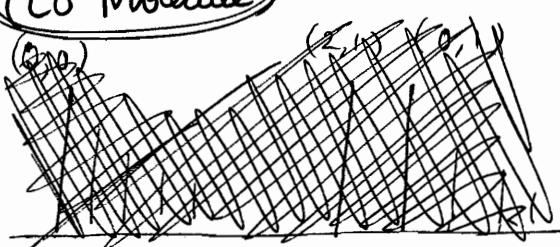
$(x \leftarrow y)$: Absorption spectra
 $(x \rightarrow y)$: emission spectra

Vertical lines from turning point of V' cut at $V = 1, 2$ respectively.

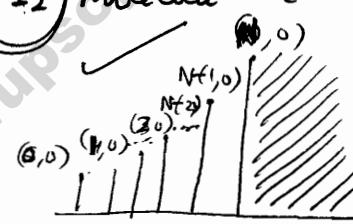
⇒ $(1,1)$ & $(2,1)$ have equal intensity !!



(CO Molecule)



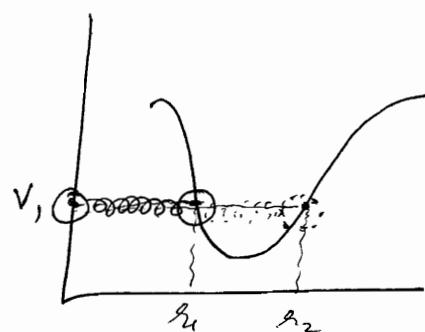
I₂ Molecule (very heavy)



Absorption
spectra

Continuous due
to dissociation limit
has been crossed.

→ Note that in vibrational energy state graphs, bond length is shown by a component of points on curve



Bond length a_1 and a_2 have
same Potential Energy.

→ Order of gap of spectral lines :- $\approx 20 \text{ cm}^{-1}$: rotational
 $\approx 1000 \text{ cm}^{-1}$: vibrational
 $\approx 50,000 \text{ cm}^{-1}$: electronic

★ Homonuclear molecules (H_2, O_2, N_2) which give neither rotational nor vibrational spectra b'coz they do not have permanent dipole moments. give electronic spectra b'coz the instantaneous dipole moments change during the redistribution of electronic charge which accompanies electronic transition.

★ Same Δv , different $\Delta J \Rightarrow$ Branch : Which is a Band
 $(V' = \text{const.})$ $\Delta J = 1$ Branch R
 $(V'' = \text{const.})$ $\Delta J = -1$ Branch P

while

$\Delta v = \text{const.}$ $v' = \text{const}$ or $v'' = \text{const}$ Progression
 $(v' \text{ and } v'' \text{ varying})$ $(v'' \text{ varying})$ $(v' \text{ varying})$ which are
 ↑ ↑ ↑
 [This is also called] [v'' progression] [v' progression]
 a sequence Band systems
 जो vary कर रही है, उसमें
 Progression
 i.e. जो Progression कर रही है !!

Molecular Physics (4)

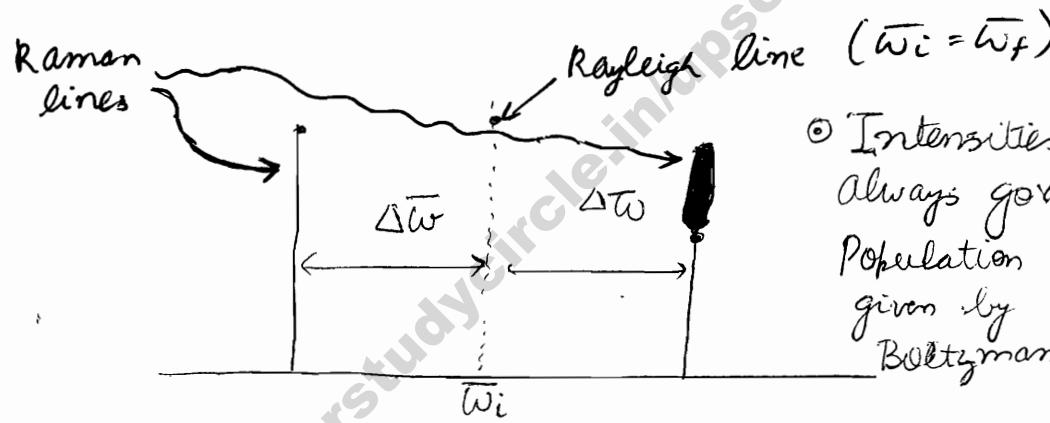
28/02/12

Raman Spectra

- ① In rotation, generally specimen is taken in vapour state.
- In Raman Spectroscopy, we can take in any phase.
- ② Here, permanent dipole moment is not required. Induced Dipole Moments are reason for Raman Spectra

$$\gamma_i \rightarrow \text{Specimen} \rightarrow \gamma_f$$

if γ_f comprises higher as well as lower freq. waves \Rightarrow Raman Scattering



④ Intensities are always governed by Population criteria given by Maxwell Boltzmann Dist?

$\Delta\omega$ is called Raman Shift

It typically lies in infrared region.

It is a characteristic of molecule.

Intensity wise $\bar{\omega}_i \approx \bar{\omega}_i - \Delta\bar{\omega}$: intensity STOKES

$\{\bar{\omega}_i + \Delta\bar{\omega}\}$: lower intensity ANTISTOKES

✓ Typical freq. in Photo Electric Effect : UV

✓ If freq. is higher, say γ-ray \Rightarrow Electron is removed as well as the photon comes out with reduced frequency.

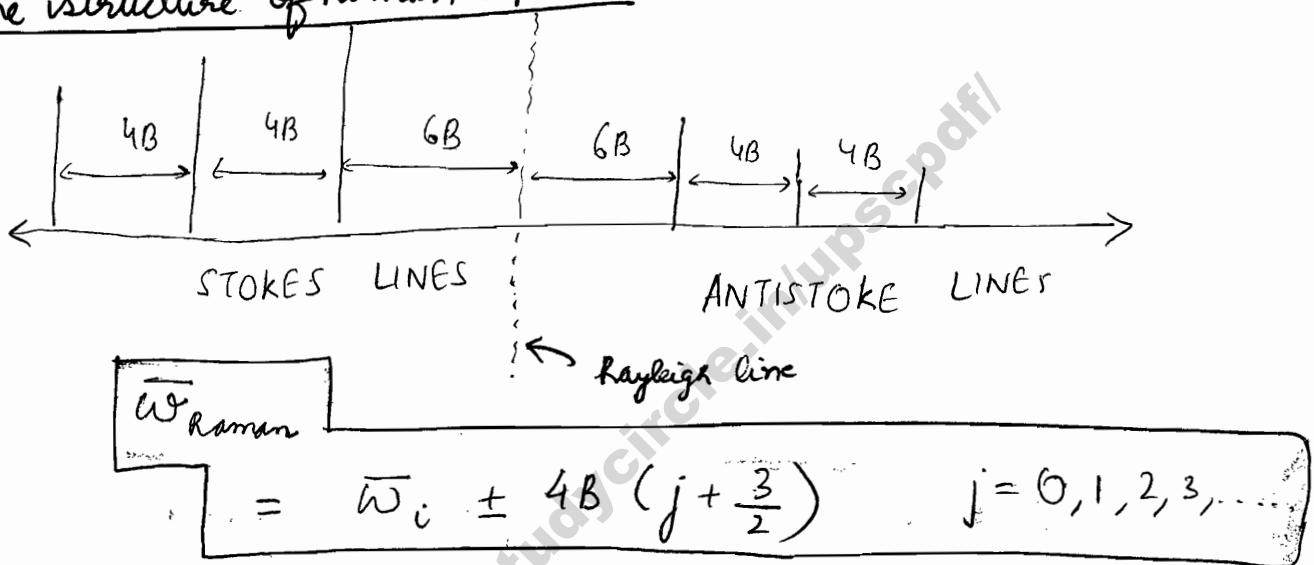
Its called Compton Effect.

✓ But in Raman spectra, the unusual thing is that some photons comes out with higher energy, though intensity is less.

✓ { Atomic Phenomenon
In Compton Effect, interaction with atoms (particularly e^-) }
{ In Raman Effect, interaction with molecules
Molecular Phenomenon }

Also $\Delta\bar{\omega}$ lies in infrared region \Rightarrow vibrational energy levels.

Fine structure of Raman Spectra



Note that Stokes lines are not confirmation of Raman Effect. Only once Antistokes are obtained, we are confirmed of Raman Effect. But Antistokes lines are low intensity lines, hence difficult to observe. When lasers come, then it become possible to detect them. Hence, we call it Laser Raman Spectroscopy.

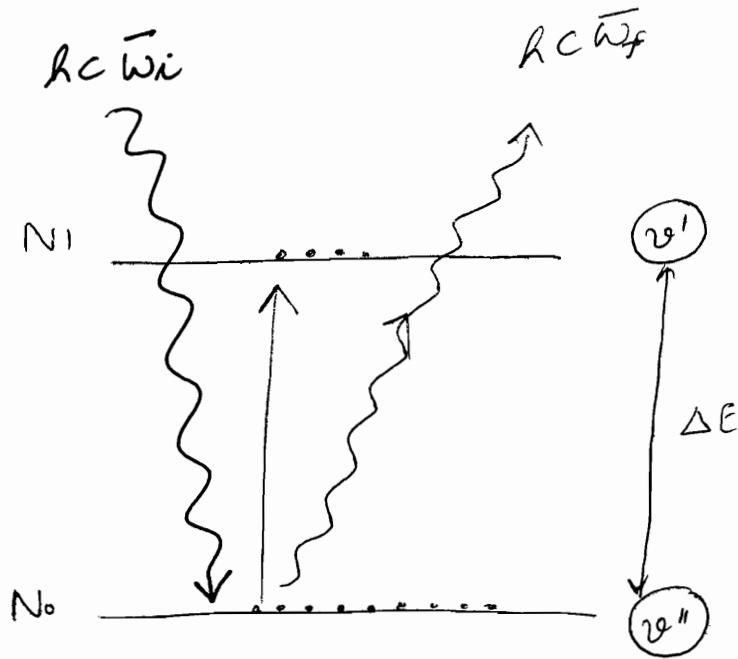
Quantum Mechanical Explanation

$\Delta v = \pm 1$ Vibrational Raman spectra

$\Delta J = \pm 2$ Rotational Raman spectra

For vibrational $\bar{\omega}_f = \bar{\omega}_i \pm [G(v+1) - G(v)]$

$$\Rightarrow \underline{\Delta\bar{\omega}_{\text{Raman}}} = \pm \bar{\omega} \left[v + \frac{3}{2} - v - \frac{1}{2} \right] = \pm \bar{\omega}$$



$$N_1 = N_0 e^{-\left(\frac{AE}{kT}\right)}$$

2 vibrational levels
 v' and v'' are shown.

$$\text{d}E = E(v') - E(v'') = \cancel{h} \cancel{c} \bar{w}$$

Suitable light is incident upon v'' i.e. $\bar{w}_i > \bar{w}$

If elastic collision, no energy transfer

$$hc\bar{w}_i + E(v'') = E(v'') + hc\bar{w}_f : \text{Rayleigh Scattering}$$

$$\Rightarrow \overline{\omega_i} = \overline{\omega_f}$$

If inelastic collision

$$\hbar c \bar{\omega}_i + E(v'') = E(v') + \hbar c \bar{\omega}_f$$

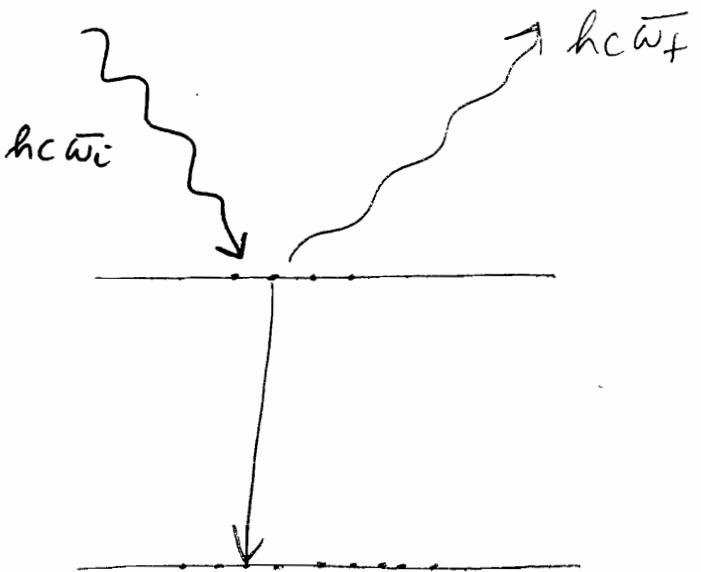
$$\Rightarrow \bar{\omega}_f = \omega_i + \left(\frac{E(v') - E(v)}{hc} \right)$$

: Stokes line of Raman scattering

Raman Shift : characteristic of molecule
 $\Delta \nu_{\text{Raman}}$

✓ { High intensity b'coz maximum population in ground state.
Incident & scattered light has nearly same energy.

$$hc\bar{\omega}_i + E(v') = E(v'') + hc\bar{\omega}_f$$



$$\Rightarrow \bar{\omega}_f = \bar{\omega}_i + \frac{(E(v') - E(v''))}{hc} \quad \Delta\omega_{\text{Raman}}$$

Anti-Stokes line

lower intensity line due to lower population in excited levels

→ Inelastic collision b/w photon & molecules is, therefore, responsible for Raman Effect.

- Note that NO NEW PHOTON IS SCATTERED AND NO PHOTON IS COMPLETELY _(photoelectric) ABSORBED.

Selection Rule for Fine Structure

$$\Delta v = \pm 1 \quad [0 \text{ for Rayleigh}]$$

$$\Delta J = \pm 1, \pm 2 \quad [0 \text{ for Rayleigh}]$$

Selection rule is due to induced dipole moment. Hence occur in all molecules irrespective of possession of permanent dipole moment.

For vibrational Raman spectrum,

$$\bar{\omega}_f = \bar{\omega}_i \pm [G(v+1) - G(v)]$$

$$\bar{\omega}_f = \bar{\omega}_i \pm \bar{\omega} \quad \Rightarrow \quad \Delta\omega_{\text{Raman}} = \bar{\omega}$$

For fine structure, or Rotational Raman Spectrum,

$$\bar{\omega}_{\text{Raman}} = \bar{\omega}_i \pm [F(J+2) - F(J)] \quad \text{Note that we are not talking about fine lines within coarse vibration lines. We are talking about only fine}$$

where $F(J) = BJ(J+1)$

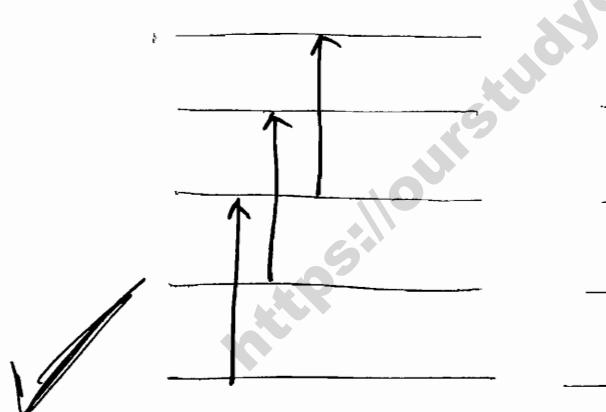
$$\Rightarrow \bar{\omega}_{\text{Raman}} = \bar{\omega}_i \pm B [(J+2)(J+3) - J(J+1)] \quad \text{lines on both of Rayleigh line in far-IR end spectra.}$$

$$= \bar{\omega}_i \pm B [4J+6]$$

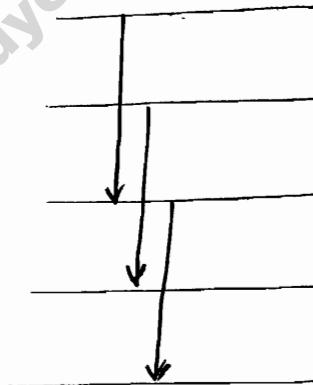
$$\boxed{\bar{\omega}_{\text{Raman}} = \bar{\omega}_i \pm 4B \left(J + \frac{3}{2} \right)}$$

$$\Rightarrow \bar{\omega}_{\text{Raman}} = \bar{\omega}_i \pm 6B, \quad \bar{\omega}_i \pm 10B, \quad \bar{\omega}_i \pm 14B, \dots$$

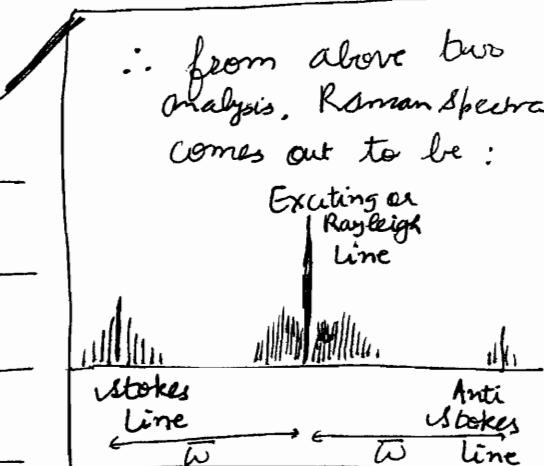
From given lines, we can calculate $B \Rightarrow I_{cm} \Rightarrow \text{Bond length}$



$\Delta J = +2$
"S Branch"
Stokes lines



$\Delta J = -2$
Anti-Stokes lines



Both are

Homonuclear diatomic molecules do not give vibrational rotational spectra but give Raman spectra.
Called Infrared Inactive but Raman Active.

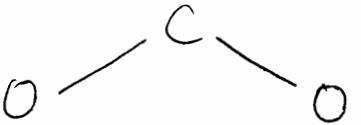
For CO_2 molecule



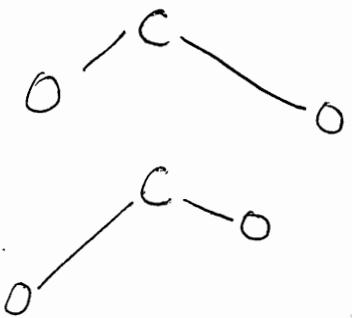
linear mode

Symmetric linear molecule.

Permanent Dipole Moment \Rightarrow Only Raman spectra



Bend Mode (Symmetric or Asymmetric)



No Centre of Symmetry } \Rightarrow Both active

Centre of Symmetry } \Rightarrow Only Raman Active

Here apart from ν_{cm} , Bond-length, type of symmetry is also known from spectra.

→ Mercury Arc was initial source of light. It had drawbacks:

① Its extended source of light \Rightarrow large quantity of sample is required, leading to wastage of precious materials.

② Some of the light of incident rays enter spectrometer tube. It will mask weak raman lines.

③ If total energy = E_{h} , incident \Rightarrow whole incident photon between v and v' is absorbed completely \Rightarrow fluorescent effect

may be caused i.e. if excitation f matches with absorption f . Fluorescent will mask Raman's weak lines.

~~④ Analysis of Coloured salt solutions was difficult due to limited frequency available in mercury arc. Lasers are available over a wide range of frequencies.~~

All these drawbacks were removed after the use of LASERS began. Hence before 1966, Raman Spectroscopy was finding little use in molecule structure determination.

Ar and kr Lasers (inert) are used. They can be focussed on small area with wide power range. Hence normal devices like gratings can be used to record spectra. Also they have wide frequency range.

$$23 \quad \omega_i = \frac{1}{514.5} \text{ nm}$$

24 Fine Structure cannot be resolved otherwise

$$\frac{h^2}{8\pi^2 I} = B = 1.43 \times 10^{-5}$$

$$\gamma_0 = 8.4 \times 10^{12} \text{ Hz}$$

$$E(J) = \frac{J^2}{2I} = j(j+1) \frac{h^2}{8\pi^2 I}$$

$$E(v=1) - E(v=0) = h\gamma_0$$

$$\text{Equating the } ①, \quad j(j+1) = \frac{6.62 \times 8.4 \times 10^6}{1.6 \times 1.43}$$

★ Vibrational Raman spectra agrees exactly with wave no. of main vibrational rotational spectra in near infra-red spectrum. while

Rotational Raman separation = 2 [separation of usual microwave spectrum]

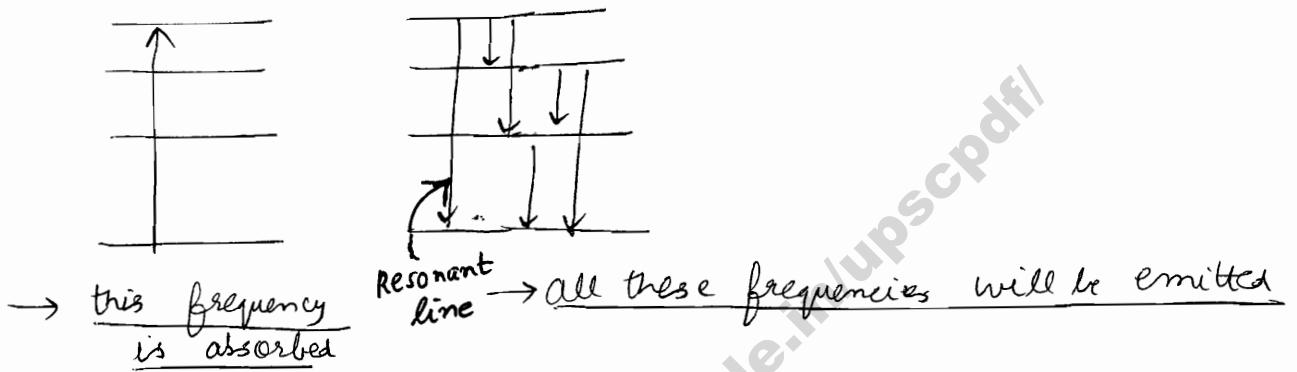
★ Induction or Polarization by incident light cause dipole moment in homonuclear molecules \Rightarrow rotational, vibrational level occur in them.

In addition, molecules like H_2, D_2, N_2, \dots the rotational ^{Raman} lines are alternately weak and strong. In extreme case like D_2 , every alternate line is missing. This phenomenon arises from symmetry properties of rotational levels of homonuclear molecules

★ Luminiscence ($21H\ h$)

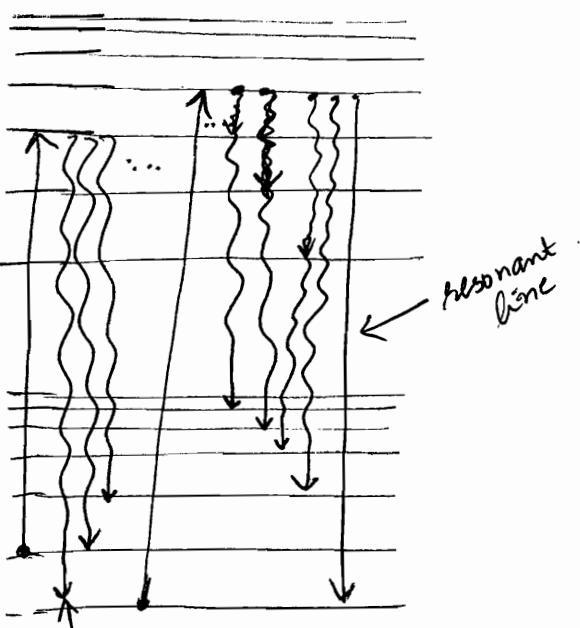
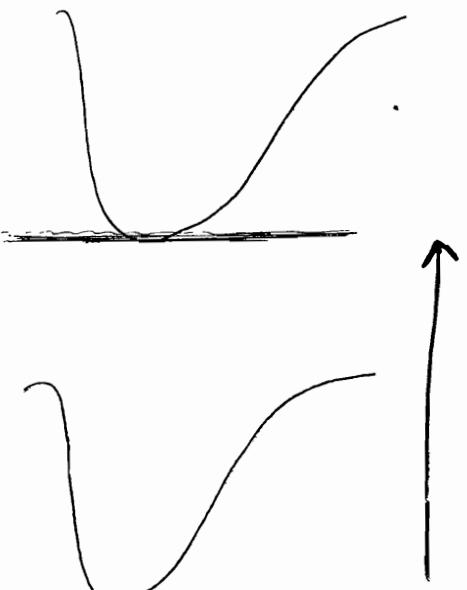
Fluorescence Phosphorescence

When a molecule is incident upon by a "suitable frequency" i.e. one of the absorption frequencies, molecule may be raised to any excited level (rot/vib/electronic).



Now, molecule has option to come down instantaneously. It's called Fluorescence. The γ released are less than incident.

In Phosphorescence, energy is emitted even after source of excitation is removed. It is delayed emission of radiation.



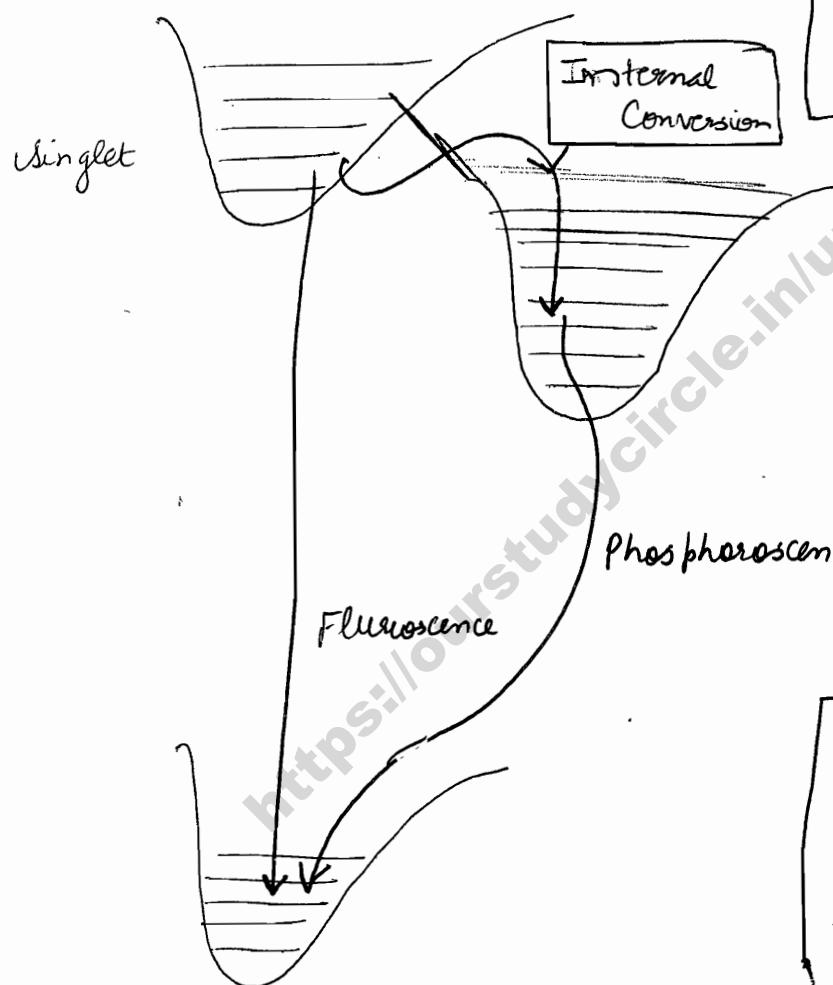
- ⑤ Intensity dist' of the bands will depend upon Frank Condon and Maxwell dist'.

Antistokes line of Resonant line

'I' photons that fall will interact with 'I' molecules. These 'I' molecules are raised to higher energy. Incident photon is absorbed.

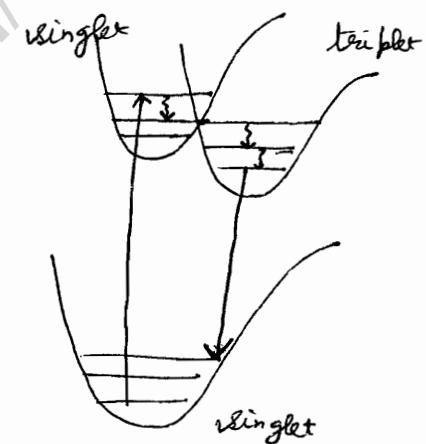
All frequencies emitted are less than that of resonant line.

Singlet, $s=0 \quad \lambda=1$



Triplet, $s=1 \quad \lambda=3$

① Delayed emission occurs due to transitions that connect electronic states of different multiplicities.



Phosphorescence arises when triplet excited state of molecule exists b/w singlet excited state and singlet ground state. Radiationless transitions to lower vibrational levels followed by internal conversion followed by further vibrational deactivation to $v'=0$. Transition from triplet state to singlet ground state are responsible for phosphorescent emission.

Remember selection rule, $\Delta s=0$

$\sigma-\sigma$ transition : same multiplicity.

It has high Probability \Rightarrow shorter time.

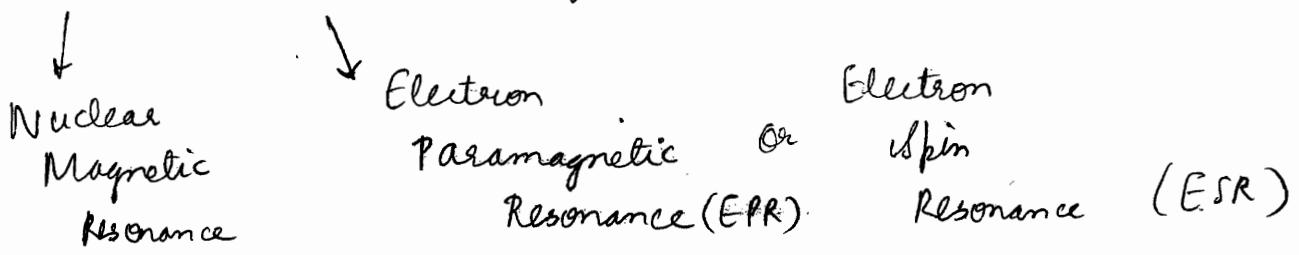
Phosphorescence occurs in violation of selection rule
 \Rightarrow low probability \Rightarrow longer time
 \Rightarrow delayed emission.

Molecular Physics (5)

29/02/2012

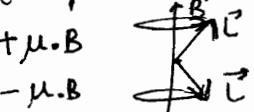
NMR and EPR/ESR

NMR and EPR are magnetic resonance techniques



✓ Resonance is matching of frequencies of source and system.

✓ Precession frequency of Nucleus is ~~is proportional to B~~ matched with f of oscillating B .

Angular Momentum precesses about field. Energy levels are separated by ΔE . 

$\Delta E_{\text{nucleus}}$: very small $\approx 10^{-8} \text{ eV}$

Remember, we mentioned it in spectroscopy

* same technique if used in
RF: NMR
mu: ESR
NMR: nuclear magnetic moment
ESR: e- spin moment Resonance

$$hy = 10^{-8} \times 10^{19}$$

$$\lambda = \frac{hc}{E} \text{ in Radio Frequency Region}$$

$$\Delta E_{\text{electron}} \text{ due to spin} \approx 10^{-3} \text{ eV} : \text{Microwave Region}$$

✓ It's also called EPR because all paramagnetic salts have $s \neq 0$, i.e. have unpaired $e^- \Rightarrow$ Spin Angular Momentum $\neq 0 \Rightarrow$ Larmor Precession $\Rightarrow \Delta E_{\text{electronic, spin}}$

$$\text{We know, } \vec{\mu}_e = -\frac{e}{2m} g_e \vec{L} \quad g_e = 1$$

$$\vec{\mu}_s = -\frac{e}{2m} g_s \vec{S} \quad g_s = 2$$

$$\vec{\mu}_J = -\frac{e}{2m} g_J \vec{J} \quad g_J = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

- ① $\vec{\mu}_J$ is component of $\vec{\mu}$ along \vec{J} . We are interested in $\vec{\mu}_J$ only as other components average out to zero.

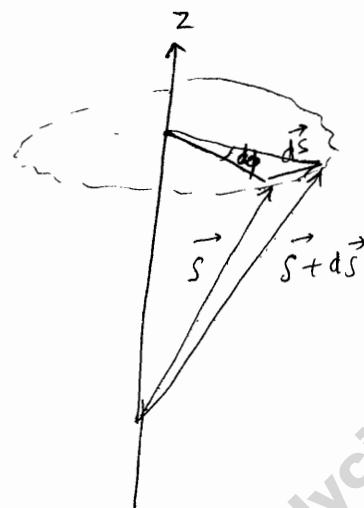
Note that prerequisite of ESR is $S \neq 0$

Atom with unpaired e^- i.e. $S \neq 0$ is kept in steady magnetic field ($\text{const } \vec{B}_0$).

$$\Rightarrow \vec{\tau} = \vec{\mu}_s \times \vec{B}_0$$

$\Rightarrow \vec{S}$ will rotate about direction of $\vec{B}_0 \Rightarrow e^-$ will precess

$$\Rightarrow \vec{\tau} = \frac{d\vec{S}}{dt} \Rightarrow d\vec{S} \perp \vec{S} \Rightarrow \underline{\text{Precession}}$$



$$\omega_p = \left(\frac{\mu_s B_0}{S} \right)$$
$$\Rightarrow \omega_p = \frac{e g_s B_0}{2 m_e}$$

✓ Precisely same derivation for Nucleus Magnetic Moment

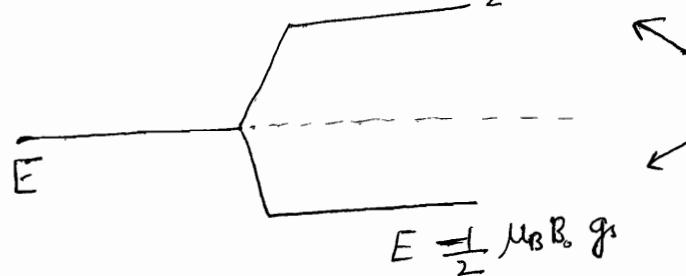
Now $\Delta E_{\text{electron spin}}$ will occur due to Potential of $\vec{\tau}$ and Magnetic field.

$$E = \omega_p S_z = \frac{e g_s B_0 m_s \hbar}{2 m_e} = \mu_B B_0 g_s m_s$$

For $e^- : m_s = \pm \frac{1}{2}$

$$\Rightarrow E = \pm \left(\frac{\mu_B B_0 g_s}{2} \right)$$

$$E + \frac{1}{2} \mu_B B_0 g_s$$



2 spin states for an electron

$$\Delta E = \mu_B B_0 g_s = h\gamma$$

This γ has no role in NMR/ESR

→ Hence by absorbing frequency γ or emitting frequency γ , e- can flip between its spin states.

Now I apply another oscillating field,

$$\vec{B}_1 = B_1 \sin(2\pi\gamma t)$$

from klystron Oscillator.

This varying field will cause magnetic resonance to its 1st field.

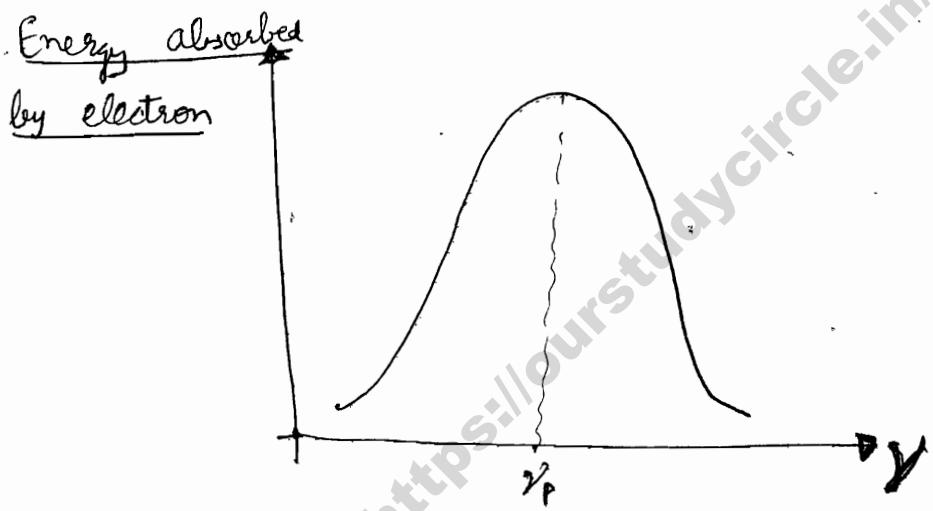
When γ of \vec{B}_1 becomes equal to $\gamma_{\text{precession}}$, then maximum absorption of energy is observed.

I am applying 2 field, 1st for creating energy separation $\Delta E = \mu_B B_0 g_s$

2nd is applied for creating resonance with the natural frequency located

$$\gamma_0 = \gamma_{\text{precession}}$$

$$= \gamma_2 \text{ for resonance}$$



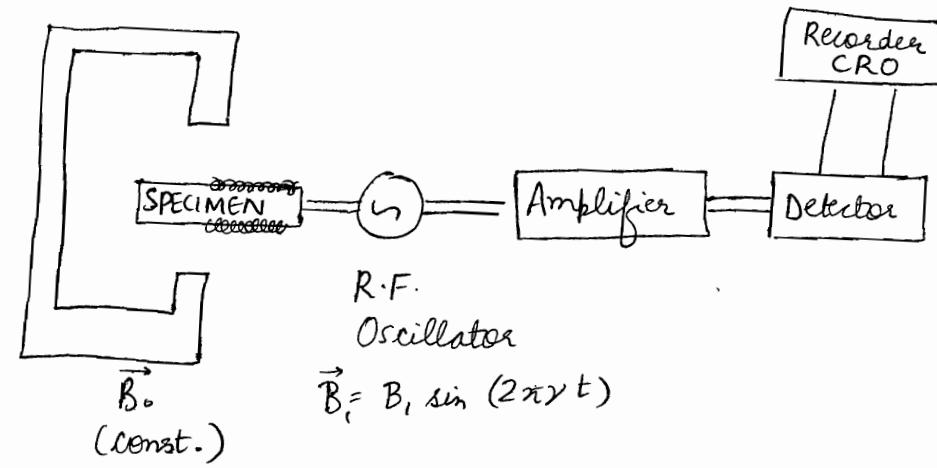
If @ $\gamma = \gamma_p$, I get maximum energy absorption

$$\Rightarrow \gamma_p = \frac{e}{4\pi m_e} g_s B_{\text{fixed}} \quad \checkmark$$

$\Rightarrow g_s$ is obtained

γ_{electron} will lie in Microwave Region ...

$$\Delta E \approx 10^{-3} \text{ eV}$$



Typical Schematic Diagram of NMR Spectroscopy

(For EPR, change the oscillator to klystron oscillation)

$$\text{Ang. Momentum } |\vec{I}| = \sqrt{I(I+1)} \hbar$$

$$\vec{\mu}_{\text{nucleus}} = \frac{e}{2m_p} g \vec{I}$$

$$\omega_p = \frac{e}{2m_p} g B_0$$

$$E + \left(\frac{\mu_N g B_0}{2} \right)$$

$$\begin{aligned} \Delta E &= \omega_p I_z \\ &= \left(\frac{e h}{2m_p} \right) g B_0 m_I \end{aligned}$$

↑
Nuclear Bohr Magneton

$$= \underline{\mu_N g B_0 m_I}$$

which can be $\pm \frac{1}{2} \mu_N g B_0$

(if only single proton)

Similarly,

$$\begin{aligned} \text{NMR frequency } \nu &= \nu_p \\ &= \frac{e}{4\pi m_p} g B_0 \end{aligned}$$

⑥ In chemical analysis and Biological Analysis, NMR and EPR are greatly used as low Energy levels of microwave and Radio wave, hence no potential damage to living tissues.

MRI = NMR used in Medical Diagnosis

→ NMR is a technique in spectroscopy where RF fields induce transitions b/w Nuclear Energy levels causing absorption of energy whereby maximum energy absorption occurs at resonant level.

$$B) \vec{J} \Rightarrow \vec{\mu}_S \Rightarrow \vec{T} \text{ in } B \Rightarrow T \perp S \Rightarrow dS \perp S$$

⇒ Precession

22) $\gamma_p = \frac{e}{4\pi m_p} g_p B_0$

$$= \frac{1.6 \times 10^{-19}}{4\pi \times 1.6 \times 10^{-24}} \times g_p \times 1.5$$

$\mu_p = \frac{e}{2m} g \vec{I}$

$$(\mu_p)_z = \frac{e}{2m_p} g I_z = \frac{e\hbar}{2m_p} g m_I$$

$$2.793 \mu_N = \mu_N g m_I$$

$$m_I = \left(\frac{1}{2}\right) \quad (\text{No value of } m_I = \frac{-1}{2})$$

$$\Rightarrow g = 2 \times 2.793 = \underline{\underline{5.586}}$$

★

$$\begin{aligned} \gamma_p &= \frac{\Delta E}{h} \\ &= \frac{(2\mu \cdot B)}{\hbar} \\ &= \frac{2e\hbar}{2m} g_I \cdot m_I B \end{aligned}$$

$$\frac{e}{4\pi m_p} g B$$

अरे आप $m_{top} - m_{bottom}$ तो
1 की होता हमेशा !!

In water NMR occurs due to Proton

$$g_{\text{proton}} = 5.586$$

$$\begin{aligned} \text{Hence } \mu_p &= \frac{e}{2m} \times 5.586 \\ &= \underline{\underline{\mu_N. 2.793}} \end{aligned}$$

Chemical shift

⇒ due to shielding : $B = B_0(1-\sigma)$

Magnetic field encountered by Bare nucleus due to shielding effect of outer electrons

$$\Rightarrow \gamma_p = \frac{e}{4\pi m_p} g_p B_0(1-\sigma)$$

We take 2 nucleus A and B

$$B_A = B_0(1-\sigma_A)$$

$$B_B = B_0(1-\sigma_B)$$

$$\Rightarrow B_A - B_B = -B_0(\sigma_A - \sigma_B)$$

$$\Rightarrow (\sigma_A - \sigma_B) = -\left(\frac{B_A - B_B}{B_0}\right)$$

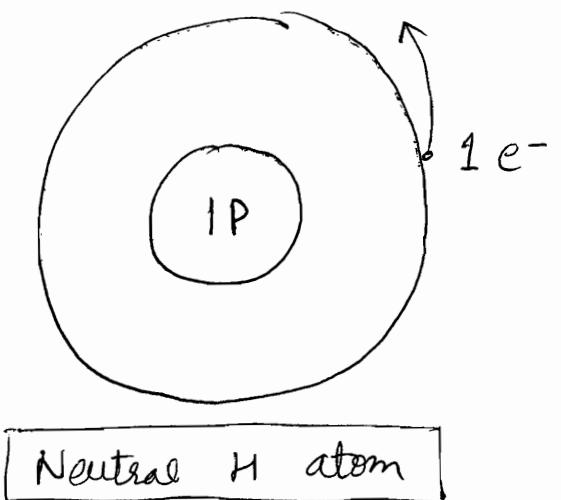
B_0 : applied

B_A, B_B : fields at which resonance was observed.

Its important in chemical analysis.

Importance of Neutral H atoms in Astronomy

In start of Universe, abundance of H (neutral) Nuclear Fusion to form He atoms and then further elements were formed.



Till now, we have neglected motion of Nucleus.
If I use Ultra-high resolution spectroscope, I see hyperfine lines further than what explained by

$$H = \frac{\vec{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} + \alpha(\vec{l} \cdot \vec{s}) + [\text{Lamb shift}]$$

It is due to motion of nucleus.

$$\vec{J} = \vec{L} + \vec{s} \dots \text{Fine Structure}$$

$$\begin{aligned} \vec{I} &= \sqrt{I(I+1)} \quad \text{Total Ang. Momentum of Atom} \\ \Rightarrow \boxed{\vec{F}} &= \vec{L} + \vec{s} + \vec{I} \\ &= (\vec{J} + \vec{I}) \end{aligned} \quad \dots \text{Hyperfine structure}$$

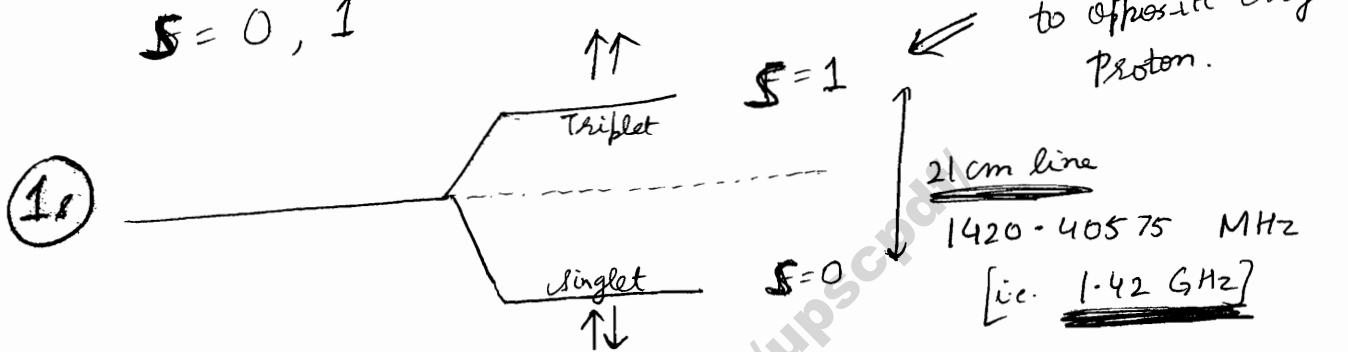
$$\Rightarrow |J-I| < F < |J+I|$$

$$\Delta F = 0, \pm 1$$

Now,
For 1s, 2s : $l=0$
[closest states]

Hyperfine Structure of Neutral Hydrogen Atom

$$S = 0, 1$$



New selection rule: $\Delta S = 0$

MICROWAVE
It lies in ~~radio~~ Frequency Region

$$\text{Transition Probability} = 2.9 \times 10^{-15} \text{ per second}$$

$$\Rightarrow \text{Transition Time} \leq 10^{14} \text{ second} = 10^7 \text{ years}$$

$$10^7 \text{ seconds} \approx 1 \text{ year}$$

hence, importance only in astronomy where such time periods are important.

Due to interatomic collisions, transition time is reduced by a little amount.

- a little amount.

of matter power spectrum in period

 - ① It can provide clear picture after recombination, ~~it~~,
~~it~~ by mapping ~~red-shifted~~ 21 cm radiation
 - ② It can provide picture of how universe was reionized,

as neutral H atom which were ionized due to radiation from quasi-stellar sources which will appear as holes in 21 cm background.

21 cm line

- ★ Hydrogen in our galaxy has been mapped by the observation of 21 cm wavelength line of hydrogen gas. At 1420 MHz, this radiation can penetrate the dust clouds (very low) and gives us a more complete map of H than that of the stars themselves since their visible light is not able to penetrate the dust clouds. (ionization)

The 1420 MHz radiation comes from the transition between the 2 levels of the H 1s ground state, slightly split due to interaction between electron spin and nuclear spin. This splitting is known as hyperfine structure. This splitting of H ground state is extremely small compared to ground state energy of -13.6 eV (about $\frac{2}{10 \text{ lakh}}$ ratio). 2 states come from the fact that both the e^- and proton have $(\frac{1}{2})$ spin, so there are 2 possible states, spin parallel (slightly high energy) and spin anti-parallel
 \downarrow
less tightly bound

NMR

When the nuclear magnetic moment associated with nuclear spin is placed in an external magnetic field, the different spin states are given different magnetic potential energies. In the presence of such static magnetic field which produces a small amount of spin polarization, an R.F. signal of proper frequency can induce a transition

between spin states.

This "spin flip" places some of the spins, in their higher energy states. If the R.F. signal is then switched off, the relaxation of the spins back of the lower state produces a measurable amount of RF signal @ the resonant frequency associated with the spin flip. This process is called Nuclear Magnetic Resonance (NMR)

It is used to study Chemical's structure i.e. composition of different compounds & polymers
Also chemical shifts measurement in high resolution NMR Spectroscopy is major source of chemical's information

Laser Raman Spectroscopy and Molecular Structure

Raman effect is an important tool to determine molecular structure information of diatomic and polyatomic molecules.

- The vibrational and rotational Raman spectra enable us to determine ω_c and $B \Rightarrow$ to determine force constant k , bond length, I_{cm} for diatomic molecules.
- For polyatomic molecules, Raman spectra and IR data (vibrational) give information regarding shape (linear or bent) and symmetry of the molecules.
According to 'Mutual Exclusion Principle', for molecules with a centre of symmetry the frequencies of IR spectra are not observed in Raman spectra and vice versa. This enables us to deduce structure of molecules.

e.g. Molecules of CO_2 and C_2S_2 are found to have 2 strong IR bands that are not observed in Raman spectra
 \Rightarrow Centre of Symmetry \Rightarrow $O=C=O$ $S=C=S$

Molecules H_2O show 3 IR bands that coincide with Raman spectra \Rightarrow



(no centre of symmetry)

Raman Spectroscopy technique used to study vibrational, rotational and other low frequency modes of a system. It relies on inelastic scattering, or Raman scattering of monochromatic light from a laser in the visible, near infrared, or near UV range. The shift in energy of photons gives information about vibrational modes in the system. IR spectroscopy yields similar but complimentary results.

The main difficulty of Raman scattering is the separation of weak inelastically scattered light from the intense Rayleigh scattered [redacted] light. With the advent of lasers and notch filters, it has become an important instrument of spectroscopic analysis.

Uses of Raman Spectroscopy :

- (i) determination of molecular structure
- (ii) Raman Gas Analyzers use real time monitoring of anaesthetic and respiratory gas mixtures during surgery.
- (iii) In solid state physics, Raman Scattering is used to characterise materials, and thereby Temperature measurement and finding crystallographic orientation
- (iv) Non invasive way of monitoring of biological tissue; and historical documents to determine best way of preservation.