Physics - 6

- $\hat{H}$ means 'Operator H' i.e Hamiltonian.

  eg. $\hat{p} = -i\hbar \frac{\partial}{\partial x}$

- BOSON : Integral Spin $s = 0, 1, 2, 3, \ldots$

  eg. Photon, Ground State He atom

  FERMION : Half Integral Spin

  eg. Electron

  Proton

  Neutron

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

-

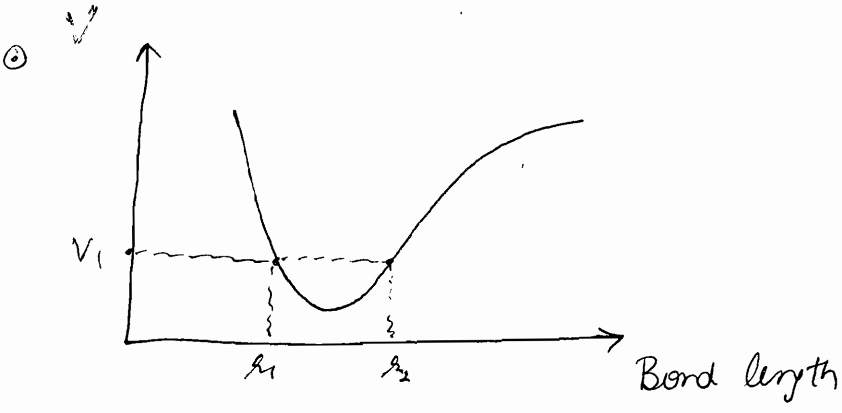
$$\begin{tikzcd}
\boxed{\nu_\gamma \simeq 10^{20}\,Hz} \arrow[r] & \nu_{Xray} = 10^{18}\,Hz \arrow[r] & \nu_{UV} = 10^{16}\,Hz \arrow[d] \\
\boxed{\nu_{radio} = 10^{6}\,Hz} & & \text{Visible } 10^{15}\,Hz \arrow[d] \\
 & \nu_{MW} = 10^{10}\,Hz \arrow[ul] & \nu_{IR} = 10^{12}\,Hz \arrow[l]
\end{tikzcd}$$

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

- Value of R_0

  m_π : 1.4 fm

  Fission parameter : 1.5 fm

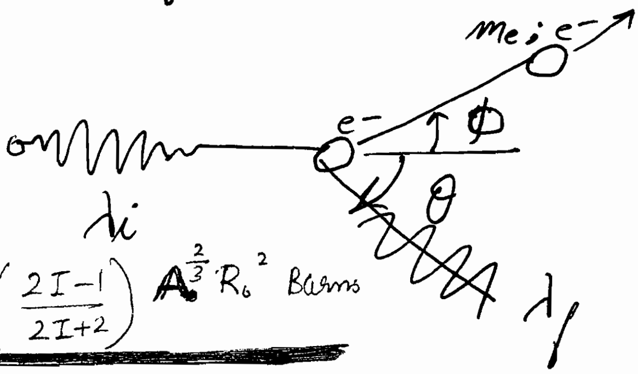
- 

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

- Visible lights range = 4000 Å − 7000 Å

- Compton Scattering : $\lambda_f - \lambda_i = \frac{h}{m_e c}\left[1-\cos\theta\right]$

θ: scattering angle of photon



- $Q = \frac{3}{5}\left(\frac{2I-1}{2I+2}\right) A^{\frac{2}{3}} R_0^{2}$ Barns $= \frac{1}{e}\int (3z^2 - r^2)\,\rho(r)\,d\tau$

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	

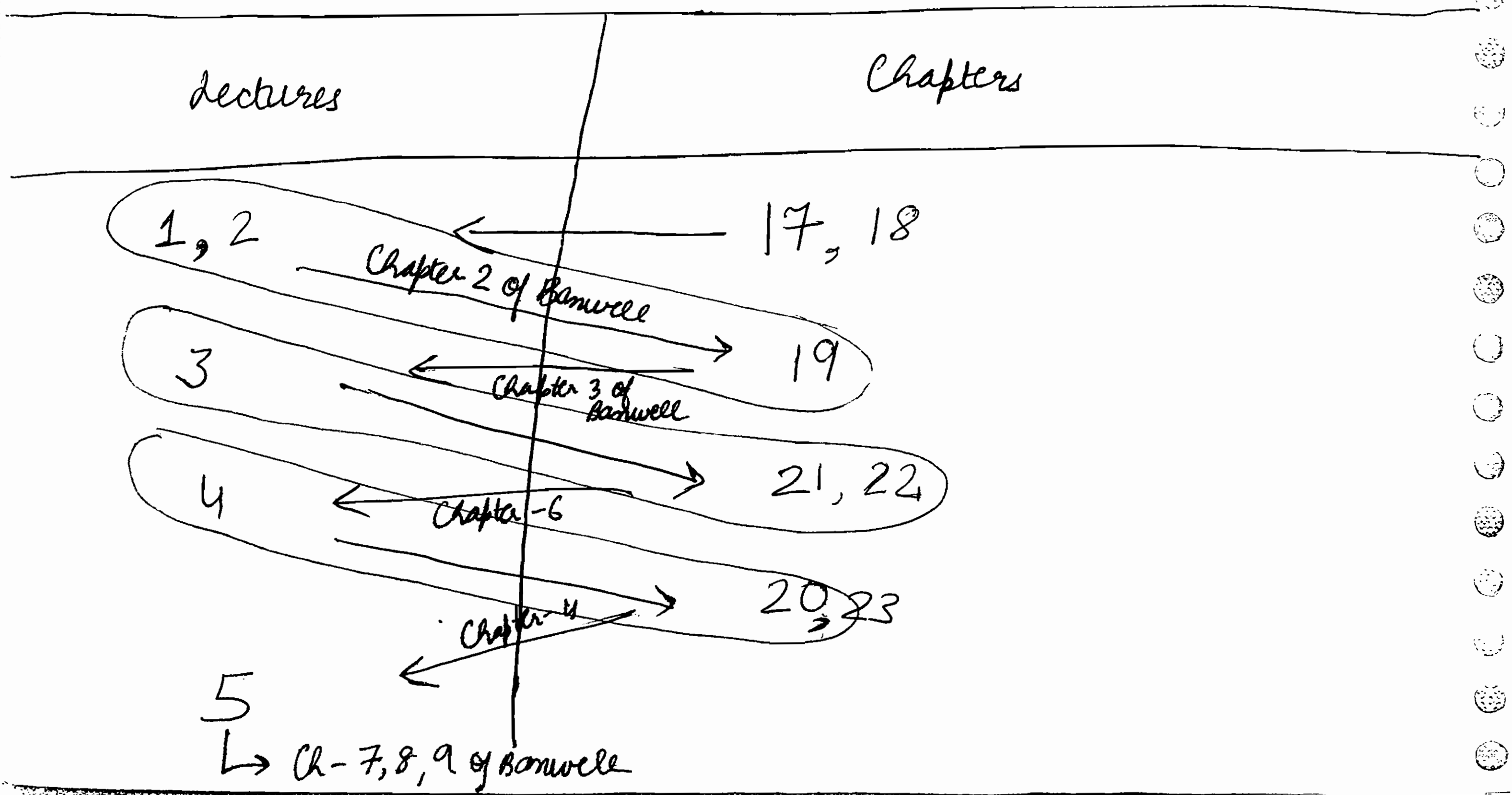
PARTICLE PHYSICS

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, $[\text{half of } 3]_A$	5, 6, 7, 8
$[\text{half of } 3]_B$, [first page of 4]	9
[Rest of 4]	12, 15 ↓ Chapter 5 of Banwell

Molecular Physics



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

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

Molecular Physics

- ✓ Elementary idea about rotational, vibrational and electronic spectra of diatomic molecules : ③
  Frank Condon Principles
- ✓ Raman Effect & Laser Raman Spectroscopy ①
- ✓ Fluoroscence & Phosphorescence : 21 cm line of H_2 ①
- ✓ NMR / EPR ①

$$\boxed{\vec{\mu_J} = -g_J \frac{e}{2m} \cdot \vec{J}}$$

$$\boxed{\Delta E = \mu_B B \, g_J m_j}$$

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 ν or ω or λ.

○ Every field of science has its own notations !!

$$\boxed{\frac{\nu}{c} = \bar{\omega} = \frac{1}{\lambda_{vacuum}}}$$

✱ Called wave number, $\bar{\omega}$ = no. of waves per metre or centimeter

○ It remains const. irrespective of medium.

○ $\bar{\omega}$ is a replacement of frequency which is usually a large number.

(✱) 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

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

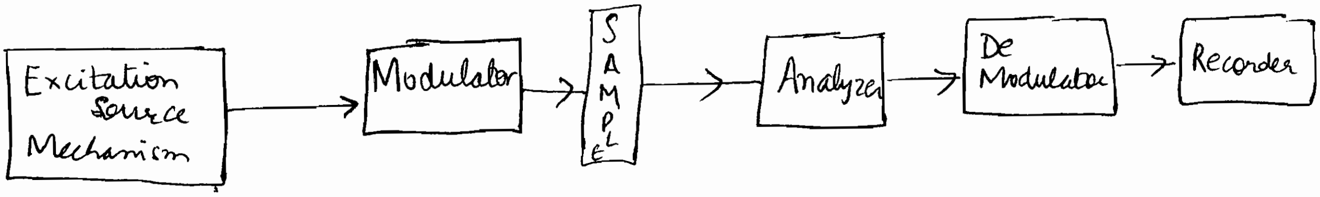
- Same specimen can give spectra of e^-, atoms, molecules & nucleus.

- [redacted] 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



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

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

Then ΔE : molecular

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

$\Delta E_{nucleus} \simeq 10^{-8} eV$

$\lambda = \frac{hc}{\Delta E}$: Radio Frequency Regions

⊛ 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 that of radio frequency rays.

Hence, Radio Frequency Spectra of nuclear energy levels

Therefore suitable source is Radio Frequency Oscillator.

example NMR.

$\Delta E_{molecular} \simeq 10^{-3} eV$

3 types of energy: ① Rotational ~ MICROWAVE SPECTRA

eg. Klystron Oscillator : Microwave Source

② Vibration $10^{-1} eV$ ~ Infrared Region

③ Electronic Energy levels ~ several eV

i.e. $10^{1} eV$

i.e. Visible or UV range.

$\Delta E_{atomic} \simeq$ many eV — Balmer — Paschen, Brackett, Pfund ....

Lyman ← UV, visible and Infrared Spectrum

due to jumping of e^-

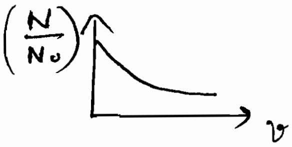
eg. $\left(13.6 - \frac{13.6}{4}\right)$ eV in H atom

If $T = 300\,k = 27°C$

Equivalent $= kT = 0.026$ eV

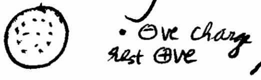
It is sufficient to cause rotation of molecules but not vibration.

⇒



Atomic Models

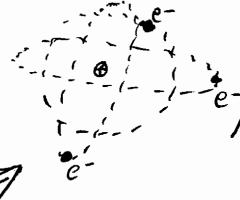
Thomson Model (Plum Pudding Model



)

↓

Rutherford Model (Based on scattering experiment



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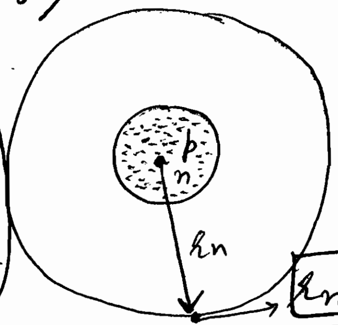


$\boxed{r_n = a n^2}$

$\boxed{a = 0.53 Å}$

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

↓

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

↓

Somerfield'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 $|\vec{L}| = |\vec{r} \times \vec{p}| = n\hbar$

$$\Downarrow$$

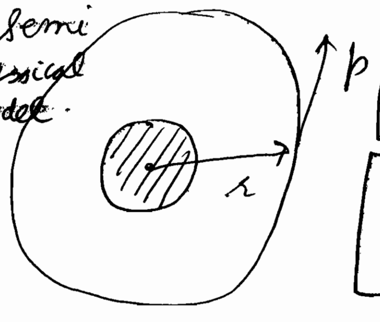
$$E_n = -\left(\frac{13.6}{n^2}\right)$$

② $\Delta E = \left(\frac{hc}{\lambda}\right) \Rightarrow E_f \sim E_i = \frac{hc}{\lambda}$

$$= 13.6\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\left.\begin{array}{l} \frac{mv^2}{r} = \frac{Zq^2}{4\pi\varepsilon_0 r^2} \\ mvr = n\hbar \end{array}\right\} \quad n\hbar v = \frac{Zq^2}{4\pi\varepsilon_0} \Rightarrow v = \frac{Zq^2}{n\hbar 4\pi\varepsilon_0} \qquad r = \frac{n^2\hbar^2 4\pi\varepsilon_0}{Zme^2}$$

Classical } Semi
Quantization } Classical Model.



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

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

$a_0 = 0.53$ Å

$v_0 = 2.18 \times 10^6$ m

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

$$= \frac{p^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$= \frac{1}{2}mv^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$= \frac{1}{2}m_e \frac{Z^2e^4}{n^2\hbar^2(4\pi\varepsilon_0)^2} - \frac{e^4 Z^2 m_e}{(4\pi\varepsilon_0)^2 n^2\hbar^2} = -\frac{1}{2}\frac{Z^2 m_e e^4}{n^2\hbar^2(4\pi\varepsilon_0)^2}$$

$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \simeq \frac{1}{137}$ dimensionless number : FINENESS CONSTANT.

$$\boxed{E_n = -\frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\left(\frac{Z^2}{n^2}\right) = -Rhc\left(\frac{Z^2}{n^2}\right)}$$

R = Rydberg Const.
$= (me^4/8\varepsilon_0^2 c h^3$

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

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

Remember,
$\boxed{E_n = -(K.E.)_n}$

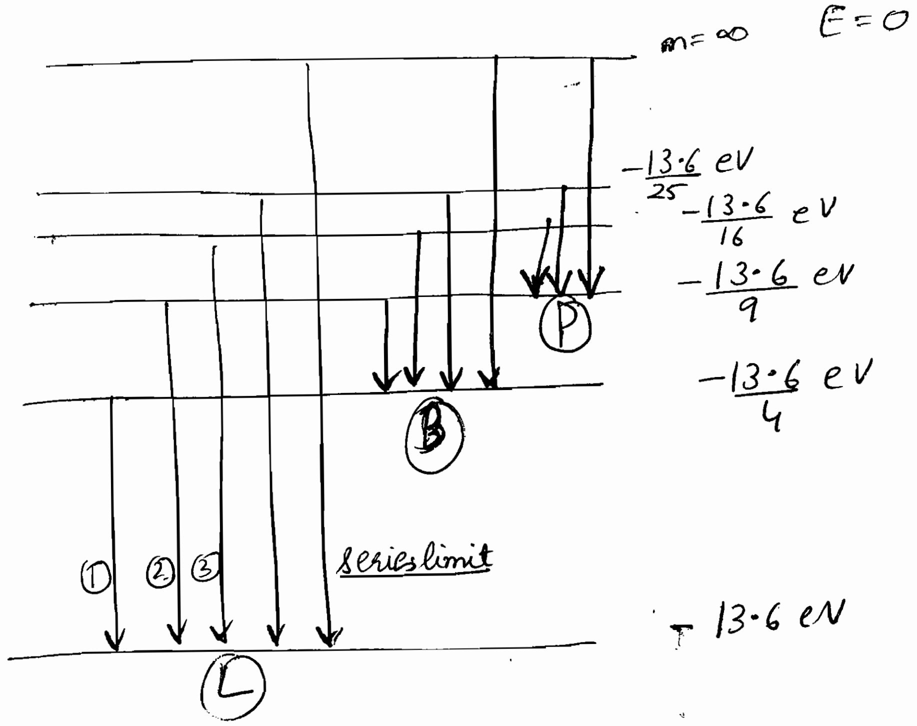
$1 \leq n < \infty$

For e- to move out of atom, K.E. > P.E.

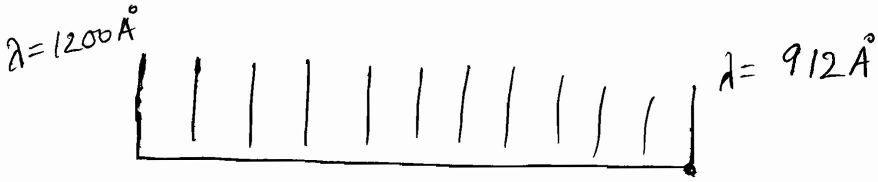
@ $n = \infty$

$E = 0$ $\qquad \frac{1}{2} m v^2 = \frac{Z e^2}{4\pi \varepsilon_0 r}$

Atomic spectra is line spectra



n=n to n=1 :	Lyman Series	UV Region	912 - 1200 Å
n=n to n=2 :	Balmer 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	



lowest wavelength
i.e.
Highest wavenumber

Lyman Series
[U.V.]

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

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

$$\frac{1}{\lambda_{min}} = R\left[\frac{1}{1^2} - \frac{1}{\infty}\right] = R \Rightarrow \lambda = \frac{1}{R} = \frac{1}{1.09\times10^7}$$

$\simeq 912$ Å → UV

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

⊙ note that we are always interested in this series. ∴ α $(n=3 \text{ to } n=2)$, β $(n=4 \text{ to } n=2)$ refer to this serie

Balmer Series
[Visible Region]

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

$$\Rightarrow \lambda_{min} = \frac{4}{R} \simeq 4000 \text{ Å}$$

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

$$\Rightarrow \lambda_{max} = \frac{36}{5R} \simeq 7000 \text{ Å}$$

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.

③ ~~Does not talk about intensity of lines.~~ No logic or reason given for quantization of angular momentum

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 $\left(\frac{p^2}{2m} + V_r\right)$ (H-atom Problem), 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-o coupling we add the term $\propto \frac{\vec{L}\cdot\vec{S}}{r^3}$ in Hamiltonian)

- Electron Spin introduced in 1925 by Gaudsmidt & Uhlenbeck.

(1) To correct Gyromagnetic [redacted] Ratio

$$\left(\frac{\text{Magnetic Moment}}{\text{Angular Momentum}}\right) = \frac{\mu}{L} = -\frac{e}{2m}$$

$$\vec{\mu}_l = -\frac{e}{2m}\vec{L} \qquad \vec{\mu}_s = \underbrace{\frac{-e}{2m}2\vec{S}}_{\text{it needed to be introduced}}$$

(2) To [redacted] explain fine structure of atomic spectra

(3) To explain Zeeman Effect

(4) To explain Stern-Gerlach Experiment.

Now $\vec{\mu}_l = -\frac{e}{2m}\vec{L} = -\frac{e}{2m} g_l \vec{L}$ $\quad g_l = 1$

Quantum Mechanically $\vec{\mu}_s = -\frac{e}{2m} 2\vec{S}$

$= -\frac{e}{2m} g_s \vec{S}$ $\quad g_s = 2$

S Orbital $\quad l = 0 \Rightarrow L = 0 \Rightarrow \mu_l = 0$

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

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

$\boxed{\uparrow\downarrow}$

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

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

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

This is called Vector Model of Atoms
for Multi Electron Atom : LS Coupling
for Single-Electron Atom : Spin-Orbit Coupling

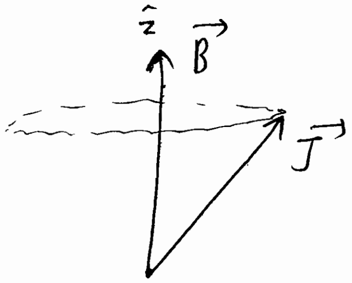
If I keep the atom in Magnetic Field ($\vec{B}$),

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

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

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

Torque will try to align $\vec{\mu_J}$ along $\vec{B}$. Hence $\vec{\mu_J}$ will presess 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~~ at specific angles to that direction s.t.
$J = \sqrt{j(j+1)}\,\hbar \qquad J_z = m_j \hbar$
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

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

<u>**Potential Energy of Orientation of Dipole**</u>

$$\boxed{E = -\vec{\mu_J} \cdot \vec{B}}$$

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

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

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

Stern Gerlach Experiment

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

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

defn of Vector Model

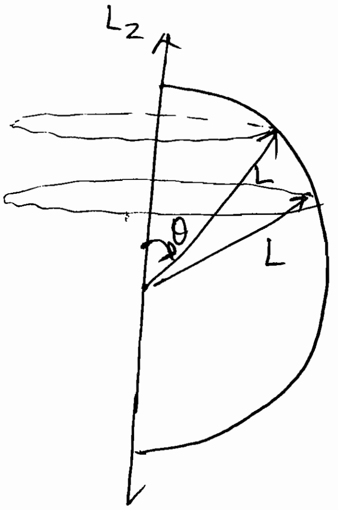
★ Total angular momentum of an atom results from the combination of spin and orbital angular momenta of its electrons. Since ang. momentum is a vector quantity, we can represent the total angular momentum as addition of orbital and spin angular momentum vectors.

[In Bohr Model, S was not there;
only $L = n\hbar$
$E = -\frac{13.6}{n^2}$ Coming out due to quantization of $\vec{L}$]

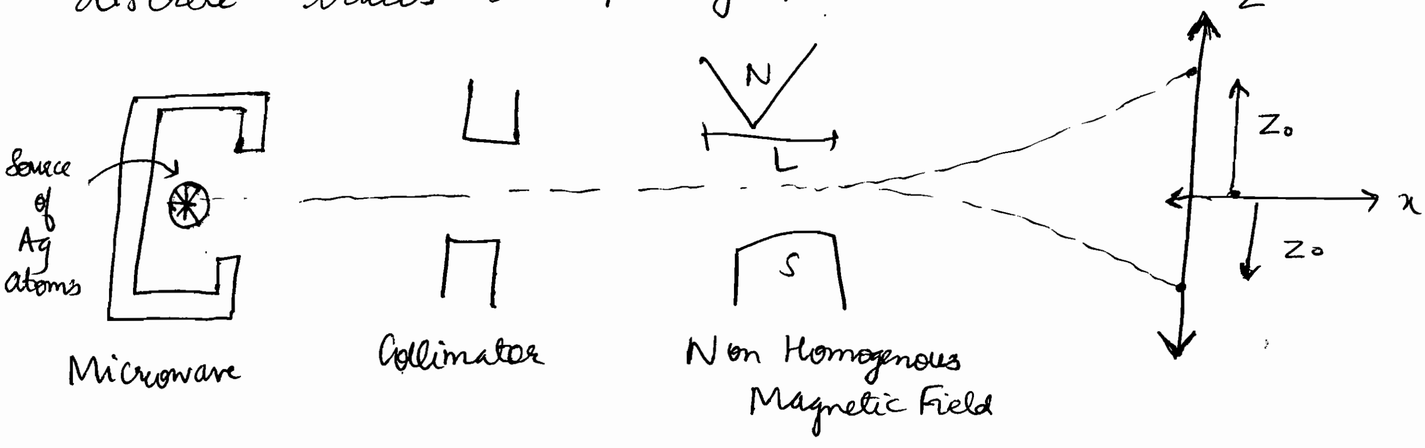
It is demonstrating : ① Orbital Motion or Space Quantization
② Spin Motion governed by

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

$$S_z = m_s\hbar \qquad -s < m_s < s$$



"Beam of neutral Silver (Ag) Atoms is passed through non-homognous 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. $J = 0$

$$\left.\begin{matrix} ns^2 \\ np^6 \\ nd^{10} \end{matrix}\right\} \begin{matrix} L = 0 \\ S = 0 \end{matrix}$$

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, $L = 0$ (s orbital) $\vec{J} = \vec{L} + \vec{S} = \vec{S}$

$S_z = m_s \hbar$

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

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

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

$$E = -\vec{\mu_s}\cdot\vec{B} = -(\mu_s)_z B$$
$$(\text{if } \vec{B} = B\hat{z})$$

$$(\vec{\mu_s})_z = -\frac{e}{2m} g_m \vec{S_z}$$

$$(S_z = m_s\hbar)$$

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

★ 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. for e^-

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

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

$\frac{e\hbar}{2m_p}$: 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 in $\vec{B}$ is Homogenous, because otherwise no net Force will act on dipole moment.

$$\vec{F} = (\vec{\mu}\cdot\vec{\nabla})\vec{B}$$
$$\vec{F} = 0 \text{ for homogenous field}$$

$$\vec{F} = \vec{\nabla}(\vec{\mu}\cdot\vec{B}) = \frac{\partial}{\partial z}(\mu_z B_z) = \mu_z\left(\frac{\partial B_z}{\partial z}\right)$$

$\vec{F}$ is non homogenous

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

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

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

remember its μ_z

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

distance$_x$ = L

velocity$_x$ = v_x (const.)

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

$$v_{z_i} = 0$$

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

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

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

Normally, it is $\frac{3}{2}kT$ $\left[\begin{array}{l}\text{till } 300\,k: \frac{3}{2}kT \\ >300\,k: \frac{4}{2}kT\end{array}\right]$

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

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

$g_s = 2$

- Cadmium } fully
Mercury } filled orbitals

$\Rightarrow S=0, L=0$

NO deviation in stern Gerlach

Now we will get m_s no. of traces.

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

Hence 2 traces.

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

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

(4 Quantum numbers) (j dependent) (B applied $\Rightarrow m_j$ dependent) $^{(2S+1)}L_j$

State, level, sub level, Spectral Term

State : Complete description $\psi(n, l, m_l, m_s)$
We require all the 4 set of quantum numbers.

Energy level : $\boxed{\text{Energy level defined by } \vec{J} \; (= \vec{L}+\vec{S})}$ ★

more the j,
more the energy
hence in general
$E_s < E_p < E_D$ for same n

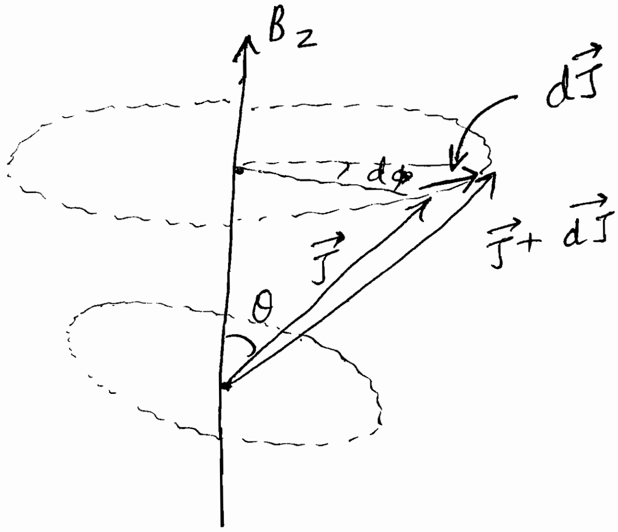
If $\vec{J}$ exists $\Rightarrow$ μ_J exists

If $\vec{B}$ exists $\Rightarrow$ $\vec{J}$ will precess about $\vec{B}$

Its called Larmer Precession

Refer to P-77 and 78 of Rajkumar

→ 2 levels (defined by j) को बीच में line ; 2 subLevels (define by m_j) (of different levels ofcourse) को बीच में component.



EXTERNAL MAGNETIC FIELD

$$\vec{dJ} \perp \vec{J}$$

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

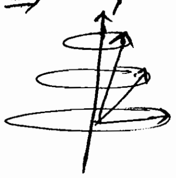
$$\tau = \frac{dJ}{dt} = \vec{\mu}_J \times \vec{B} = \mu_J B \sin\theta$$

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

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

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

⇒ ω_p is independent of m_j



all have same ω_p

[redacted]

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

✓ $= \frac{e}{2m} g_J m_J \hbar \vec{B}$ $\quad -j \leq m_j \leq j$

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

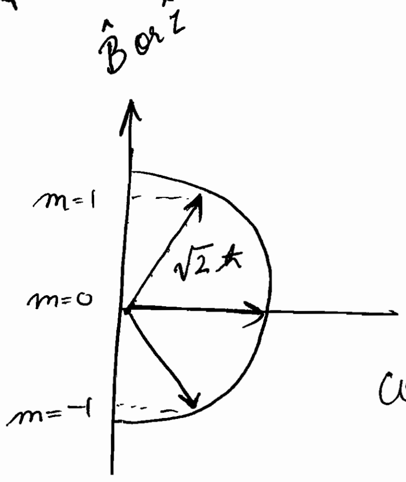
$$\nu_p = \frac{e}{4\pi m} B\, g_J$$

m_j : Magnetic Moment Quantum No.

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

⊛ $(2j+1)$ gives different orientation of $\underline{j}$ i.e. no. of values of $\underline{m_j}$ 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

r = Multiplicity $= (2S+1)$ for single e^- atom

Many electron atoms : $2S+1 \; (L>S)$

$2L+1 \; (S>L)$

⊙ $r = 2S+1$ always

⊙ multiplicity =

$$\boxed{r = 2*(\text{छोटा वाला}) + 1 = \text{no. of energy levels}}$$

eg. Na :

$\underline{1s^2\ 2s^2\ 2p^6}\ 3s^1$

X

$L=0$

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

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

- 1 term symbol corresponds to 1 energy level i.e. 1 particular value of J
- When subjected to $\vec{B}_{ext}$, each J i.e. each level will break into $(2J+1)$ sublevels

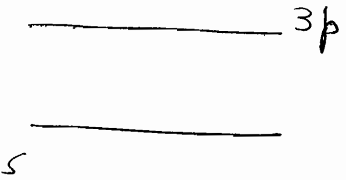
Term Symbol : $3\,^2S_{\frac{1}{2}}$

orbital

J

Multiplicity

n.



For excited Na atom,

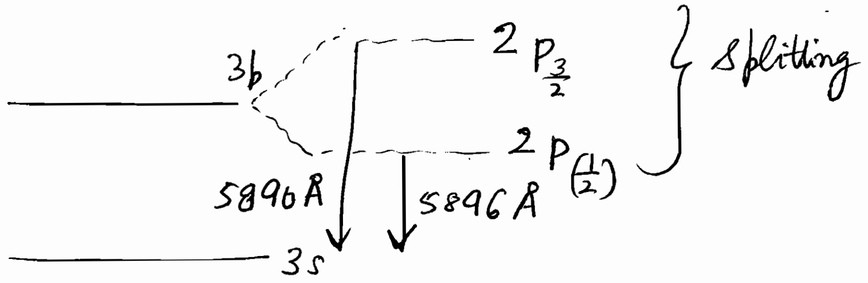
$l=1$ (p)

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

[redacted] $=\frac{1}{2}, \frac{3}{2}$

$j = l \pm s =$

hence



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

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

$\underbrace{D_1 \text{ and } D_2 \text{ lines}}$

This is called Fine Structure caused due to spin

Energy level "j" : transition between 2 energy levels : <u>line</u>

(Note that Sodium transitions are 2 lines)

Energy sublevel : <u>Component</u> : transition b/w 2 sublevels

(Components are those that is Zeeman effect on Sodium Transitions)

(of course, not 2 sublevels of same level)

Spectral Term $^{\gamma}L_j$: <u>Multiplets</u> : transition b/w 2 spectral levels.

But what are allowed transition?

It is governed by Selection Rule

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

initial

final

Reason for transition

laporte's rule

eg. $\langle i | \mu_z | f \rangle \neq 0$

For allowed transition $\int \Psi_i^* \, \mu_z \, \Psi_f \, d\tau > 0$

we get, $\Delta m_j = \pm 1, 0$ for Zeeman Effect

When 2 e^- are said to be equivalent ?

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

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

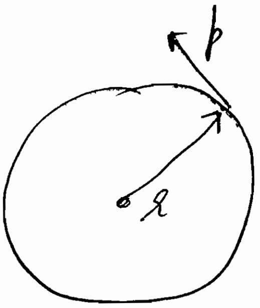
Equivalent means :- n and l quantum numbers are same.

IT IS APPLICABLE AND OBSERVABLE IN ALL ATOMS..... IT IS MORE DOMINANT IN HEAVIER ATOMS WHERE $\vec{L}$ and $\vec{S}$ ARE INDIVIDUALLY [redacted] NON EXISTENT FOR INDIVIDUAL ELECTRONS AND ONLY $\vec{J}_{electron}$ IS OBSERVABLE. THIS COUPLING IS NOT STRONG IN MULTI ELECTRON LIGHT ATOMS WHERE $\vec{L}$'s and $\vec{S}$'s INDIVIDUALLY COUPLE AND THEN COMBINED $\vec{L}$ AND $\vec{S}$ INTERACT...

Spin Orbit Coupling

Spin e^- produces its own $\vec{\mu}_s$ ~~which is double of~~

~~produced by orbital motion $\vec{\mu}_L$~~.



Orbiting e^- ⟺ Current loop ⟺ creates its own magnetic field

⊛ For current loop, $B = \left(\frac{\mu_0 I}{2r}\right)$

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

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 $-\omega$. Hence it will experience force due to field created by nucleus.

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

$$\boxed{\begin{aligned} E &= -\vec{\mu}_s \cdot \vec{B} \\ &= 2\frac{e}{2m} \vec{S} \cdot \vec{B} \end{aligned}}$$

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

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

$$dW = \tau d\theta = -\vec{\mu}_s \cdot \vec{B} = \frac{e}{2m} \cdot 2\vec{S} \cdot \vec{B}$$

INTERNAL MAGNETIC FIELD

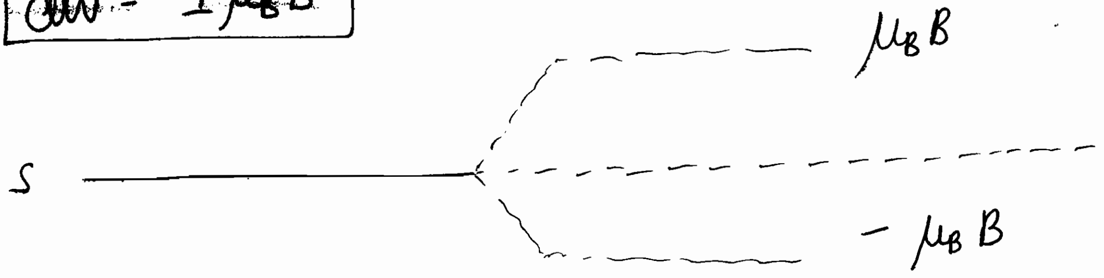
$$= \frac{e}{2m} 2 S_z B$$

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

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

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

✓ $\boxed{dW = \pm \mu_B B}$



It will result into fine structure doubling.

This analysis for single valence e^-.

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

Its a weak interaction.

Refer last Page

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

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

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

Hence its called spin Orbit Coupling.

○ Now $E_{l,s}$ is the correction factor in Hamiltonian. It will now give Fine Structure, Quantum Mechanically.

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

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

from, $H\psi = E\psi$

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

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

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

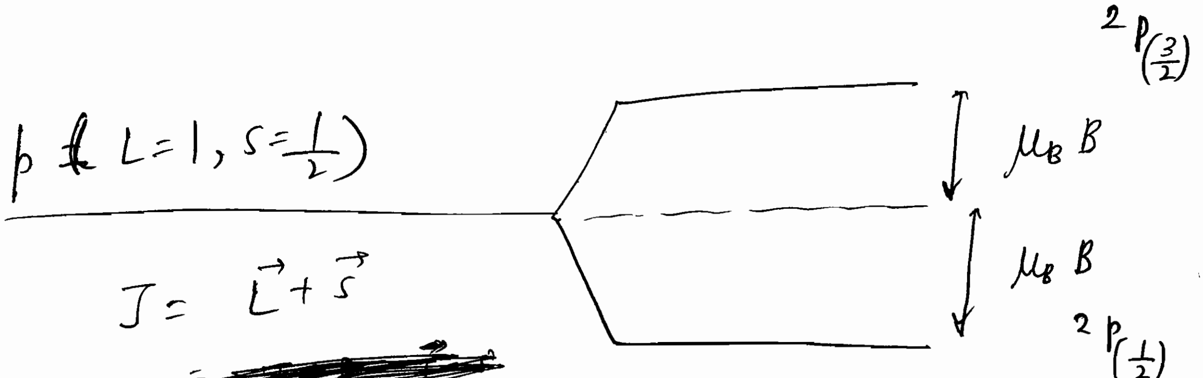
$$J^2 = L^2 + S^2 + 2\vec{L}\cdot\vec{S}$$

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

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

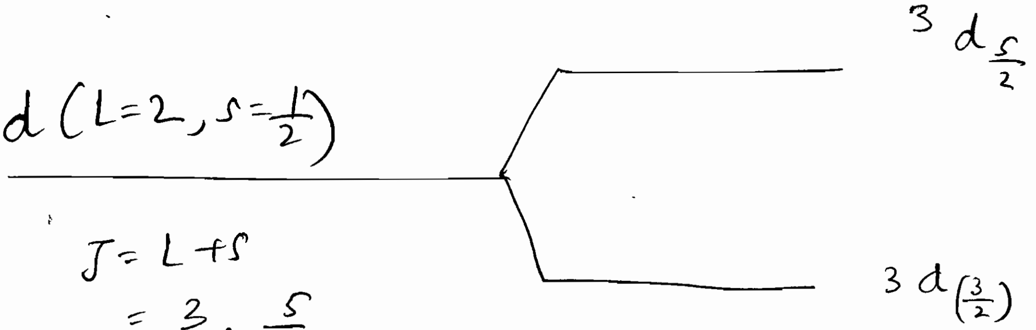
$$= \alpha \left\langle \frac{1}{r^3}\left[j(j+1) - l(l+1) - s(s+1)\right]\right\rangle$$

$p\ (L=1, s=\frac{1}{2})$



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

$d\ (L=2, s=\frac{1}{2})$



$J = L + S$

$= \frac{3}{2}, \frac{5}{2}$

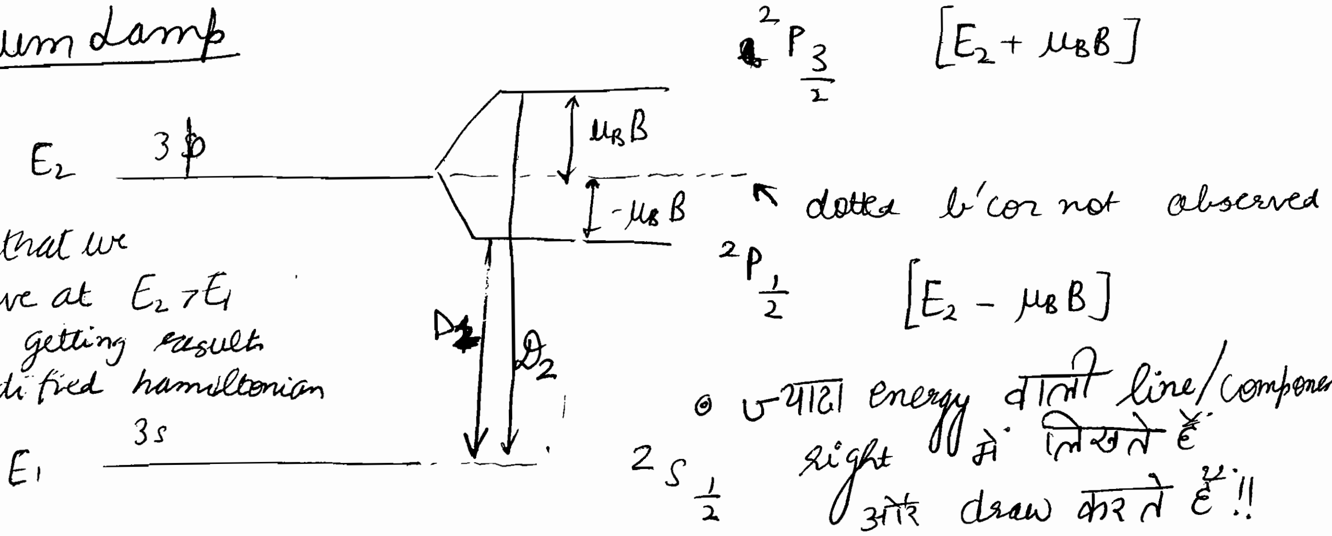
$$= \alpha\left[j(j+1) - L(L+1) - s(s+1)\right]\left\langle\frac{1}{r^3}\right\rangle$$

eg.

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

⊛ Perfect Example for Spin Orbit Coupling are d_1 and d_2 lines of sodium lamp.

Sodium Lamp



⊙ Note that we achieve at $E_2 > E_1$ after getting result of modified hamiltonian

⊙ ज्यादा energy वाली line/component right में ~~लिखते हैं~~ ओर draw करते हैं!!

⊙ For Spin Orbit Coupling

$$\boxed{\begin{cases} \Delta l = \pm 1 \\ \Delta j = 0, \pm 1 \\ \Delta s = 0 \end{cases}}$$

Selection rules

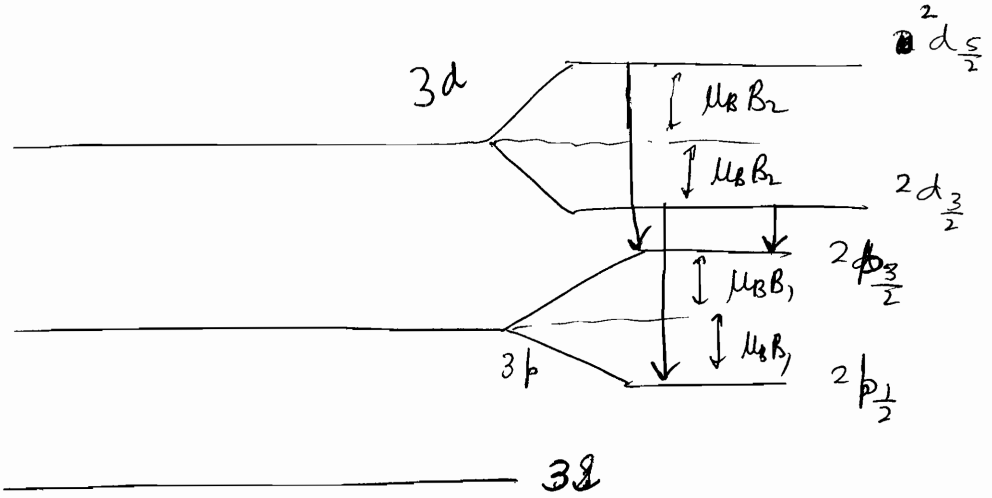
$$\lambda_1 : \quad \frac{hc}{\lambda_1} = (E_2 - \mu_B B) - E_1 = (E_2 - E_1) - \mu_B B$$

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

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

B_{int} can be calculated which is felt by p electrons

No coupling in s electron.



3 spectral lines for d→p transitions

B_1 and B_2 are not equal in general.

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

Fine Structure of H atom

Dirac's Quantum Mechanical Model

① Spin Orbit Coupling

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

$$= Z^4 R \alpha^2 / n^3 l(l+1) = \frac{5.84 Z^4}{n^3 l(l+1)} \text{cm}^{-1}$$

② Relativistic correction in Hamiltonian.

$$H = E - m_0c^2 + V$$

$$= c^2(m - m_0) + V$$

$$= m_0c^2\left[\left(1 - \frac{v^2}{c^2}\right)^{-\frac{1}{2}} - 1\right] + V$$

$$= m_0c^2\left[\cancel{1} + \frac{v^2}{2c^2} - \frac{3}{8}\frac{v^4}{c^4} + \dots \cancel{-1}\right] + V$$

$$= \frac{1}{2}m_0v^2 \boxed{- \frac{3}{8}\frac{v^4 m_0}{c^2}} + V$$

Relativistic Correction $= \frac{-3}{8 m_0^3 c^2} p^4$.

$$\langle H' \rangle = \frac{-3}{8 m_0^3 c^2} \langle p^4 \rangle$$

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 :

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

$$\boxed{\Delta E \simeq -\frac{5 \cdot 84 Z^4}{n^3} \left[\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right] \text{cm}^{-1}}$$

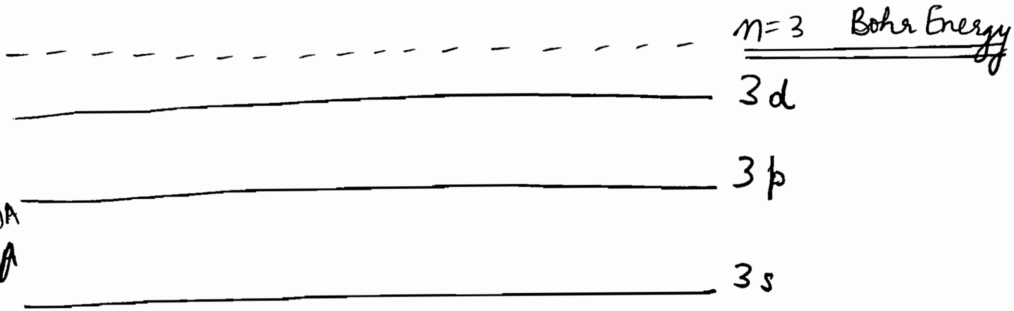
Dirac's Quantum Mechanical Model

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

eg. $n = 3$ and 's' ignored

$\Rightarrow$ for $l = 0, 1, 2$

$\Delta E = \underbrace{-\frac{3}{4}A}_{3s}, \underbrace{-\frac{5}{4}A}_{3p}, \underbrace{-\left(\frac{11}{4}\right)A}_{3d}$

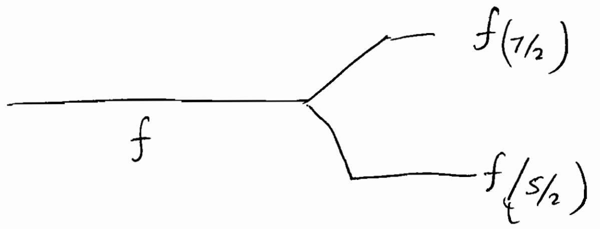


Hence Energy depends on BOHR n value ; then on a finer level it depends on DIRAC QUANTUM j values ; then on a further finer level E depends on l values (lamb effect)... finally it further depends on m_j (Zeeman)

A & M Physics (3)

22/02/2012

- 's' values have no spin orbit coupling



- Spin Orbit Coupling only for single e⁻ atoms.

- Spin Orbit Coupling Rules of Selection:

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

($^{j=0}_{j=0}$ is not allowed)

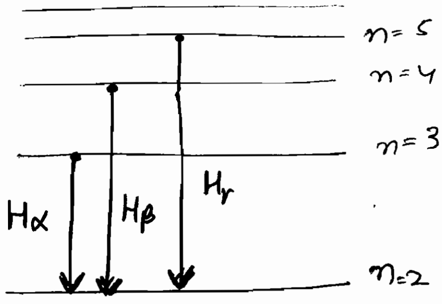
- $$\Delta T = -\frac{R_\infty \alpha^2 Z^4}{n^3}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right]$$ Departure from Bohr's n^{th} level

$$= -\frac{5.84\ Z^4}{n^3}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right]$$

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

Hα, Hβ and Hγ lines come in the **BALMER series** of H spectrum

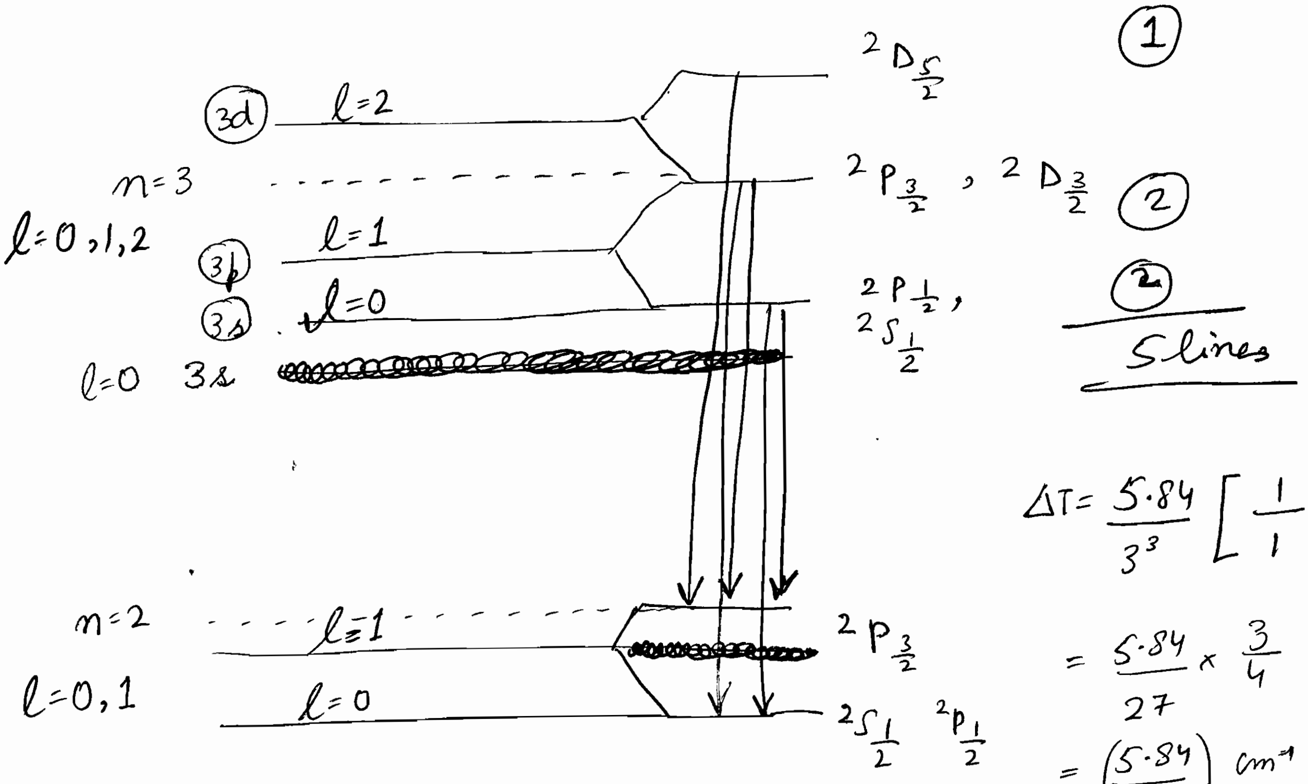
Hα : n=3 to n=2
Hβ : n=4 to n=2
Hγ : n=5 to n=2



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

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

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



$$\Delta T = \frac{5.84}{3^3}\left[\frac{1}{1} - \frac{8}{4}\right]$$

$$= \frac{5.84}{27} \times \frac{3}{4}$$

$$= \left(\frac{5.84}{36}\right) \text{cm}^{-1}$$

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 & Retherford.

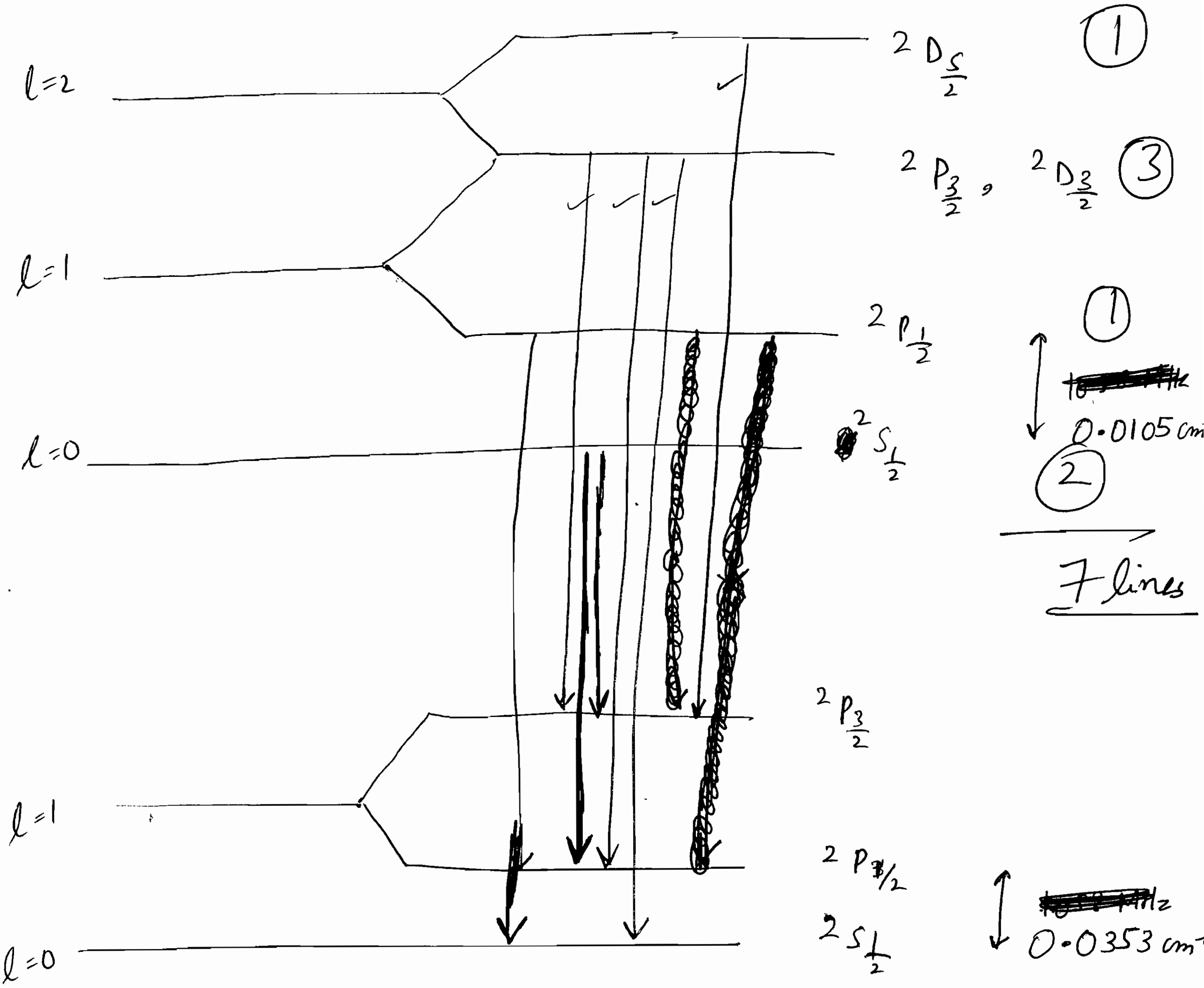
Its called LAMB SHIFT.

✓ 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

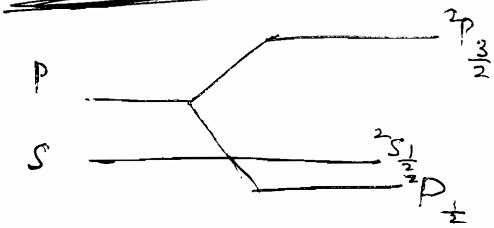
⊙ Note that $\Delta l \neq 0$ it should be ± 1



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

Explanation for lamb shift

✓ ⊙ 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.



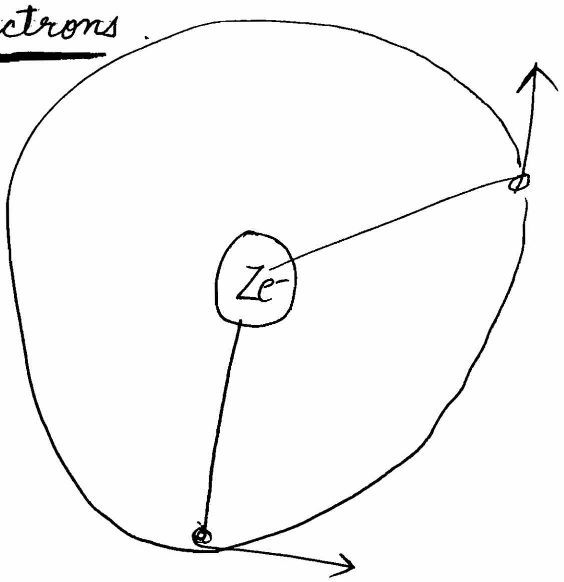
★ Note that in lamb shift, the level of $^2P_{(\frac{1}{2})}$ energy is actually lower than $^2S_{(\frac{1}{2})}$ energy.

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

Its called Orbital- Orbital interaction: **electrostatic interaction**

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V(r_1, r_2)$$: unperturbed Hamiltonian

all $\vec{l}$ in same direction ⇒ N+N+N ⇒ repulsion ⇒ low energy as $E \propto \left(\frac{1}{r}\right)$

$|\vec{L}_{max}| = |\vec{L}_1| + |\vec{L}_2|$: lowest energy (due to d_{max})

$|\vec{L}_{min}| = |\vec{L}_1| - |\vec{L}_2|$; highest energy (due to d_{min})

$\vec{l}\uparrow$ and other $\vec{l}\downarrow$ ⇒ N+S ⇒ attraction ⇒ more energy

② ✓ $\vec{S}_{spin} = \vec{S}_1 + \vec{S}_2$ Its called **spin spin interaction**

$S_{min} = S_1 - S_2 = 0$ Max. Energy

$S_{max} = S_1 + S_2$ Min. Energy → These 3 are perturbations in H operator.

③ ✓ Spin Orbit Interaction * Hence more 'l' or more 's' implies ~~less~~ energy. ∴ order is ex. $\overset{0}{\underset{2}{1}} \leftarrow \overset{0}{\underset{2}{1}}$

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

✓ Heavier Atoms : Spin Orbit ~~Coupling~~ Interaction high

LS coupling: also called Russel Saunder Coupling

① For **lighter atom**, where Spin-Orbit interaction is lowest.

$\vec{S} = \vec{S_1} + \vec{S_2}$

$|S_1 - S_2| \leqslant S < |S_1 + S_2|$

$\vec{L} = \vec{L_1} + \vec{L_2}$

$|L_1 - L_2| \leqslant L \leqslant |L_1 + L_2|$

$\vec{L} + \vec{S} = \vec{J}$
(LS coupling)

$E = \alpha[\vec{L} \cdot \vec{S}]$

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

JJ Coupling

Spin Orbit Coupling dominates over others, in ~~heavier~~ atoms.

$\vec{l_1} + \vec{S_1} = \vec{J_1}$

$\vec{l_2} + \vec{S_2} = \vec{J_2}$

$\vec{J_1} + \vec{J_2} = \vec{J}$

[redacted]

$|J_1 - J_2| < |\vec{J}| < |\vec{J_1} + \vec{J_2}|$

Individual e⁻'s angular momenta couple and form whole angular momentum of atom. Its called JJ Coupling.

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

2p 3p : Terms due to LS Coupling

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

3p: $l_2 = 1$ $s_2 = \frac{1}{2}$

$S = 0, 1$ ← BOSON

$r = 1, 3$

Singlet Triplet

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

Triplet lies below singlet $S=0 > S=1$

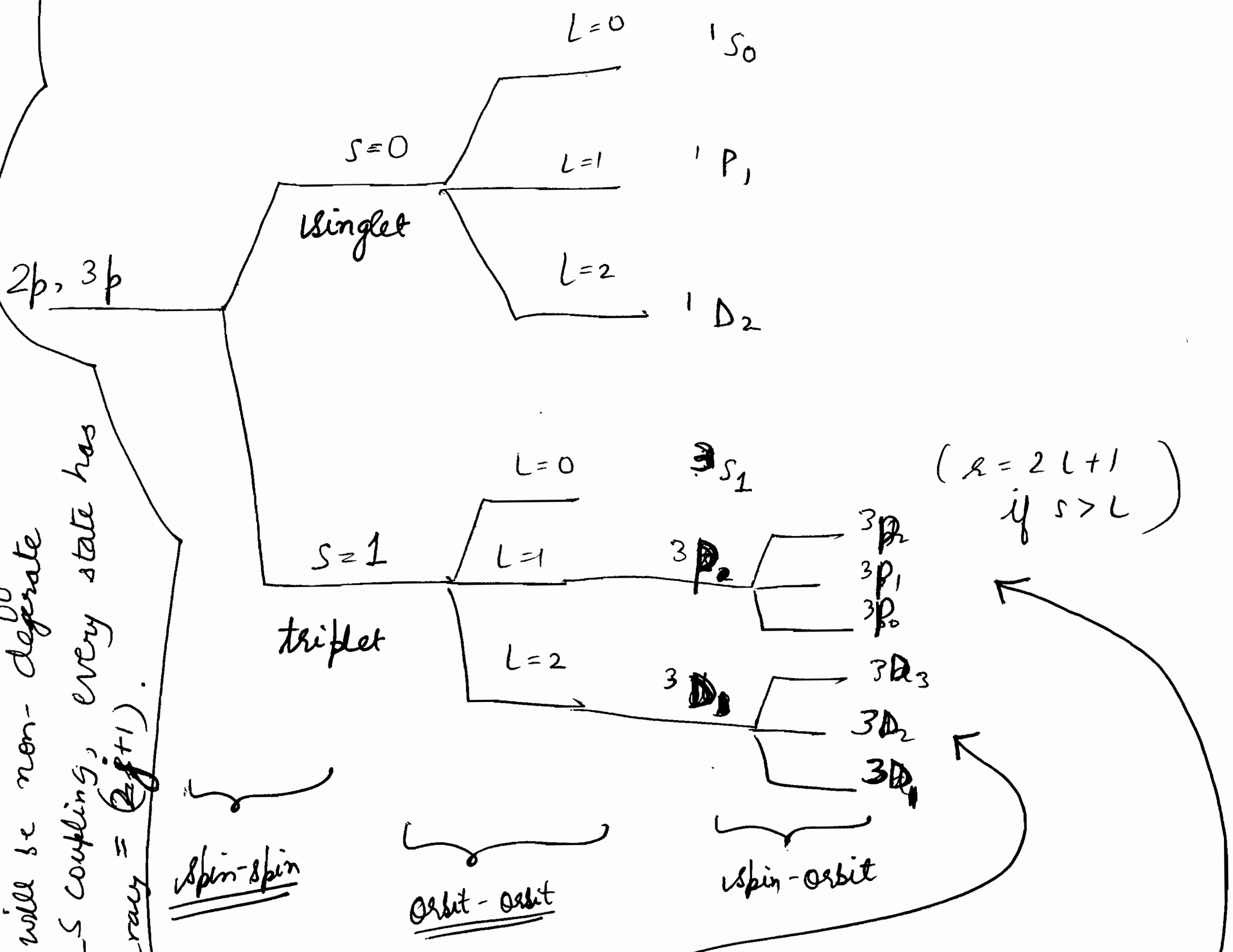
$L = l_1 + l_2$

$= 0, 1, 2$

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

$0 \leq L \leq 2$

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



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

$0 \leq J \leq 2$

$1 \leq J \leq 3$

* 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 Hα was a special case of general LS coupling.

⊙ $\underbrace{1s^2\ 2s^2\ 2p^6\ 3s^2}, 3p^2$

Completed subshells
NO contribution to $\vec{L}$ or $\vec{S}$
Only Contribution from
$3p^2$ electrons.

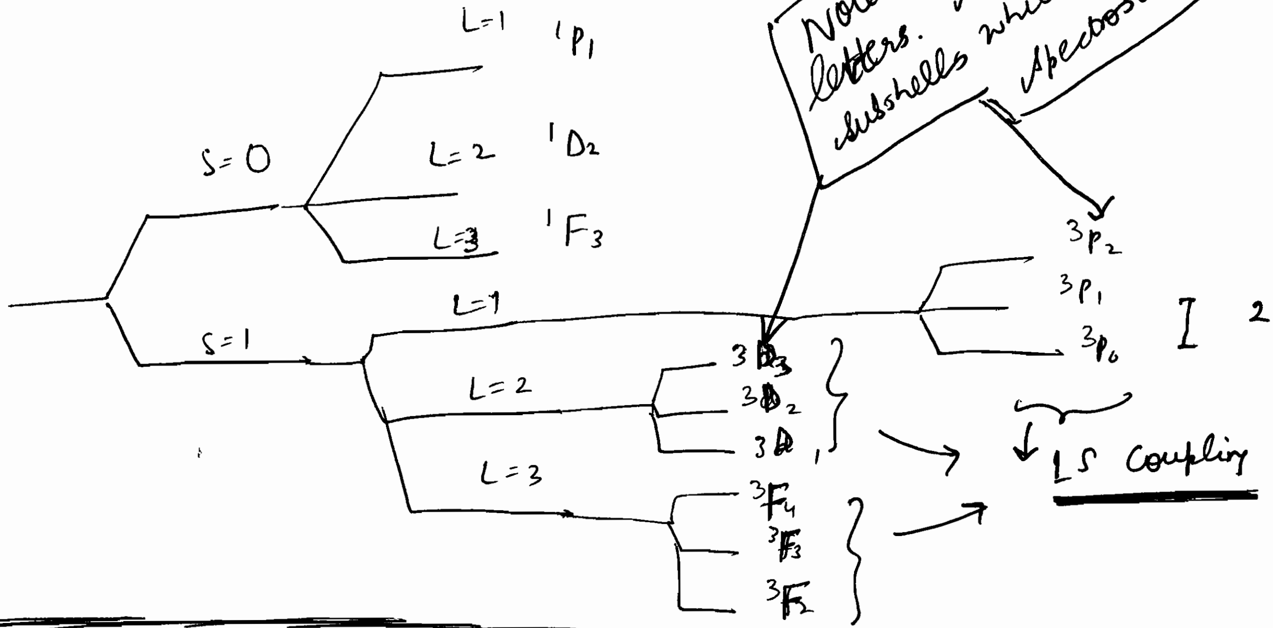
pd

$l_1 = 1 \quad l_2 = 2$

$L = 1, 2, 3$

$s_1 = \frac{1}{2} \quad s_2 = \frac{1}{2}$

$S = 0, 1$



Note that capital letters. Small alphabets for subshells while capital for spectroscopic Notations

LANDÉS INTERVAL RULE

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

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

$$= \alpha \left[J(J+1) - \underbrace{L(L+1) - S(S+1)}_{\text{remain same for successive terms}} \right]$$

$$E_{(J+1)} - E_{(J)} = \alpha \left[(J+1)(J+2) - J(J+1) \right]$$

$$= 2\alpha \left[J+1 \right]$$

i.e. $\boxed{\Delta E \propto (J+1)}$

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

L-S coupling selection rules:
$\Delta L = 0, \pm 1$
$\Delta J = 0, \pm 1$
$\Delta S = 0$

$\Delta L = 0$ भी allowed है इसमें

Spectral terms of Equivalent electrons due to LS coupling

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

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

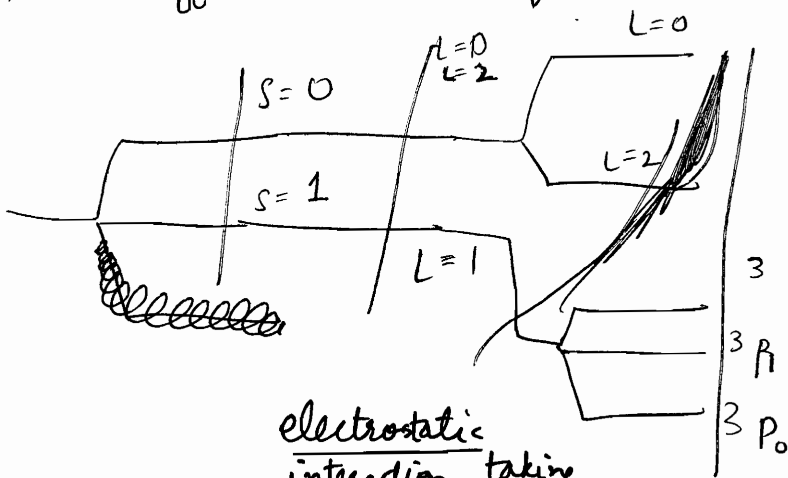
$S = 0$: m_s values for both e- are different
$m_1 = \left(+\frac{1}{2}\right)$ $m_2 = \left(-\frac{1}{2}\right)$

$S = 1$: m_s values same

$\vec{L} = l_1 + l_2 = 0, 1, 2$

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

Multiplet terms of
$p^2 \Leftrightarrow p^4$
$d^4 \Leftrightarrow d^6$
$(nl)^q \Leftrightarrow (nl)^{\kappa - q}$ κ: maximum no. of electron in l subshell



	$(2J+1)$
$^1S_0$	1
$^1D_2$	5
$^3P_2$	5
$^3P_1$	3
$^3P_0$	1
	15

from lande's internal rule
⇓
I (4α)
I 2α

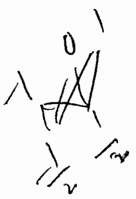
electrostatic interaction taking into account
$= \vec{L} = \vec{l_1} + \vec{l_2}$

Pauli Exclusion Principle

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

Total number of possibilities are less.

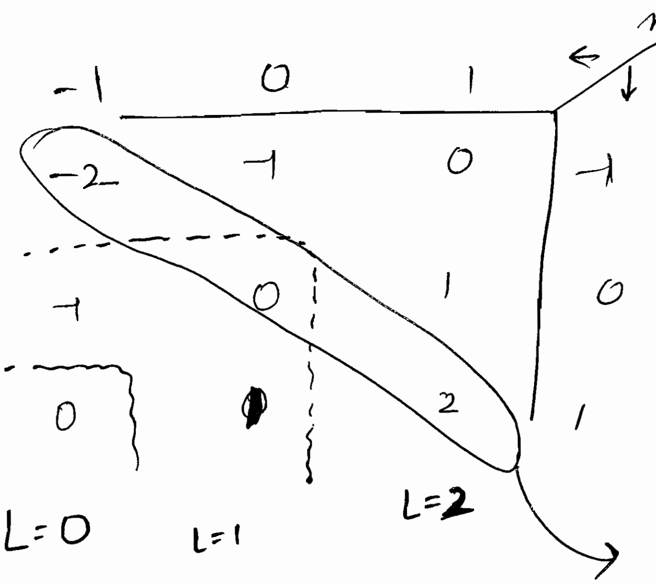
1L 1L 1L



[6 possibilities for 1 e-]
⇒ [For 2e⁻ $^6C_2 = 15$]
= [Can be seen from $\sum (2J+1)$]

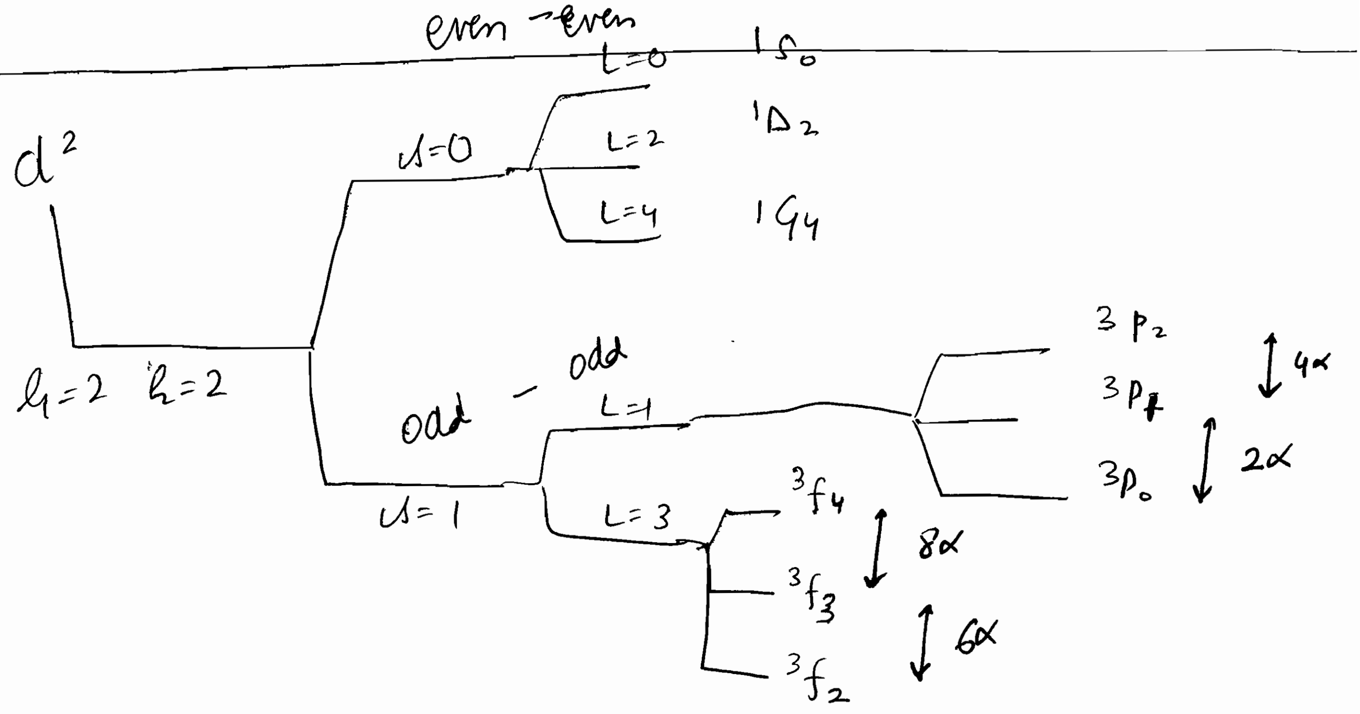
$l_1 = 1, \; l_2 = 1$

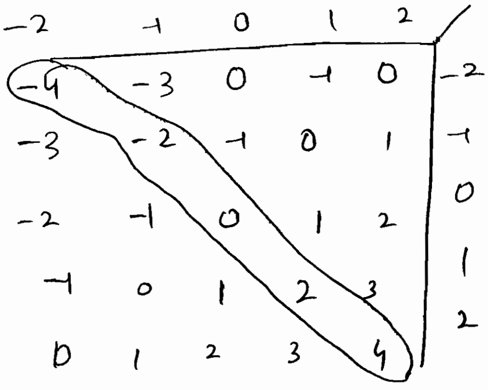
Breit's Scheme



Obtained when both have same ~~me~~ values.

Will not go along with s = 1 where m_s have same values.





⊛ Note that in ~~pd~~ 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.

[redacted]

Same states

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 corelation.

~~[illegible]~~

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

$\vec{J_1} = \vec{l_1} + \vec{s_1}$

$\vec{J_2} = \vec{l_2} + \vec{s_2}$

$\vec{J} = \vec{J_1} + \vec{J_2}$

eg. $\boxed{4p\,5d}$

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

$\boxed{|l-s| \text{ to } |l+s|}$

⇑

J variation

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

⊛ We cannot write finally common integral J terms as even 'same J' terms are distinct

J : Combinations

$\left(\frac{1}{2}, \frac{3}{2}\right)$ — J = 1, 2

$\left(\frac{1}{2}, \frac{5}{2}\right)$ — J = 2, 3

$\left(\frac{3}{2}, \frac{3}{2}\right)$ — J = 0, 1, 2, 3

$\left(\frac{3}{2}, \frac{5}{2}\right)$ — J = 1, 2, 3, 4

⊛ Each of the four levels are further splitted by residual electrostatic interaction and spin spin corelation into a no. of integral J levels.

⊛ Selection rule for J-J coupling :

① $\Delta J = 0, \pm 1$

$J = 0 \not\leftrightarrow J = 0$

thats it .....

NO rule for ΔS, ΔL, as they are no longer good Quantum numbers

$$\boxed{|J_1 - J_2| \leq J \leq (J_1 + J_2)}$$

⊛ 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.

After Carbon, atoms typically show J-J coupling.

Zeeman Effect

Behaviour of atom in external weak/ intermediate magnetic field.

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

If Field is external ⇒ Zeeman Effect

(Internal में तो spin-Orbit interaction)

$$\omega_p = \frac{e}{2m} g B \checkmark$$ [Angular Velocity of LARMER PRECESSION]

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

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

$$\boxed{E = \mu_B g B m_j}$$

Note that if field is strong, its called Paschen Back Effect.

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

Selection Rule comes out to be:

$$\boxed{\Delta m_j = 0, \pm 1}$$

For complete answer, we have to mention selection rule.

0 → π component

±1 → σ components

linearly polarized

⊛ Note that spectroscopic notation represented levels. Now, in zeeman effect, we have sublevel

⊛ 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

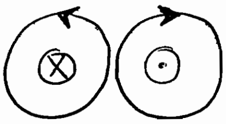
Spectra is viewed perpendicular to direction of applied magnetic field.

It will give plane polarized π and σ components $\boxed{\Delta m = 0, \pm 1}$

Longitudinal Zeeman Effect:

↑ parallel

Spectra is viewed parallel to direction of applied magnetic field.



It will give circularly polarized components. RCP and LCP

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

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) eg. p^2 ↑|↑ even but $S \neq 0$

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.

नाम के विपरीत !!

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

Quantum Mechanical Explanation

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

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

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 $\vec{B}$!!

$$\vec{\mu} = \vec{\mu_l} + \vec{\mu_s}$$

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

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

Both will individually precess about $\vec{B}$

$$= \cancel{-\frac{e}{2m} B (L_z + 2S_z)}$$

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

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

This is Paschen Back Effect

But Zeeman Effect has :

$$\mu = \frac{-e}{2m}\left(\underbrace{\vec{L} + \vec{S}}_{\downarrow} + \vec{S}\right)$$

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

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

[L-S coupling : a weak field effect]

[In strong field, they will individual precess]

⊛ 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, Coupling will break down and $\vec{L}$ and $2\vec{S}$ will individually precess

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

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

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

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

$$dW = \tau\, d\theta = \mu_J B \sin\theta\, d\theta$$

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

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

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

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

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

$$\left[\begin{aligned} \vec{L} &= \vec{J} - \vec{S} \\ \vec{L}\cdot\vec{L} &= (\vec{J}-\vec{S})\cdot(\vec{J}-\vec{S}) \\ \Rightarrow \vec{S}\cdot\vec{J} &= \frac{J^2 + S^2 - L^2}{2} \end{aligned}\right]$$

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

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

$$\boxed{\vec{\mu}_J = -\frac{e}{2m}\, g_j \vec{J}}$$

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

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

$$\Rightarrow \boxed{\begin{aligned} \vec{\mu_l} &= \frac{-e}{2m} g_l \vec{L} \\ \vec{\mu_s} &= \frac{-e}{2m} g_s \vec{S} \end{aligned}}$$

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

$$\Rightarrow \boxed{\vec{\mu_J} = \frac{-e}{2m} g_J \vec{J}}$$

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

$$\boxed{\begin{aligned} &{}^4D_{\frac{1}{2}} \\ &\Rightarrow g = 0 \end{aligned}}$$

[redacted] 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

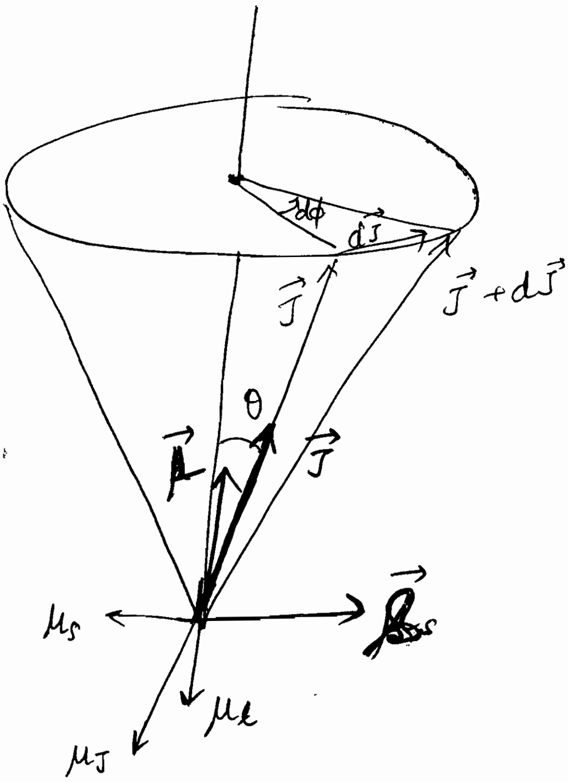
$J_z = m_j \hbar$

$$E = \omega_p J_z$$

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

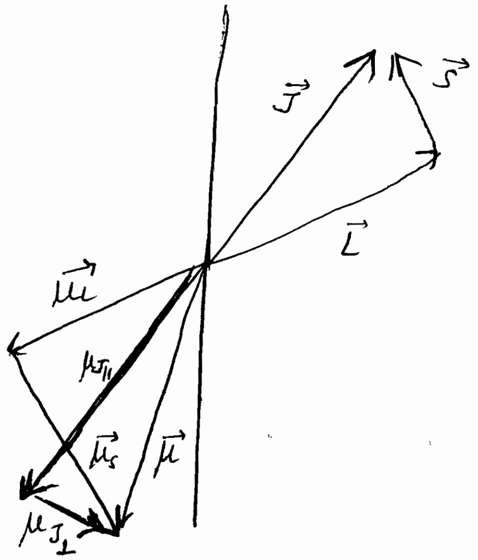
$$= \left(\frac{e\hbar}{2m}\right) g_J B m_j$$

$$\boxed{E = \mu_B B \left(g_J m_J\right)}$$



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?



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

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

while

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

But, $\vec{L}, \vec{S}, \vec{\mu_L}, \vec{\mu_S}$ and therefore $\vec{\mu}$ all precess about $\vec{J}$.

($\vec{J}$ in turn precesses about $\vec{B}$)

$\Rightarrow \vec{\mu} = \vec{\mu_{J_\parallel}} + \vec{\mu_{J_\perp}}$

The $\vec{\mu_{J_\perp}}$ averages to zero due to the precession motion

$\Rightarrow \Delta E = \vec{\mu_{J_\parallel}}\cdot\vec{B}$

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

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

$$\boxed{E = \mu_B B \left(g_J m_j\right)}$$

Normal Zeeman Effect

$E = \mu_B B \; g_J m_J$

Normal Zeeman Effect $\Delta E = \mu_B B \; \Delta m_l$ (if $s=0$) i.e. $g_J = g_l = 1$

$\Delta m_l = 0, \pm 1$

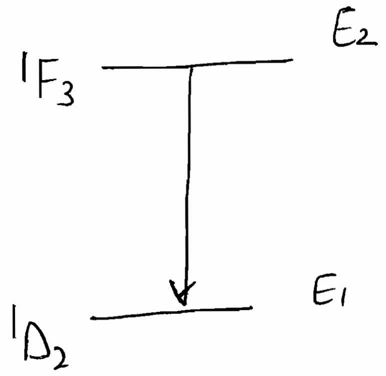
Transverse Normal Zeeman Effect : $\underbrace{\pi, \; 2\sigma}_{\text{3 components}}$

Longitudinal Normal Zeeman Effect: 2 circularly polarized components

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

Q Draw Zeeman pattern of $^1F_3 \longrightarrow {}^1D_2$

A



Unpeturbed line

$\boxed{\text{Now in presence of } \vec{B}\text{, it will split into } (2J+1) \text{ sublevels}}$

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

Hence Normal Zeeman Pattern

$\Rightarrow J = l = 3$ for $^1F_3$

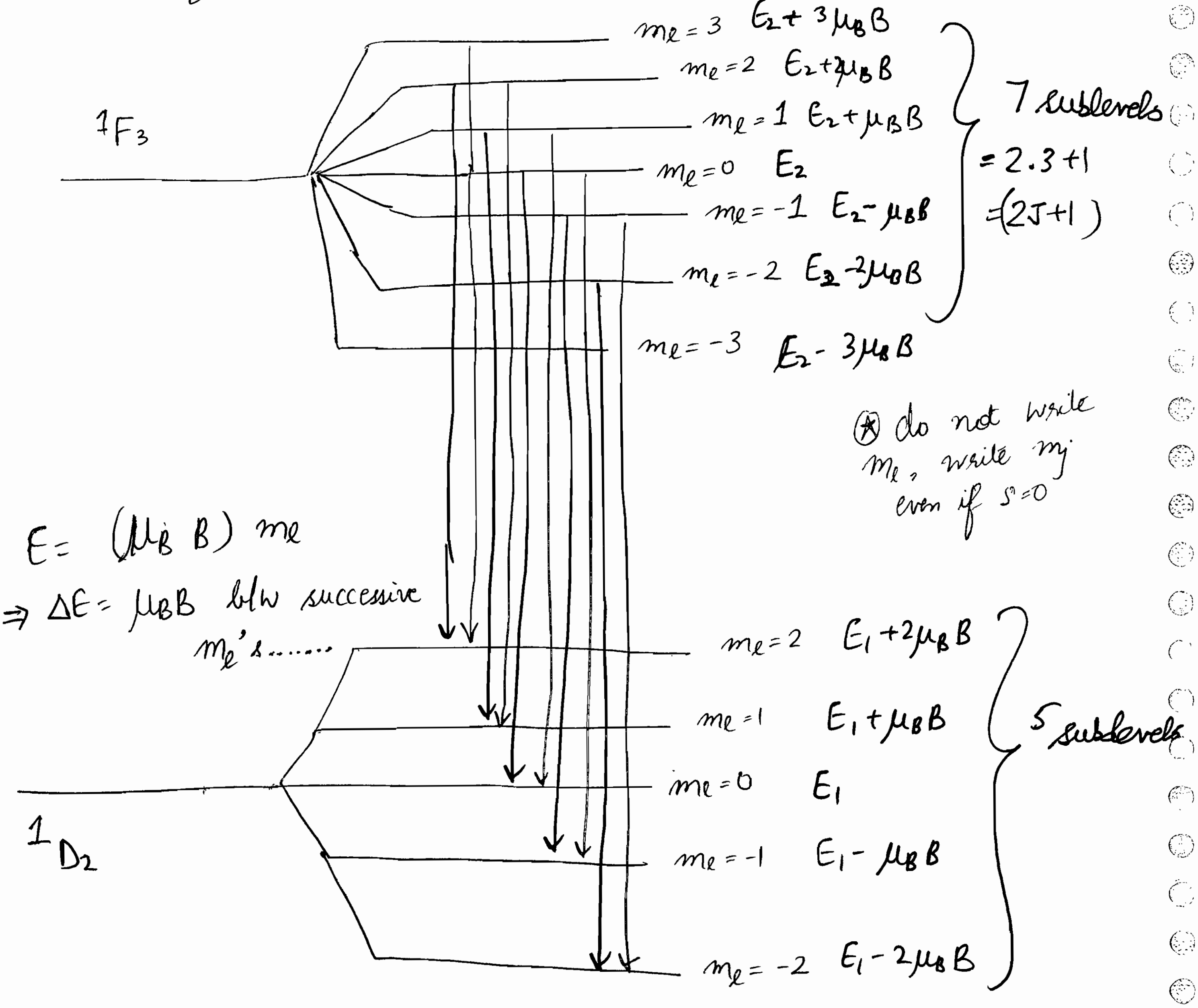
$J = l = 2$ for $^1D_2$

⊛ π component : $\vec{E}$ parallel to External Magnetic Field ∏

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.



⊛ do not write m_l, write m_j even if $S=0$

$E = (\mu_B B)\, m_l$

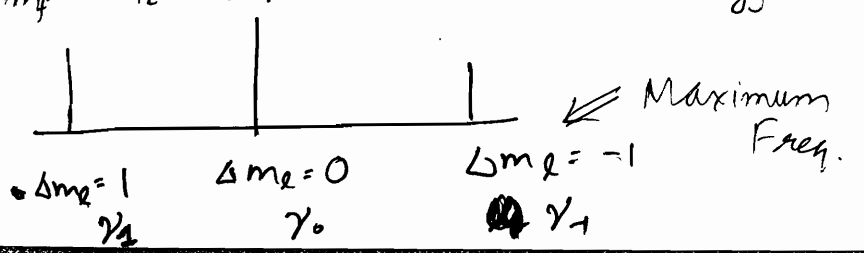
$\Rightarrow \Delta E = \mu_B B$ b/w successive m_l's......

$\boxed{\Delta m_l = 0, \pm 1}$

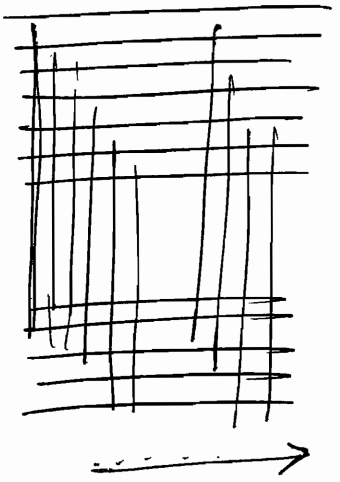
⊛ Note that $m_l = 0 \rightarrow m_l = 0$ is allowed !!

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

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



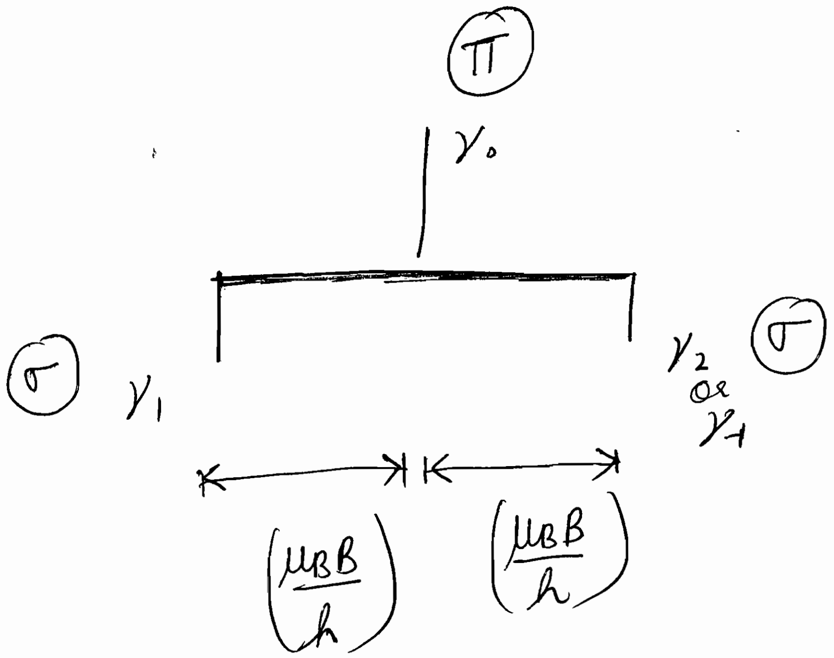
⊙ In exam draw more energy lines on right and less energy lines on left.



$$\nu_0 = \frac{\Delta E}{h} = \left(\frac{E_2 - E_1}{h}\right)$$

$$\nu_{-1} = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} + \frac{\mu_B B}{h}$$

$$\nu_1 = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} - \frac{\mu_B B}{h}$$



⊙ π represented above horizontal line while σ are represented below this line.....

In longitudinal, ν_0 will be missing

$$\boxed{\text{Zeeman Shift (in Frequency)} = \frac{\mu_B B}{h} = \left(\frac{eB}{4\pi m}\right)}$$

⊙ 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.

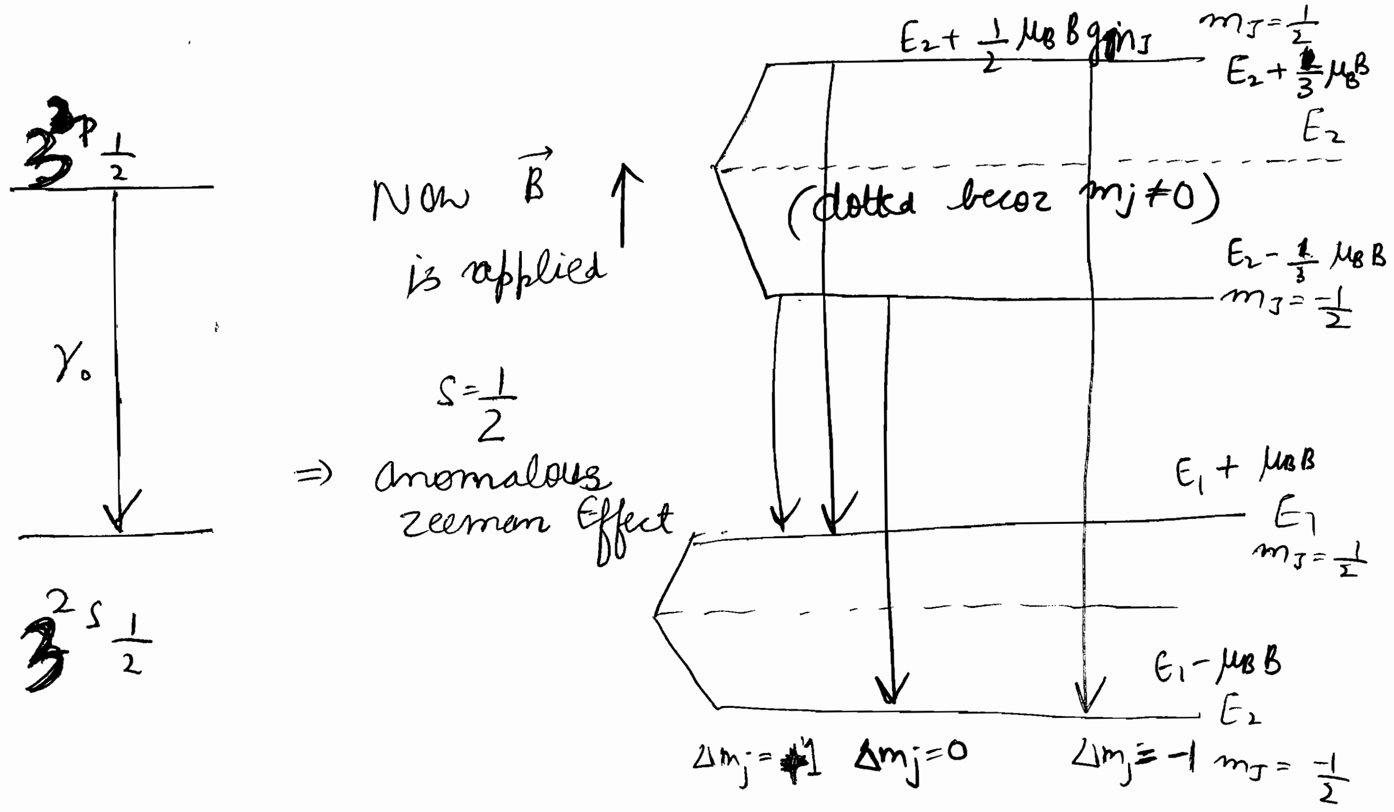
Anomalous Zeeman Pattern

Q Zeeman Effect of Sodium lines D_1 and D_2

D_1: 4 components $\qquad$ D_2: 6 components

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

$\boxed{D_1 \text{ line}}$



Now $\vec{B}$ ↑ is applied

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

⇒ anomalous Zeeman Effect

Now note that $\boxed{E = -\mu_B B(g m_j)}$

We have to take g into account for both levels

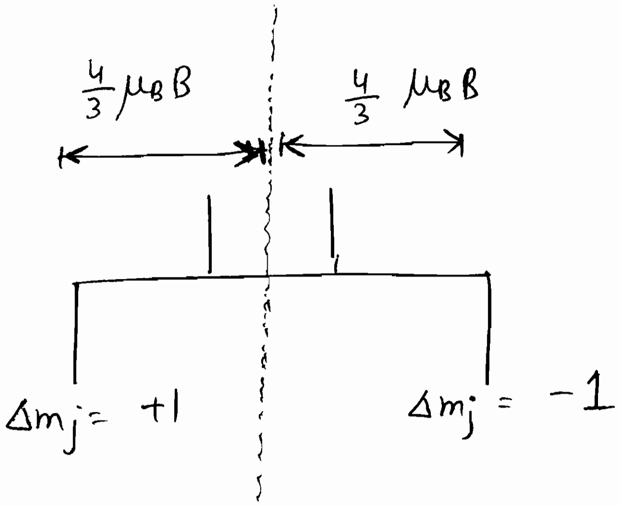
Hence 2 differente components for $\Delta m_j = 0$

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

$$= 1 + \frac{\frac{3}{4} + \frac{3}{4} - 2}{3/2} = 1 - \frac{1}{3} = \frac{2}{3}$$

D_1 : छोटी line
D_2 : बड़ी line

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



reference line
corresponding to D_1 line.

$$\gamma_1 = \gamma_0 - \frac{4}{3}\frac{\mu_B \cdot B}{\hbar} \qquad \sigma \qquad \Delta m = +1$$

$$\left.\begin{aligned} \gamma_2 &= \gamma_0 - \frac{2}{3}\left(\frac{\mu_B B}{h}\right) \\ \gamma_3 &= \gamma_0 + \frac{2}{3}\left(\frac{\mu_B B}{h}\right) \end{aligned}\right\} \pi \qquad \Delta m = 0$$

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

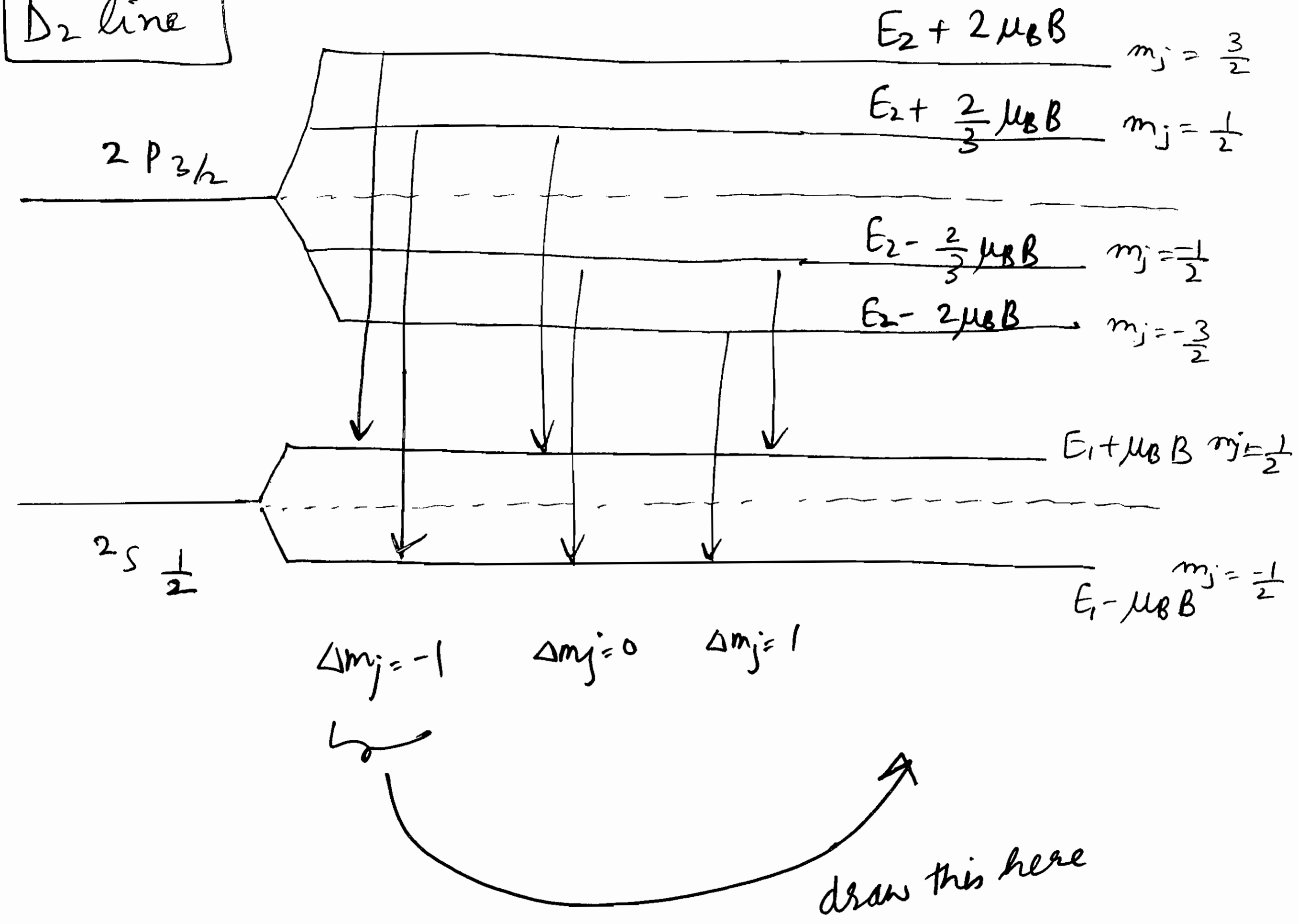
Selection rule for Zeeman :

$\Delta m = 0, \pm 1$

$M_j = 0 \not\leftrightarrow M_j = 0$ if $\Delta J = 0$

eg. $3P_1 \longrightarrow {}^3S_1$ transition

D_2 line



$$g(^2P_{\frac{3}{2}}) = 1 + \frac{\frac{3}{2}\cdot\frac{5}{2} + \frac{1}{2}\cdot\frac{3}{2} - 1\cdot 2}{2\,\frac{15}{4}}$$

$$= 1 + \frac{\frac{15}{4} + \frac{3}{4} - \frac{8}{4}}{\frac{15}{4}} = 1 + \frac{10\,\cancel{4}}{2\,\cancel{4}\cdot 15} = 1 + \frac{\cancel{1}}{3} = \left(\frac{4}{3}\right)$$

(*) 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. Its 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 equitorial velocity of spinning electron to be much greater than c. i.e. $V_{eq} >> c$ which is not possible.

(★) Spectroscopy is that branch of Physics which deals wit 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 ~~t~~transition, the parity of the state of the atom must change.

Proof Transition Rate for x-component of dipole moment $= \langle \psi_f | A \psi_i \rangle$

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

Lets say ψ_i : even

Now if $\sum_j e x_j$ is odd function

$\Rightarrow$ if ψ_f is even $\Rightarrow$ integrand $= 0$

$\Rightarrow$ ψ_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. $\frac{\mu_s}{s} = 2\left(\frac{\mu_L}{L}\right) \Rightarrow g_s = 2 g_l$ ($\because \frac{-e}{2m}$ is sam

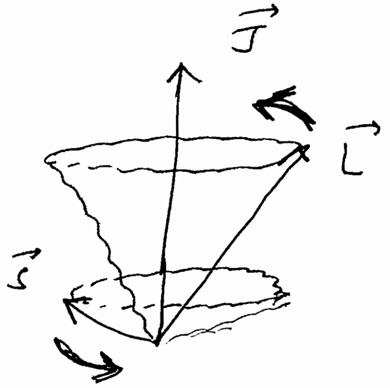
(g factor)

[redacted]

⊛ 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.

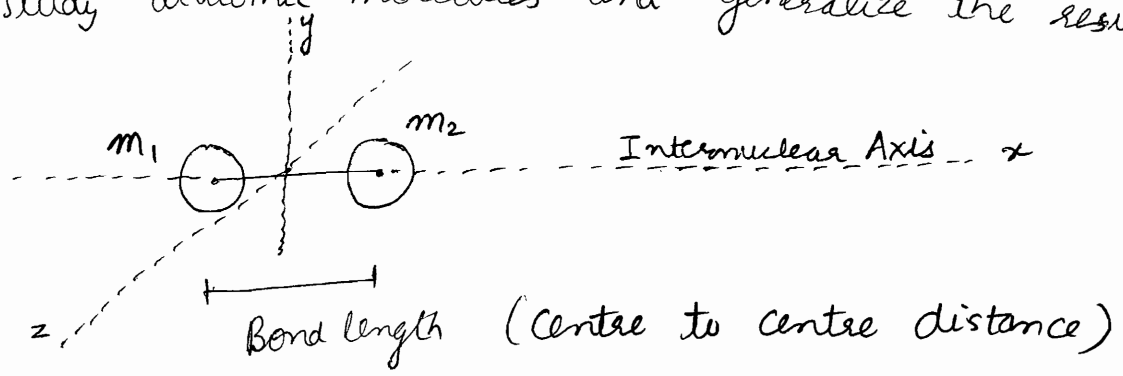
⊛ Multiplet is a collection of spectral lines or transition between two terms. eg 6 Components Comprise D2 multiplet of Na $^2P_{3/2} \rightarrow {}^2S_{1/2}$

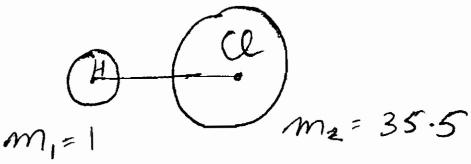
Molecular Physics (1)

24/02/2012

ROTATIONAL SPECTRA

○ We study diatomic molecules and generalize the results.





$$\bar{\omega} = [T_e' + G'(v) + F'(v,J)$$
$$-[T_e'' + G''(v) + F''(v,J$$
remember the notations...

Thank God, [its] Friday

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

Assymmetric 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.
L about internuclear axis is negligible.
Rotation is possible only along line passing through Centre of Mass, and ⊥ to internuclear axis.

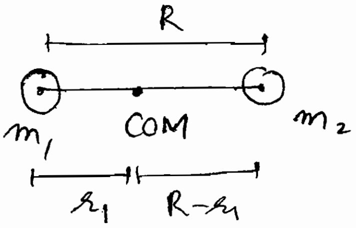
जब किसी एक Particular vibrational mode में होतो rotation करते वक्त r fix रहे!!

→ locating COM,

Now we know,

$$m_1 r_1 = m_2 (R - r_1)$$

$$r_1 = \left(\frac{m_2 R}{m_1 + m_2}\right) \Rightarrow R - r_1 = \left(\frac{m_1 R}{m_1 + m_2}\right)$$



- For rigid rotator,

$$I_{CM} = m_1 r_1^2 + m_2 (R - r_1)^2 = \frac{m_1 m_2^2 R^2}{(m_1+m_2)^2} + \frac{m_2 m_1^2 R}{(m_1+m_2)^2}$$

~~[illegible]~~

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

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

$$\boxed{I_{CM} = \mu R^2} \qquad \boxed{R : \text{Bond length}}$$

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

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

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

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

⊛ Zero Point Energy = 0

⊛ Note that J can take (0, 1, 2, 3, ...) values

We usually define Energy in Wave numbers or Term Numbers i.e.

$$\boxed{F(J) = \frac{E(J)}{hc} = \frac{h}{8\pi^2 I_{CM}\, c} j(j+1) = \underline{B\, j(j+1)}\ \text{cm}^{-1}}$$

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

Now $F(J)$ can have values $0, 2B, 6B, 12B, 20B, \ldots$

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 atom diatomic molecules do not give rotational or vibrational spectra or rotational-vibration spectra.

Only Heteronuclear Molecules possess rotation.

Heteronuclear Molecules possess dipole moment. eg. 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 $= (\vec{p} \times \vec{E})$ 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 Rotator)

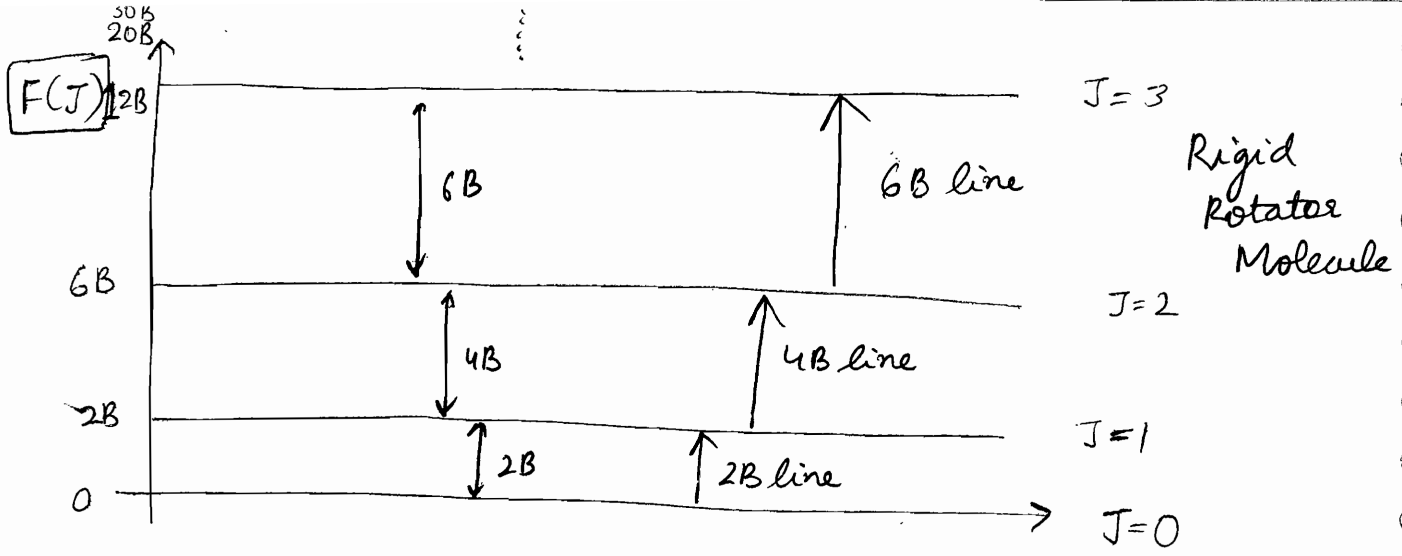
$$\frac{J_{yy}^2}{2I_{yy}} + \frac{J_{zz}^2}{I_{zz}} \Rightarrow \boxed{E = \underbrace{j(j+1)B}_{\text{only this term in rigid rotator}} - D[J(J+1)]^2}$$

↑ Centrifugal distortion coefficient [CDC] ✓

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

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

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



→ Rotational levels are increasing gaps

Order of $B \simeq 0{\cdot}001$ eV

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

⊙ Remember more $|\vec{J}|$ means more energy

$$\boxed{\Delta J = \underset{\text{(absorbtion)}}{+1}, \; -1 \text{ (emission)}}$$

Depending upon energy of klystron Oscillator [Microwave Source], the various jumps can occur.

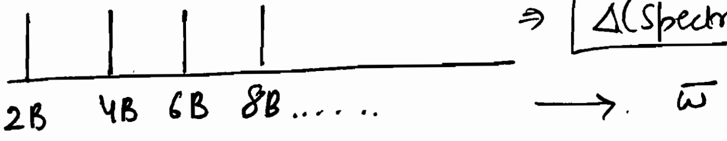
All frequencies of klystron Oscillator are not easily available. [redacted]

$\therefore \Delta J = \pm 1 \Rightarrow$ [Similar to Lande interval rule]

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

$$\Rightarrow \boxed{\Delta E = 2jB}$$

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



uniform gaps in rotational spectra of diatomic rigid rotator molecules.

→ If gap is not uniform ⇒ [redacted] molecules [redacted]
[redacted].
Non rigid rotator

If uniform gap ⇒ rigid rotator (<u>nature of molecule</u>)

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

$$\Rightarrow I_{CM} = \frac{h}{8\pi^2 c B}$$ (<u>Moment of Inertia</u>)

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

$$\Rightarrow r = \sqrt{\frac{I_{CM}}{\mu}}$$ (<u>Bond length</u>)

Hence 3 things were calculated from seeing gap.

$H^1 Cl^{35.5}$ $H^2 Cl^{35.5}$.

$\mu = \frac{1 \times 35.5}{36.5}$ $\mu = \frac{2 \times 35.5}{37.5}$

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

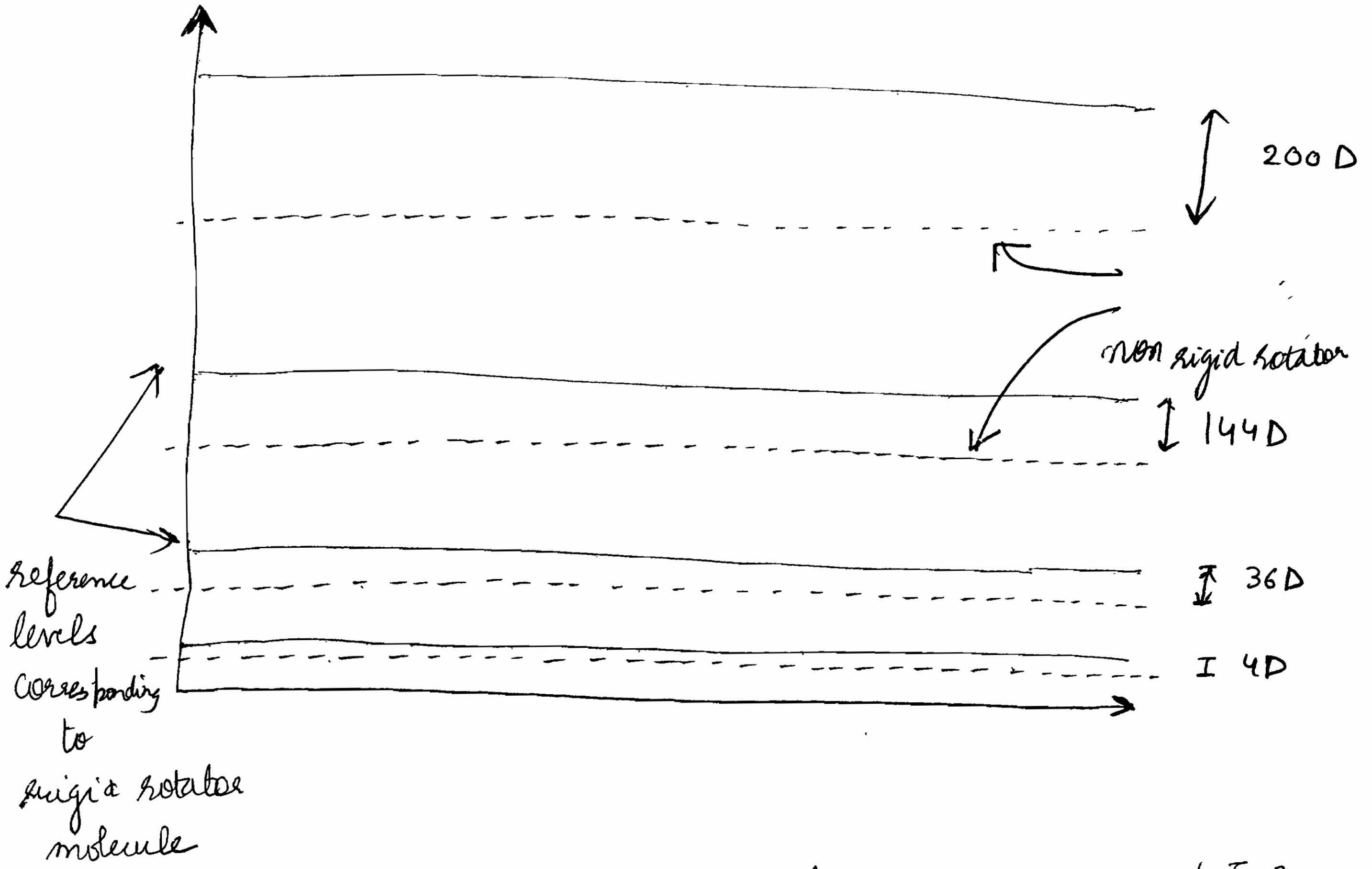
⇒ from shift in B, we can obtain <u>information about isotope</u>. This is called <u>isotope effect</u>.

⇒ 4^{th} information we got is Isotope Effect from gap.

For [redacted] (Non Rigid Rotator)

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

$F(0) = 0$; $F(1) = 2B - 4D$; $F(2) = 6B - 36D$;
$F(3) = 12B - 144D$; $F(4) = 20B - 400D$



	$\Delta J = 1$	$\Delta J = 2$
$F(0) = 0$	$2B - 4D$	$6B - 36D$
$F(1) = 2B - 4D$	$4B - 32D$	$10B - 140D$
$F(2) = 6B - 36D$	$6B - 108D$	$14B - 364D$
$F(3) = 12B - 144D$	$8B - 256D$	
$F(4) = 20B - 400D$		

gap is non uniform

$\Downarrow$

non rigid rotator molecule

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

$4B - 32D$: known

x_1

x_2

x_3

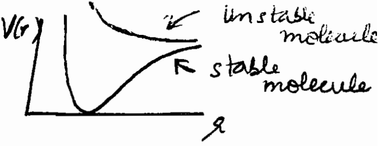
Q8) CO : $J = 0 \longrightarrow J = 1$

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

$F(0) = 0$

$F(1) = 2B$

$2BC = \nu$ 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

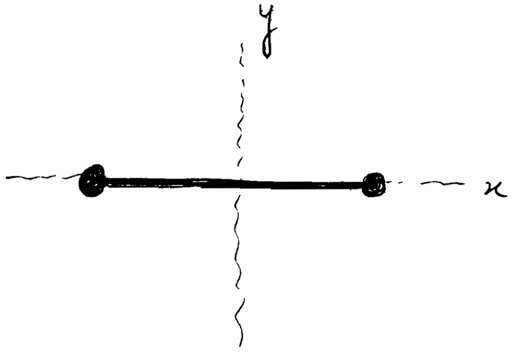
In non homogenous Electric Field, permanent dipole moment experiences $\boxed{\vec{F} = (\vec{p}\cdot\vec{\nabla})\vec{E}}$

⇒ Oscillatory Force due to oscillating $\vec{E}$.

⇒ vibration

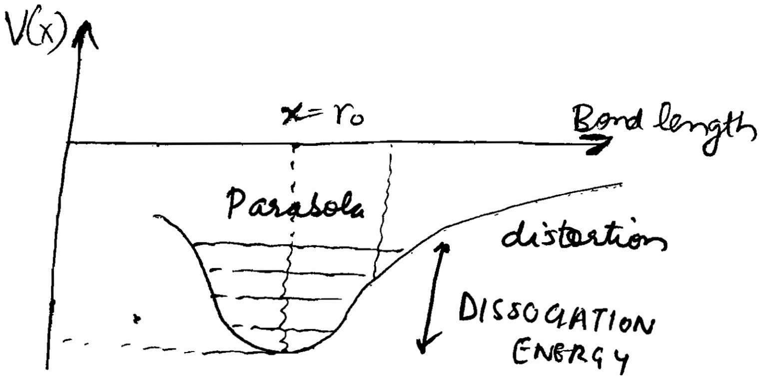
Molecule behaves like simple Harmonic Oscillator.

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



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

But molecules may not be simple harmonic oscillator



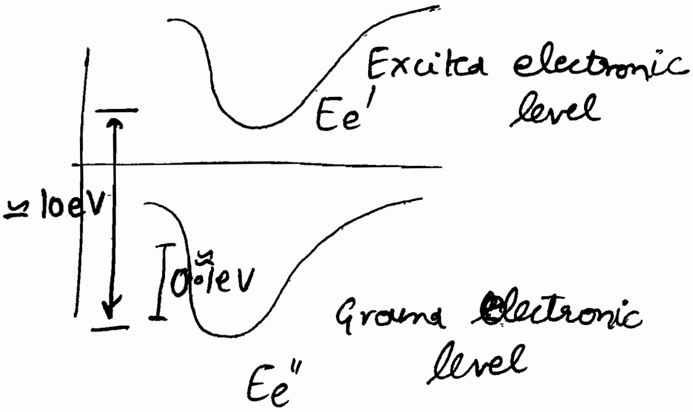
Potential for diatomic molecule

Combination of Parabolic Aparabolic curves.

$$\boxed{V(x) = Fx^2 - gx^3} \quad : x = (r - r_0)$$

<u>Dissociation Energy</u>: 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
Ee' : single prime for excited electron

Assume the primes like floors of Basement

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]

$$V = \frac{1}{2}kx^2$$

Quantum Solution

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

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

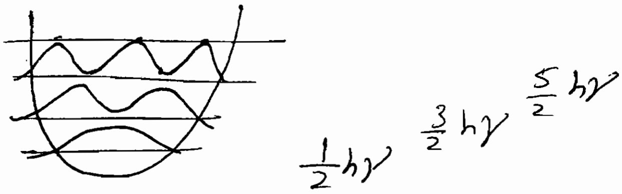
write $\hbar\omega = \bar{\omega}hc$
$\Rightarrow \bar{\omega} = \frac{1}{2\pi c}\sqrt{\frac{k}{m}}$

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

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

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

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



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

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

Anharmonic Oscillator

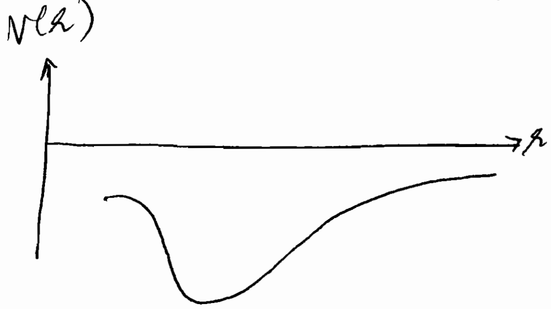
Q) $f(x)$: continuous in some interval.
Expand it about x.

⇓

$$f(x) = f(x_0) + (x-x_0)f'(x_0) + \frac{(x-x_0)^2}{\lfloor 2} f''(x_0) + \ldots + \frac{(x-x_0)^r}{\lfloor r} f^r(x_0)$$

Tailor Series

Using Taylor Series,



$$V(r) = V(r_0) + (r-r_0)V'(r_0) + (r-r_0)^2 V''(r_0) + \ldots$$

⇒ $V(r) - V(r_0) = 0$ if [illegible] $V'(r_0) = 0$

⇒ Force = 0

EQUILIBRIUM

$V''(r_0) > 0$

⇒ Put $(r-r_0)$ = displacement from equilibrium as x.

Now $V''(r_0) > 0$: Minima

$V'''(r_0) < 0$

Every subsequent coefficients are lesser in Taylor Series

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

Hence lets fix,

$$V(x) = \text{[redacted]} \; f x^2 - g x^3 \longleftarrow$$ Mechanical Anharmonicity

Eigen Value Problem has solutions,

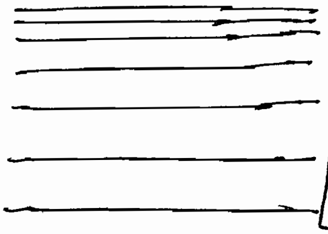
$$\boxed{E(v) = \left(v+\tfrac{1}{2}\right) hc\,\bar{\omega}_e - \left(v+\tfrac{1}{2}\right)^2 hc\,\bar{\omega}_e x_e}$$

$\omega_e x_e$: Anharmonicity Const. $\omega_e x_e \ll \omega_e$

ω_e : energy state if curve was parabola

$$G(v) = \frac{E(v)}{hc} = \left(v+\tfrac{1}{2}\right)\bar{\omega}_e - \left(v+\tfrac{1}{2}\right)^2 \bar{\omega}_e x_e$$

Quantum Number $v = 0, 1, 2, \ldots$



decreasing energy levels due to mechanical anharmonicity

[redacted] ~~Rule of Electric Dipole Moment for Vibrations~~

$\Delta v = \pm 1$; Harmonic Oscillations

$\Delta v = \pm 1, \pm 2$: Anharmonic oscillations [redacted]

[redacted]

electrical anharmonicity

$\boxed{\Delta v = +1}$ $\boxed{\Delta v = +2}$

$G(0) = \frac{1}{2}\bar{\omega}_e - \frac{1}{4}\bar{\omega}_e x_e$

$G(1) = \frac{3}{2}\bar{\omega}_e - \frac{9}{4}\bar{\omega}_e x_e$

$G(2) = \frac{5}{2}\bar{\omega}_e - \frac{25}{4}\bar{\omega}_e x_e$

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

$\omega_e - 2\bar{\omega}_e x_e$

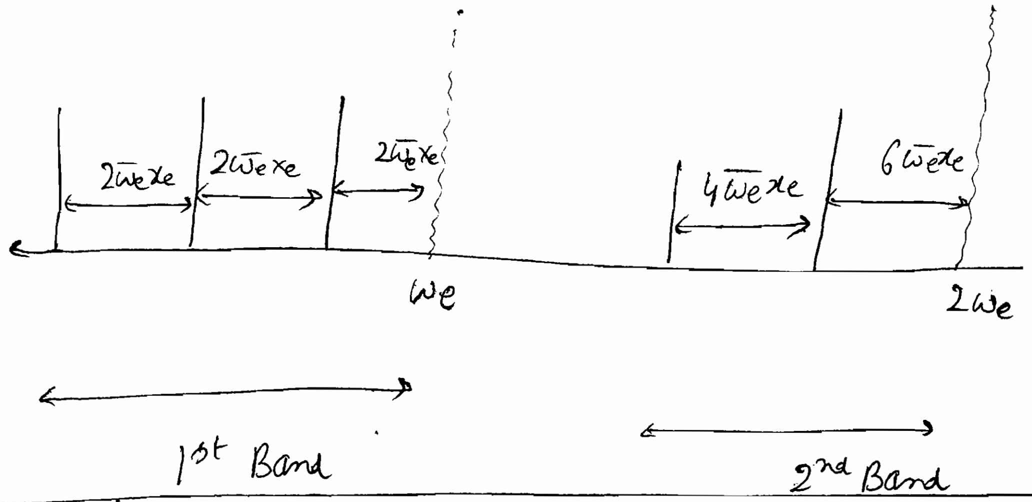
$\omega_e - 4\bar{\omega}_e x_e$

$\omega_e - 6\bar{\omega}_e x_e$

$2\omega_e - 6\bar{\omega}_e x_e$

$2\bar{\omega}_e - 10\bar{\omega}_e x_e$

- 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 v (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 Schroedinger's equation, Born Oppenheimer approximation is used, according to which:

(i) first, due to slow moving massive nuclei, the wave equation for electronic motion alone is solved, in which nuclear coordinates appear simply as parameter.

(ii) then, the wave equation for motion of nuclei alone is solved in which [redacted] eigenvalues of electronic motion occur as part of potential energy function of nuclear motion.

(iii) 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.

(★) r_e : equilibrium

@ $r < r_e$: more nuclear repulsion
@ $r > r_e$: ~~less~~ electronic attraction } ⇒ 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 $v=1$

i.e. $\bar{\omega}_1 = \bar{\omega}_e (1 - 2x_e$

$\Delta v = +2$: Band

Population is governed by Maxwell Boltzmann Statistics.

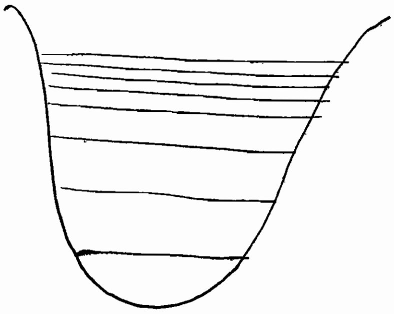
$$N_1 = N_0 e^{-\left(\frac{\Delta E}{kT}\right)}$$

ΔE : Energy b/w $v=0$ to $v=1$ transition

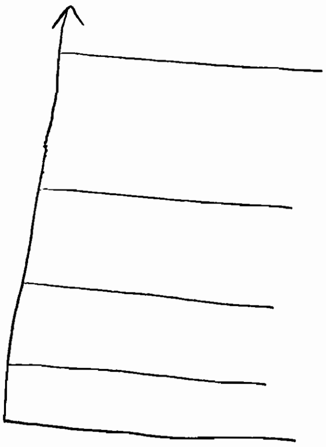
⊛ At room temperature, usually $v''=0$ is seen. But for heavier molecules like I_2, $\bar{\omega}_e$ is less ⇒ $v''=0,1,2$ can be seen at room temperature

✓ 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.



In rotation, gap ↑ with increase in quantum number J

Major difference in Spectra of Rotation & [redacted] Vibration

Vibration - Rotation Spectra

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

$$\boxed{G(v, J) = G(v) + F(J)}$$

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

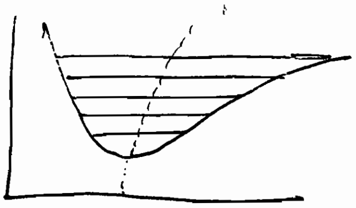
$$+ \; B\, J(J+1)$$

B: rotational constant in vibrational level v $= \left(\frac{h}{8\pi^2 c \mu r^2}\right)$

★ Overtones due to $\Delta v = 2, 3, \ldots$ 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

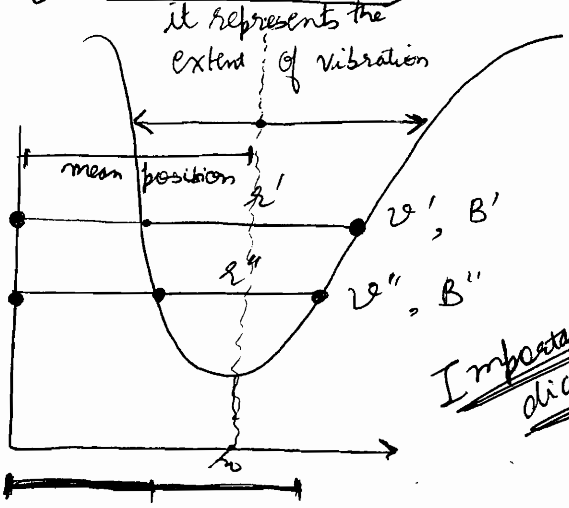
★



r_0 moves towards right

⇒ B reduces

r_0: mean position



Important diagram

Also the mean r_0 moves towards right with increasing energy levels

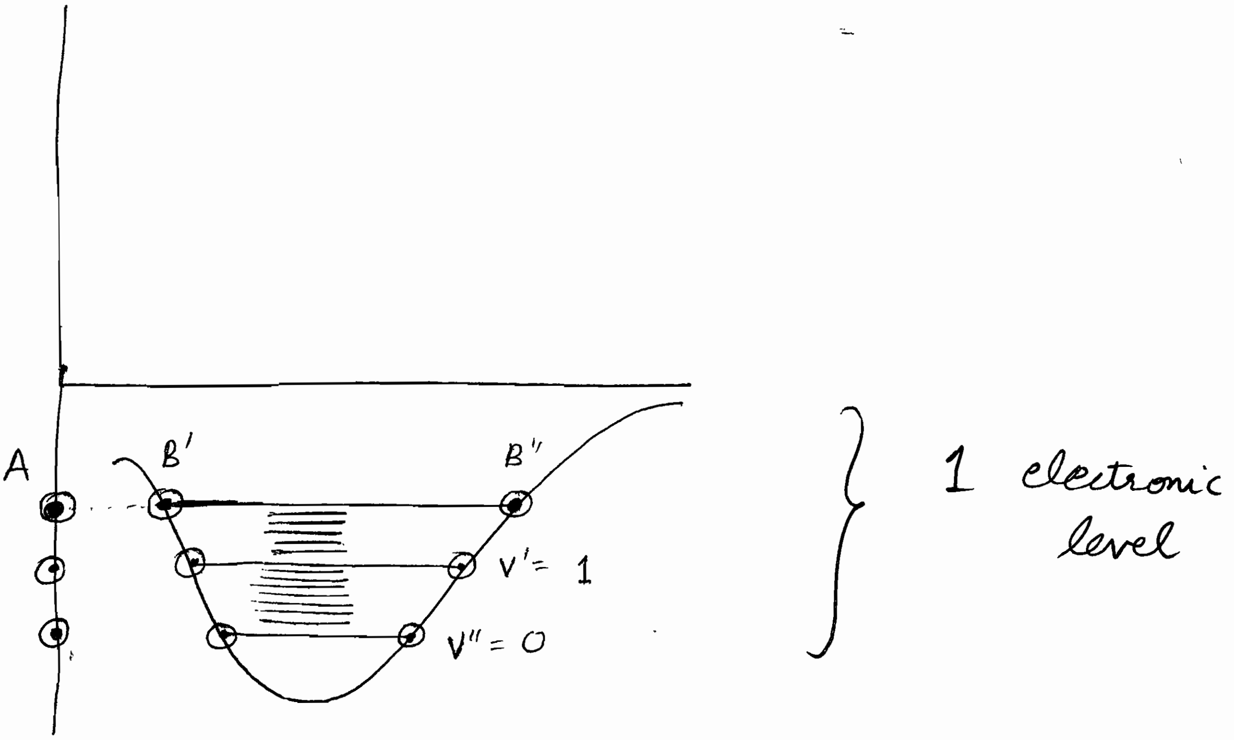
In increasing vibrational state, inter molecular distance increases. Although difference is not very significance

Now $r' > r''$
$B' < B''$ ⇒ $\boxed{B' - B'' < 0}$

⇒ $\boxed{B' - B''}$ is small negative quantity.

Molecule is stretched with every excited molecular vibrational 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 ≠ 0
Many rotational energy are inculcated in this level.] *

Writing ground state of Vibrational - Rotational level

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

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

Excited state

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

$$\overline{\omega}_{v,r} = \Delta G(v, J)$$

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

$$\boxed{\overline{\omega}_{v,r} = (v'-v'')\,\overline{\omega}_e - (v'-v'')(v'+v''+1)\,\overline{\omega}_e x_e + B'J'(J'+1) - B''J''(J''+1)}$$

[redacted]

Rigid Rotator Diatomic Molecule

$\Delta v = v' - v'' = 1$ (absorption) (−1 for emission)

$\Delta J = \pm 1$

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

For Non-Rigid Rotator Molecule

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

$\Delta J = \pm 1$

For $\Delta v = 1$

⊛ We normally study the spectra for normal absorption case $\Delta v = 1$ $\boxed{v' = 1 \leftarrow v'' = 0}$

$$\Rightarrow \overline{\omega}_{v,r} = \overline{\omega}_e - 1(2v''+2)\,\overline{\omega}_e x_e + B'J'(J'+1) - B''J''(J''+1)$$

General for $\Delta v = +1$

Specific Case

$V'' = 0$ to $v' = 1$: $\overline{\omega}_{v,r} = \overline{\omega}_e - 2\overline{\omega}_e x_e + B'J'(J'+1) - B''J''(J''+1)$

Band — Vibrational line

[redacted]

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

Now,

$$\bar{\omega}_{v,r} = \underbrace{\bar{\omega}_e - 2\bar{\omega}_e x_e}_{} + B'J'(J'+1) - B''J''(J''+1)$$

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

<u>ΔG_v will give $\bar{\omega}_v$</u>
<u>The finer lines will come from ΔG_r.</u>

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

ΔJ :	-2	-1	0	1	2
	O	P	Q	R	S

(*) सभी Occurs होते हैं !!

$\Delta J = 0$: 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 <u>in vibrational band, only P and R branch are observed to be seen.</u>

<u>R branch</u> $\boxed{\Delta J = +1}$ $\boxed{J' - J'' = 1}$

$\boxed{J'' = 0, 1, 2, \ldots}$

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

$$= \boxed{\bar{\omega}_v + (J''+1)\left[(B'-B'')J'' + (2B'-B'')\right]}$$

Put $J''=0$ $\quad = \bar{\omega}_v + 1[2B' - B'']$

⋮

Put $\boxed{\Delta J = -1}$ for P branch, $\boxed{J' - J'' = -1}$ **P BRANCH**

Here $\boxed{J'' = 1, 2, 3, 4, \ldots}$

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

$$\boxed{\overline{\omega}_P = \overline{\omega}_v - (B' + B'')J'' + (B' - B'')J''^2}$$

$$\boxed{\omega_R = \overline{\omega}_v + (B' + B'')J'' + (B' - B'')J''^2 + 2B'}$$

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

Put $$\boxed{\overline{\omega}_{v,R} = \overline{\omega}_v + (B' + B'')m + (B' - B'')m^2}$$

where m : parameter

Note that $m \neq 0$ i.e. $|m| > 0$

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

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

Its called [redacted]

For P series, replacing J values $(1, 2, 3, 4, \ldots\ldots)$

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

$$\overline{\omega}_{P(2)} = \overline{\omega}_v - 2(B' + B'') + 4(B' - B'')$$
$$= \overline{\omega}_v + 2B' - 6B''$$

$$\overline{\omega}_{P(3)} = \overline{\omega}_v - 3(B' + B'') + 9(B' - B'')$$
$$= \overline{\omega}_v + 6B' - 12B''$$

$\downarrow$ decreasing

Refer Fig. 11 on P-313

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

For R series

जहाँ से चालू होता है, उसका index

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

$$\bar{\omega}_{R(1)} = \bar{\omega}_v + 2(B'+B'') + 4(B'-B'')$$

$$= \bar{\omega}_v + 6B' - 2B''$$

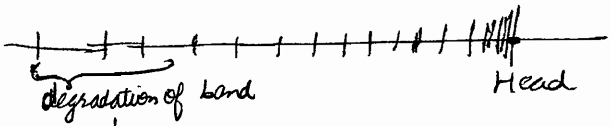
increasing

$$\bar{\omega}_{R(2)} = \bar{\omega}_v + 3(B'+B'') + 9(B'-B'')$$

$$= \bar{\omega}_v + 12B' - 6B''$$

Red degraded ←

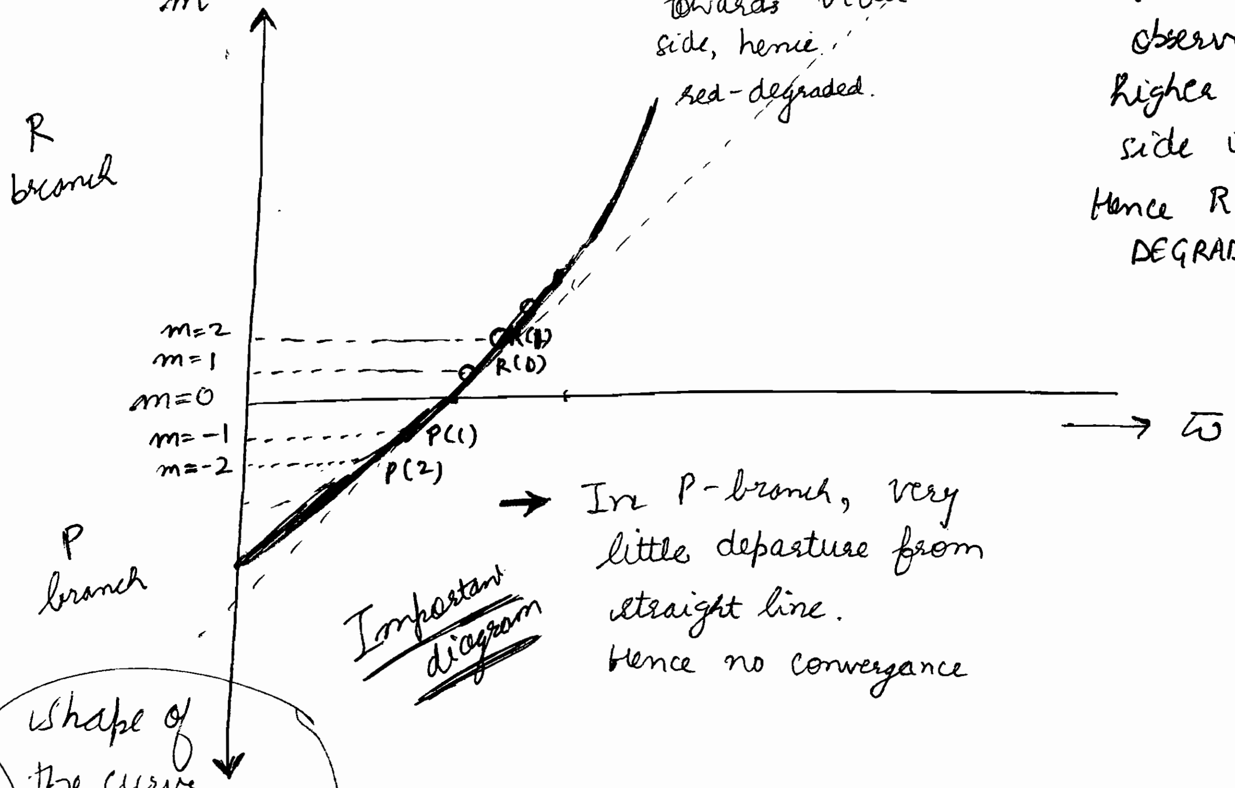
head formation tendency towards high ν side →



$\bar{\omega}_{v,R}$ vs m

In R-branch, poor convergence.
But convergence is towards violet side, hence red-degraded.

⊕ Head Formation Tendency is observed towards higher frequency side i.e. violet side.
Hence RED IS DEGRADED.



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

Important diagram

Shape of the curve should be like Fig 12, P-314

if $B'-B'' > 0 \Rightarrow$ --- (VIOLET Degraded Parabola : formed in electronic spectra

But $B'-B'' < 0 \Rightarrow$ ---) Red ~~Violet~~ Degraded Parabola ✓ FORMED here

For vertex of Parabola

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

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

⊙ [Vibration Rotation spectra shows poor tendency of head formation (but tendency is) towards higher wave number side violet side]

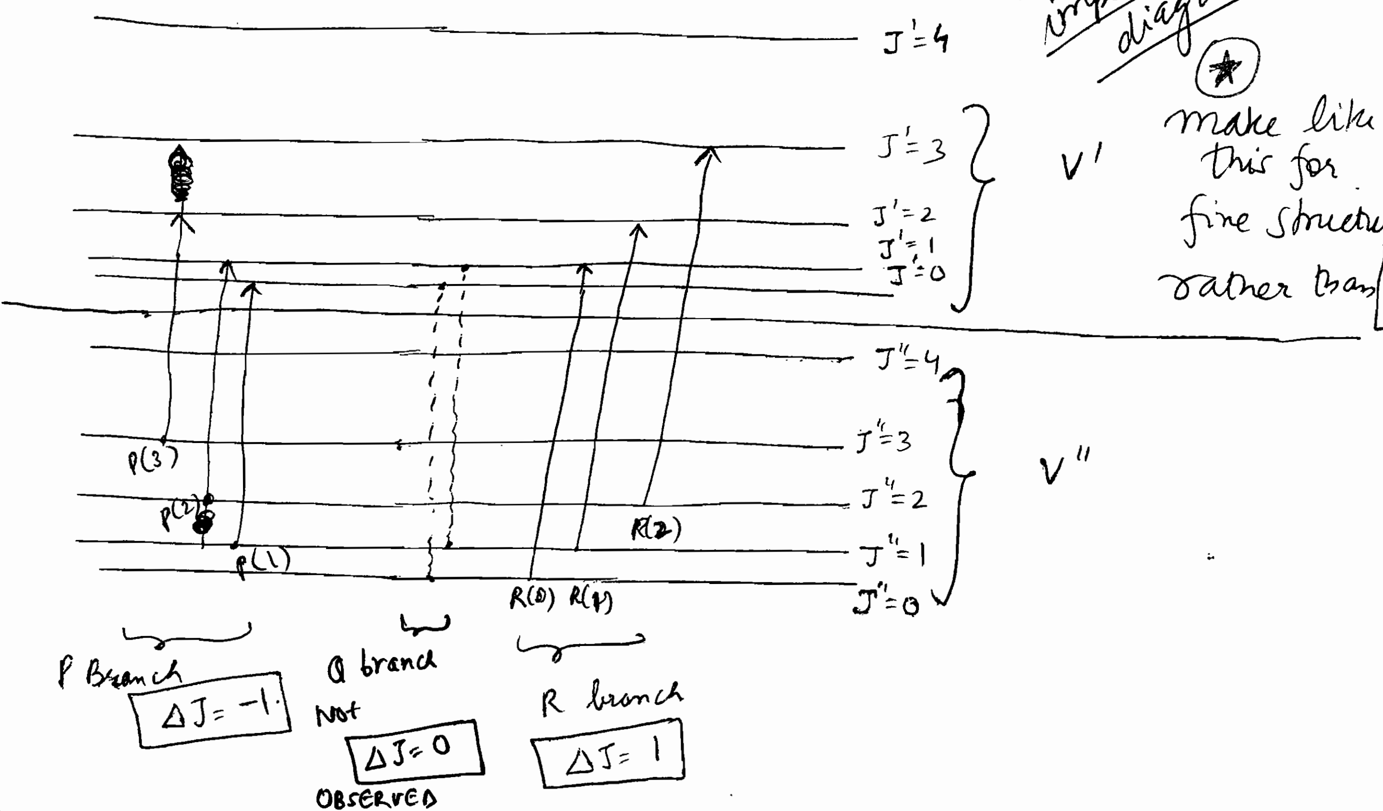
⊙ [Only bands degraded to only 1 side are formed, i.e. Red degraded only]

Reason for both is $r' > r''$ but difference is SMALL

⇒ $B' < B''$

⇒ $(B' - B'')$ is SMALL NEGATIVE QUANTITY

Spectrum



important diagram ★

make like this for fine structure rather than V

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

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

⑧ $\lambda_v = 14.7\ \mu m$

$$\frac{1}{\lambda} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2} = \checkmark$$

$\Rightarrow$ k : calculated ✓

$J=0 \rightarrow J=1$: 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. B'coz 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.

$$20.68\ (J+1)$$

$$F(J+1) - F(J) = B(J+1)(J+2) - BJ(J+1)$$

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

$$2B = 20.68 \qquad B = \frac{h}{8\pi^2 c\, I_{CM}}$$

Hence I_{CM} Obtained.

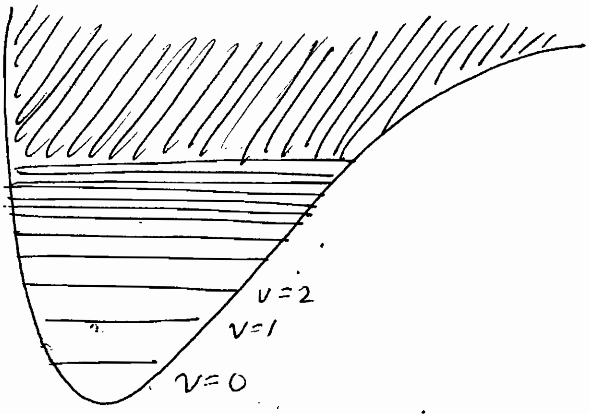
$$k_1 : k_2 : k_3 = \mu_1 \omega_1^2 : \mu_2 \omega_2^2 : \mu_3 \omega_3^2$$

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

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

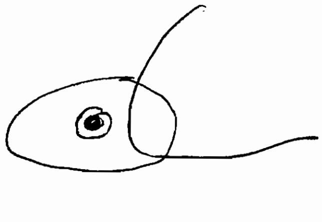
Hence most of the molecules in a sample exist in $v=0$ state, with only their zero point energies. Exceptions are heavy molecules like I_2 that have small $\overline{\omega_e}$ ⇒ they can exist @ $v=0$, $v=1$ $v=2$ at room temperature! $v=1$ पर $v=0$ से तो कम होंगे but still appreciable amount में होंगे.

(★) 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 $B_v = B_e - \alpha\left(v + \frac{1}{2}\right)$

where $B_e = \left(\frac{h}{8\pi^2 \mu r_e^2 c}\right)$

corresponding to

MOLECULAR PHYSICS (3)

27/02/2012

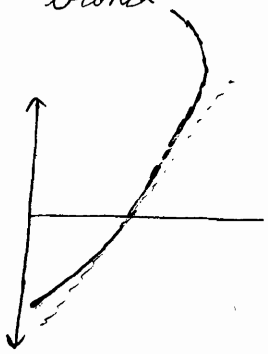
⊙ For vibrational-rotational motion,

$$\bar{\omega}_{P\ or\ R} = \bar{\omega}_V + (B' - B'')\, m + (B' - B'')\, m^2$$

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

Positive : R branch

Negative : P branch

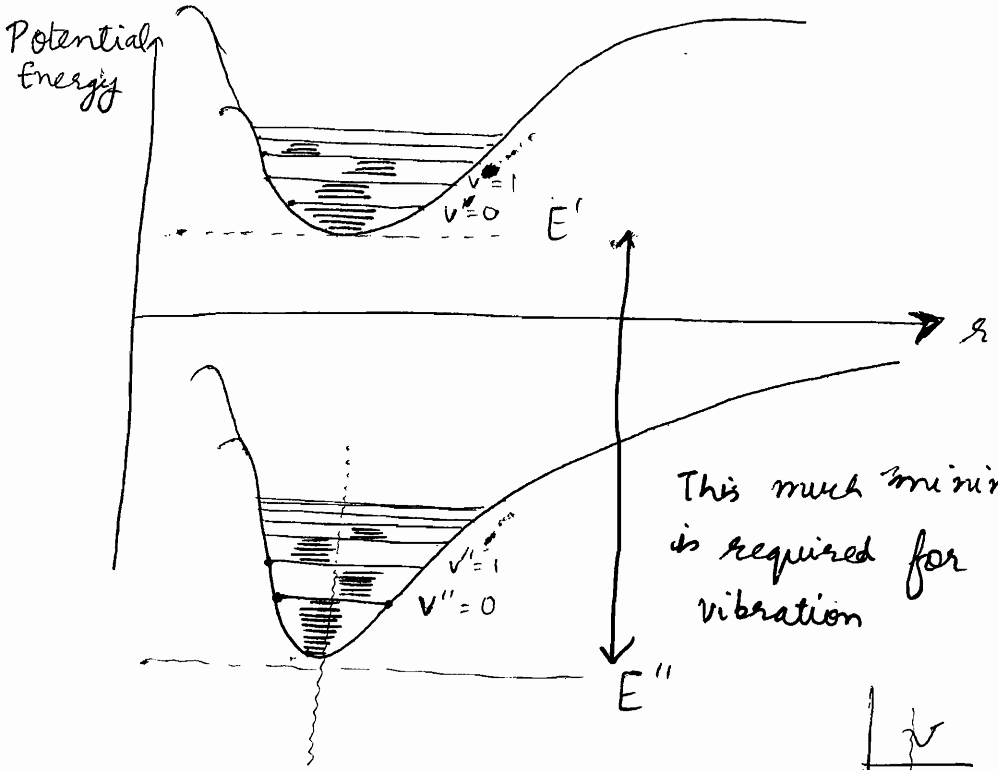


→ The spectrum formation has

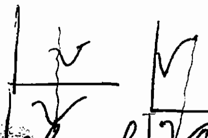
- poor tendency for head formation
- red - degraded character

Electronic Spectra

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



This much minimum energy is required for electronic vibration



In electronic motion, bond length may also be compressed.

There are 4 allowed transitions depending upon m_ℓ values. Corresponding to L_z about internuclear axis.

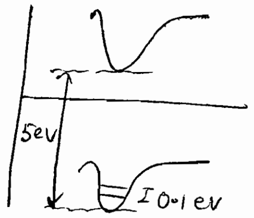
Selection Rules	S	P	D	F
Δm_l	0	1	2	3
Transition	Σ	Π	Δ	Φ

(first letters of corresponding Greek Alphabet)

In 'Σ' transition, $\Delta m_l = 0$. 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 $\Delta m_l = 0$ is allowed.

$$\boxed{E = E_{(e)} + E_{(v)} + E_{(J)}}$$



eg. if provided ⇒ 5 eV — E_e changes ⇒ new E

5·1 eV — E_e as well as E_v changes to new E, new v level

5·150 eV — E_e as wells as E_v as well as rotational E is changed ⇒ New E, new v, new J.

⊛ (Note that quantums are so small s.t such energy level continuum is possible)

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

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

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

↑ (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, Δv is unrestricted. When Δv is unrestricted & ΔJ not considered, coarse structure. When ΔJ is Considered [redacted], 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.

$$\Delta v = \text{unrestricted}$$

$$\neq 0, \pm 1, \pm 2, \pm 3, \ldots$$

(Restriction is only the no. of v levels in single electronic level)

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

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

We know $\omega = \sqrt{\frac{k}{m}}$ $\Rightarrow \bar{\omega} = \frac{1}{\lambda} = \frac{1}{cT} = \frac{\nu}{c} = \left(\frac{2\pi\nu}{2\pi c}\right)$

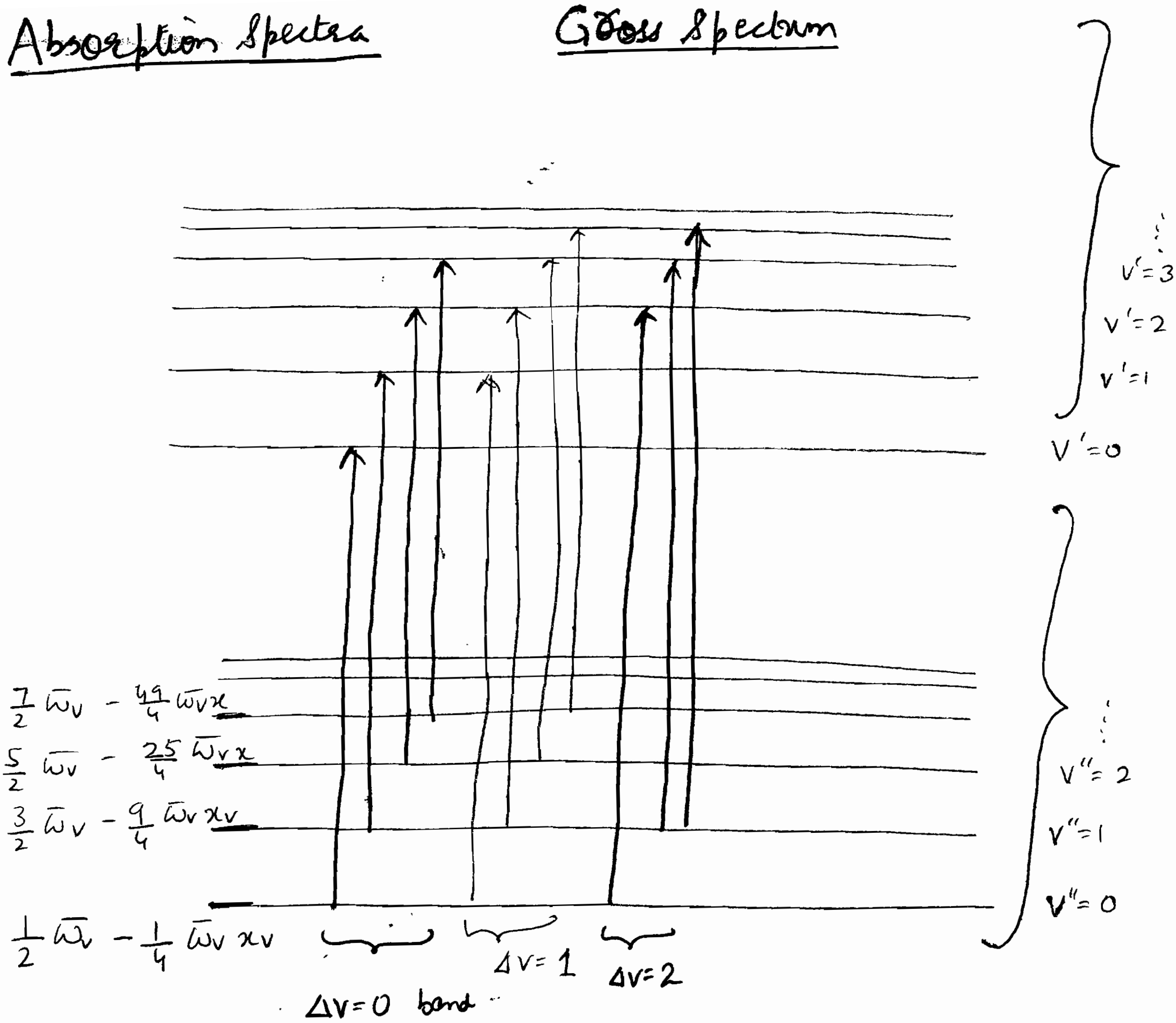
$$= \frac{\omega}{2\pi c} = \underline{\underline{\frac{1}{2\pi c}\sqrt{\frac{k}{m}}}}$$

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

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 possess if nuclei were fixed, & consists of
  - → K.E. & P.E. of extranuclear electrons
  - → P.E. of repulsion between nuclei

Absorption Spectra Gross Spectrum



↑

Note that separations are not of const. width ⇒ BAND of LINES

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

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.

$$\bar{\omega}_{e,v} = T(e') + G(v') - T(e'') - G(v'')$$

$$= [T(e') - T(e'')] + [G(v') - G(v'')]$$

$$= \bar{\omega}_e + \left(v'+\tfrac{1}{2}\right)\bar{\omega}_v - \left(v'+\tfrac{1}{2}\right)^2 \bar{\omega}_v x_v$$

$$- \left(v''+\tfrac{1}{2}\right)\bar{\omega}_v' + \left(v''+\tfrac{1}{2}\right)^2 \bar{\omega}_v' x_v$$

~~[illegible]~~

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

(different electronic levels have different curves and different ω_e, x_e 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 Band systems

eg. $\Delta v = 1$ Band Or Progression

$$v=0 \rightarrow v=1 \Rightarrow \omega = \bar{\omega}_e + \frac{3}{2}\bar{\omega}_v - \frac{9}{4}\bar{\omega}_v x_v - \frac{1}{2}\bar{\omega}_{v'} + \frac{1}{4}\bar{\omega}_{v'} x_v$$
$$= \underline{\omega_e + \bar{\omega}_v - 2\bar{\omega}_v x_v}$$

$v=1 \rightarrow v=2$
$v=2 \rightarrow v=3$

$$\omega = \bar{\omega}_e + \bar{\omega}_v - 4\bar{\omega}_v x_v$$

$$\omega = \bar{\omega}_e + \bar{\omega}_v - 6\bar{\omega}_v x_v$$

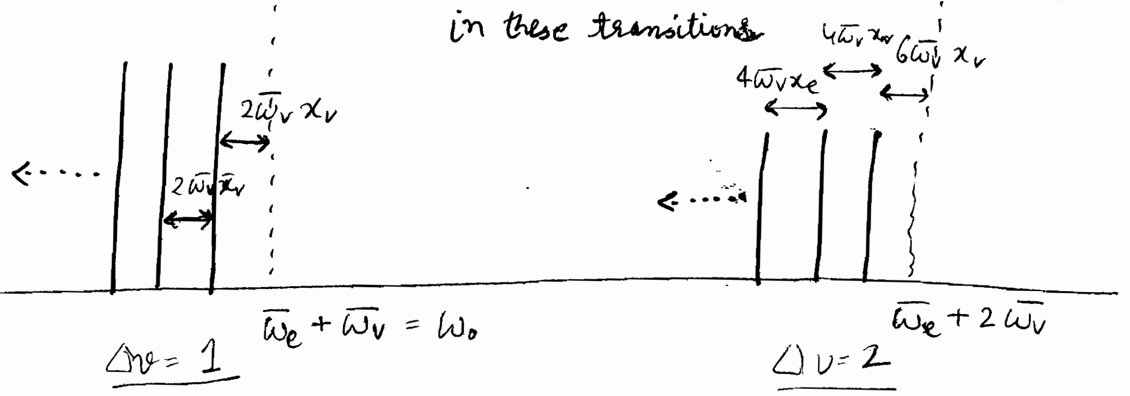
all take $v''=0$
$v' = 1, 2, 3$
Progression

v' [illegible] for $v''=0$

Let us say $(\bar{\omega}_e + \bar{\omega}_v)$ = reference level ω_0

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

Gross Spectrum of Electronic level changes



$\Delta v = 2$ Band or Progression

~~[illegible]~~

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

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

⊛ Note that $\omega_e' \neq \omega_e''$

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

$$\Delta E = \Delta T_e + \Delta G(v) + \Delta F(J)$$
$$= \bar{\omega}_e + \bar{\omega}_v + \Delta F(J)$$
$$= \omega_0 + \Delta F(J)$$
$$= \omega_0 + B'J'(J'+1) - B''J''(J''+1)$$

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

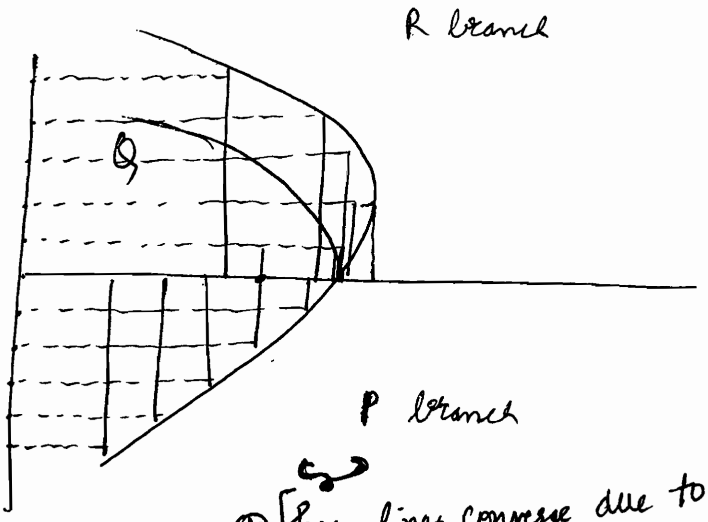
$\Delta J = -1$: P branch

Note that here $r' > r''$ (Possible Case)

$\Rightarrow (B' - B'') < 0$: Negative Quantity [Not small]

Hence good FORTRET PARABOLA is formed.

$\omega = \overline{\omega}_0 +$ [redacted] $(B' + B'')\, m + (B' - B'')\, m^2$



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

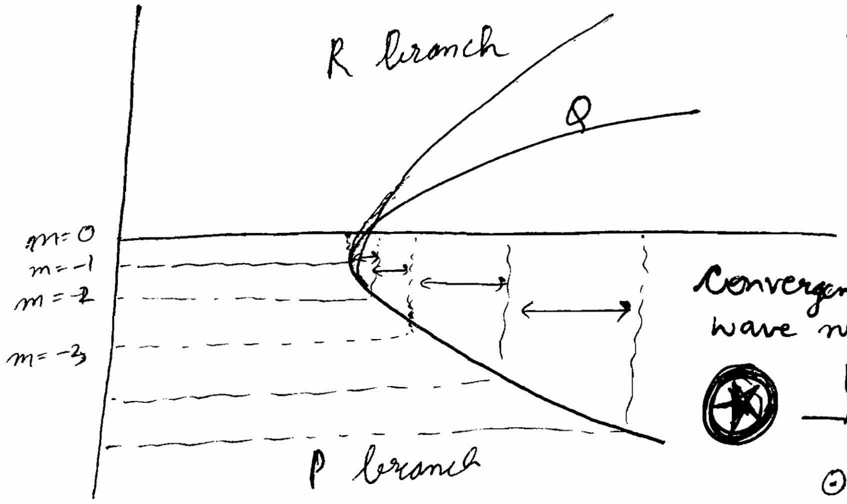
- Good tendency for head formation.
- Red degraded
- Convergence towards higher wave number side

Also $r' < r''$ (Possible)

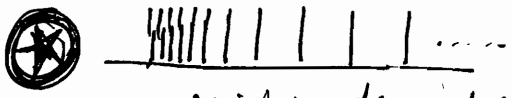
$\Rightarrow B' - B'' > 0$: Positive Quantity

$Q : m = J''$

$w = w_0 + (B' - B'')m + (B' - B'')$



Convergence towards lower wave number side.....



○ Violet degraded Parabola

✓ Vertex in P branch

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

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

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

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

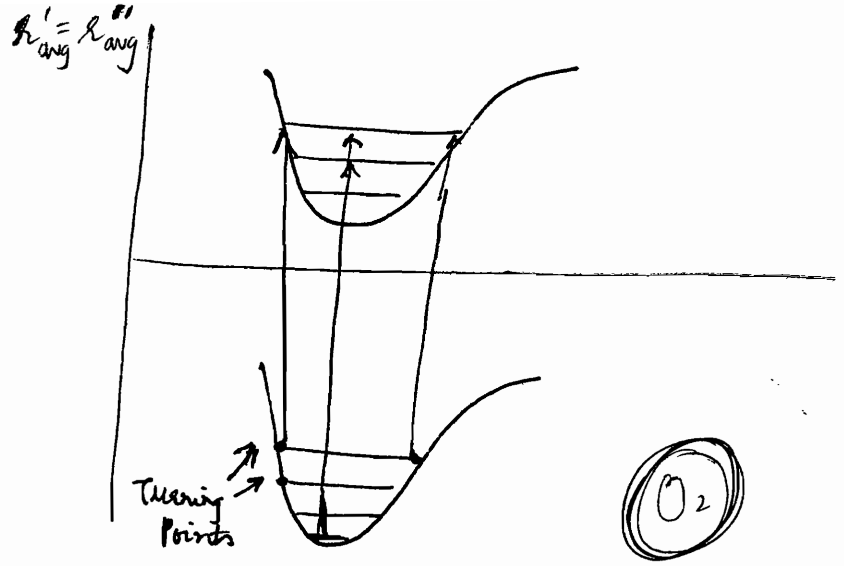
[Q branch] in (Symmetric Molecules)

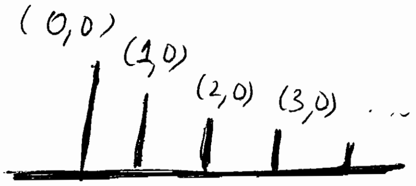
[Again $(B' - B'')$ can be negative or positive]

FRANK- CONDON PRINCIPLE

'Most favoured transitions' or 'Most Probable Transitions' in electronic spectra are given by this principle. <u>It is the secondary criteria. Primary criteria is the Population according to Maxwell Boltzmann Curve.</u>

✓ ① All transitions must be represented by vertical lines.

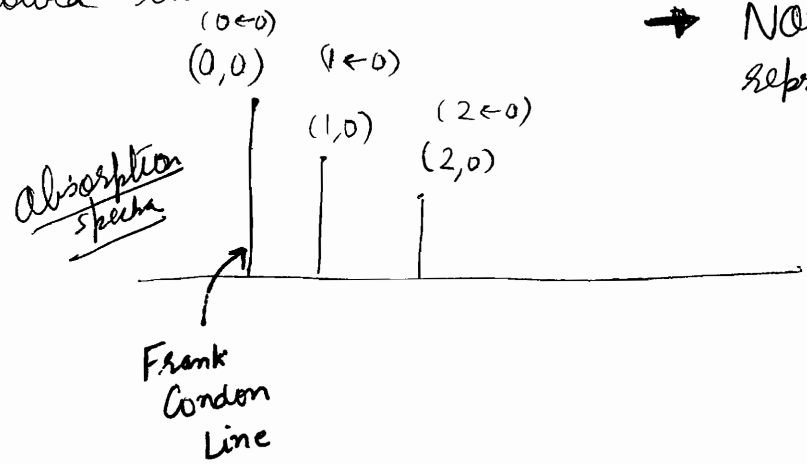




⇒ During transtions, internuclear distances are const. Electrons are so small and swift that in their time of transition, heavy nuclei remain at the same positions.

② For ground state transitions, transitions must occur from middle of level. Any other transitions occur from turning points $|\psi|^2$ is more at ends for higher state. ⇒ more prob. of transition.

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



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

x ← higher energy state

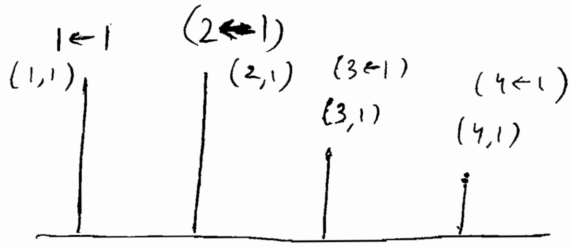
y ← lower energy state

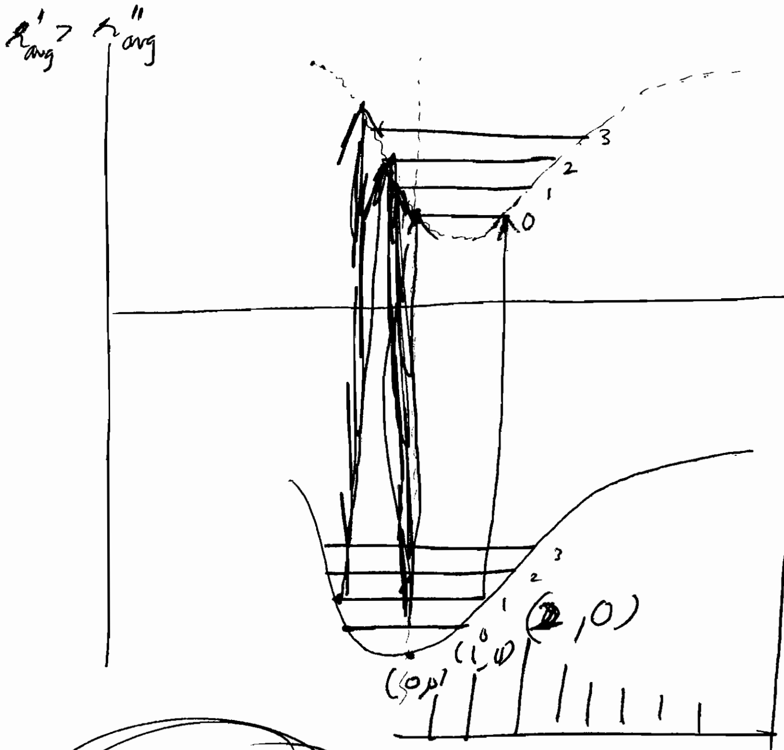
$(x \leftarrow y)$: Absorption spectra

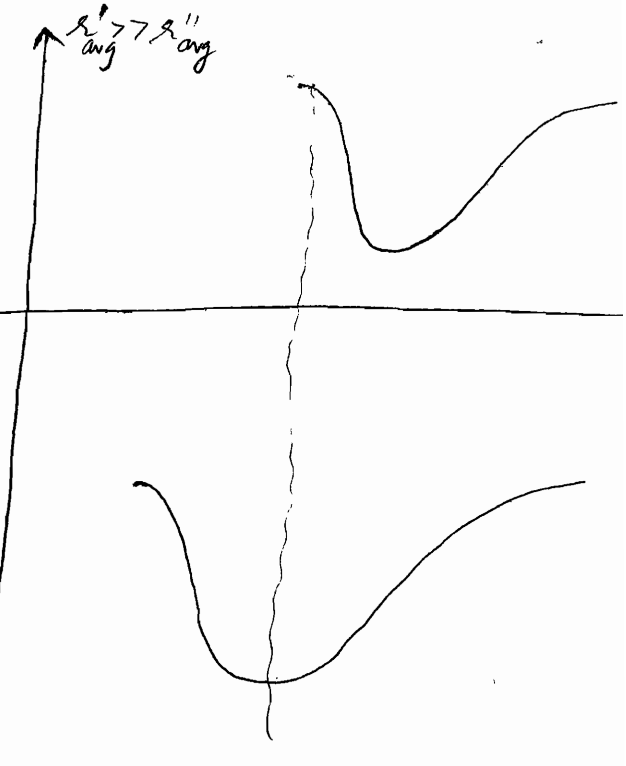
$(x \rightarrow y)$: emission spectra

<u>Vertical lines from turning point of $v''=1$ cut at $v'=1, 2$ respectively.</u>

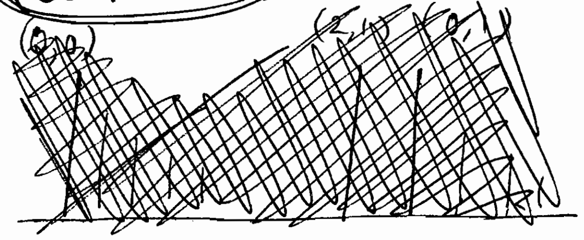
⇒ (1,1) & (2,1) have equal intensity !!



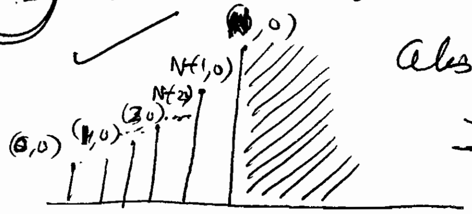




(CO Molecule)



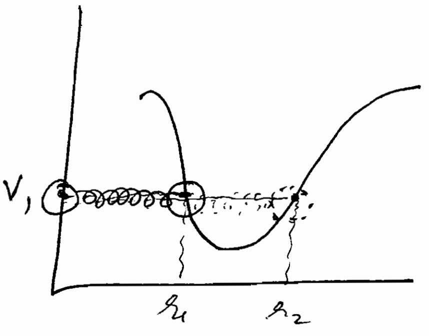
I_2 Molecule (very heavy)



Absorption spectra

Continuous due to dissociation limit has been crossed.

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



Bond length r_1 and r_2 have same Potential Energy.

→ Order of gap of spectral lines :-

≈ 20 cm^{-1} : rotational

≈ 1000 cm^{-1} : Vibrational

≈ 50,000 cm^{-1} : electronic

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

★ Same Δv, (v' = const., v'' = const) different ΔJ ⇒ Branch : which is a Band

$\Delta J = 1$ Branch R

$\Delta J = -1$ Branch P

while

Δv = const, (v' and v'' varying) ⇑ [this is also called a ~~sequence~~]

v' = const (v'' varying) ⇑ [v'' progression]

Or

v'' = const. (v' : varying) ⇑ [v' progression]

Progression which are Band systems

जो vary कर रहा है, उसका Progression

i.e. जो Progress कर रहा है !!

Molecular Physics (4)

28/02/12

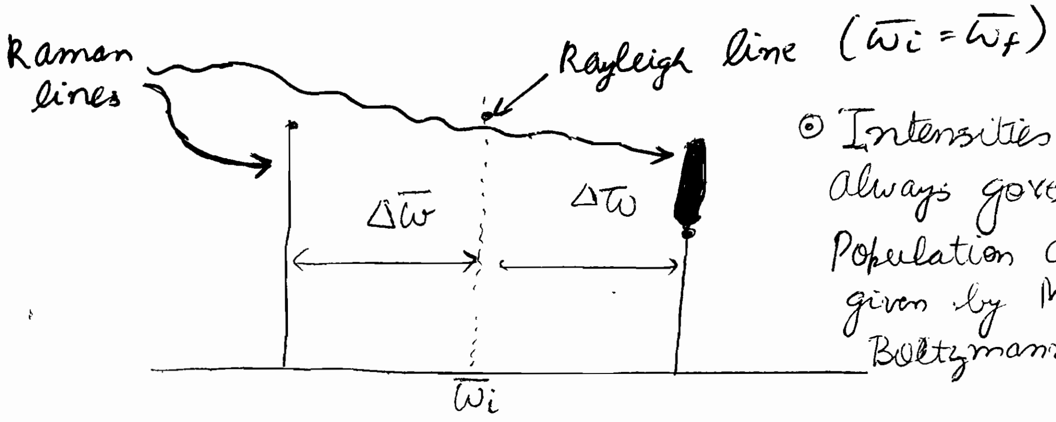
Raman Spectra

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]

$\nu_i \longrightarrow \text{Specimen} \longrightarrow \nu_f$

if ν_f comprises higher as well as lower freq. waves ⇒ Raman Scattering



⊙ Intensities are always governed by Population criteria given by Maxwell Boltzmann Distⁿ.

$\Delta\bar{\omega}$ 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 ⇒ Electron is removed as well as the photon comes out with reduced frequency.

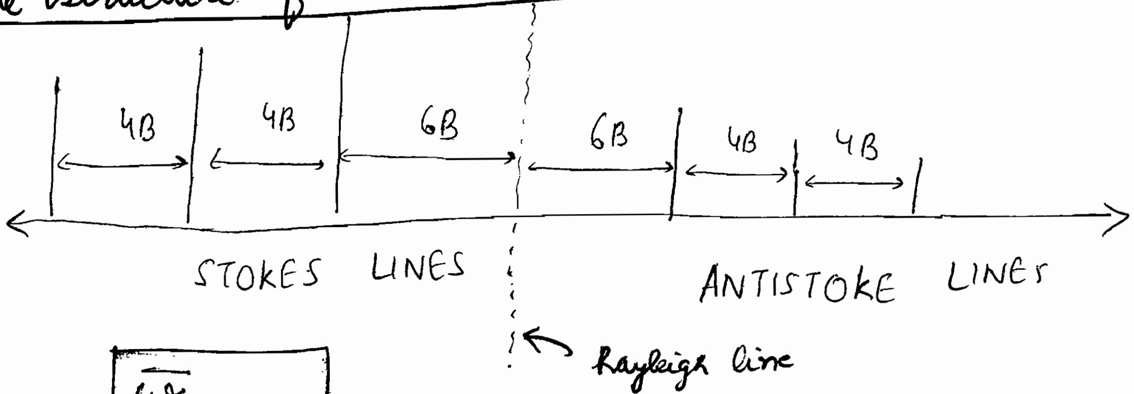
Its called Compton Effect.

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

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

<u>Also $\Delta\bar{\omega}$ lies in infrared region ⇒ vibrational energy levels.</u>

Fine Structure of Raman Spectra



$$\boxed{\bar{\omega}_{Raman} = \bar{\omega}_i \pm 4B\left(j+\frac{3}{2}\right) \qquad j=0,1,2,3,\ldots}$$

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 came, then it become possible to detect them. Hence, we call it <u>Laser Raman Spectroscopy</u>.

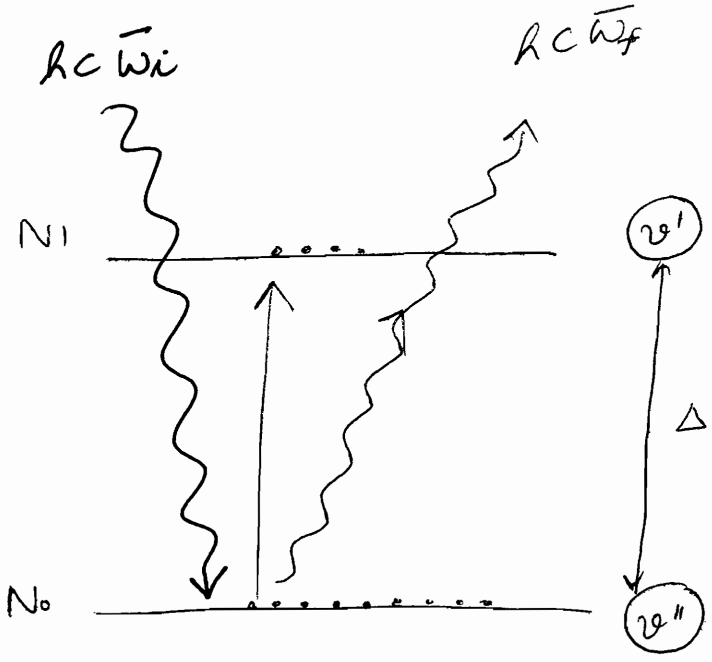
Quantum Mechanical Explanation

$\Delta v = \pm 1$ Vibrational Raman Spectra

$\Delta J = \pm 2$ Rotational Raman Spectra

For vibrational $\bar{\omega}_f = \bar{\omega}_i \pm [G(v+1) - G(v)]$

$$\Rightarrow \Delta\omega_{Raman} = \pm \bar{\omega}\left[v+\frac{3}{2} - v - \frac{1}{2}\right] = \pm\bar{\omega}$$



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

2 vibrational levels v' and v'' are shown.

Let $\Delta E = E(v') - E(v'') = \underline{hc\bar{\omega}}$

Suitable light is incident upon v'' i.e. $\bar{\omega}_i > \bar{\omega}$

If elastic collision, no energy transfer

$$hc\bar{\omega}_i + \cancel{E(v'')} = \cancel{E(v'')} + hc\bar{\omega}_f \quad : \text{Rayleigh Scattering}$$

$$\Rightarrow \bar{\omega}_i = \bar{\omega}_f$$

If inelastic collision

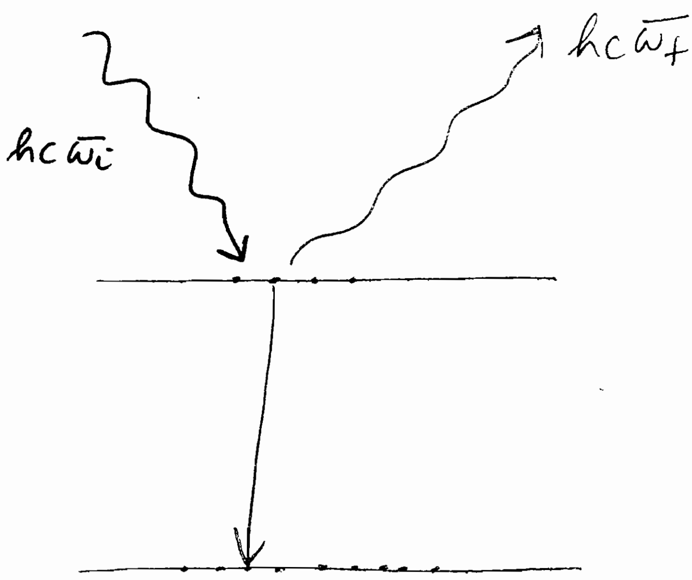
$$hc\bar{\omega}_i + E(v'') = E(v') + hc\bar{\omega}_f \quad : \boxed{\text{Stoke's line of Raman Scattering}}$$

$$\Rightarrow \boxed{\bar{\omega}_f = \omega_i + \underbrace{\left(\frac{E(v') - E(v'')}{hc}\right)}_{\text{Raman Shift } \Delta\omega_{raman}}}$$

: characteristic of molecule

✓ $\Big\{$ High intensity b'coz maximum population in ground state.
Incident & scattered light has nearly same energy.

$$hc\bar{\omega}_i + E(v') = E(v'') + hc\bar{\omega}_f$$



$$\Rightarrow \boxed{\bar{\omega}_f = \bar{\omega}_i + \underbrace{\left(\frac{E(v') - E(v'')}{hc}\right)}_{\Delta\omega_{Raman}}}$$: $\boxed{\text{Anti Stokes line}}$

lower intensity line due to lower population in excited level

→ Inelastic collision b/w photon & molecules is, therefore, responsible for Raman Effect.

⊙ Note that NO NEW PHOTON IS SCATTERED (compton) and NO PHOTON IS COMPLETELY (Photoelectric) ABSORBED.

Selection Rule for Fine Structure

$\Delta v = \pm 1$ [0 for Rayleigh]

$\Delta J = \cancel{0}, \pm 2$ [0 for Rayleight]

Selection rule is due to induced dipole moment. Hence occur in all molecules irrespective of possession of permanent dipole moment.

For vibrational Raman Spectrum,

$$\bar{\omega}_f = \bar{\omega}_i \pm [G(v+1) - G(v)]$$

or

$$\bar{\omega}_f = \bar{\omega}_i \pm \bar{\omega} \Rightarrow \boxed{\Delta\omega_{raman} = \bar{\omega}}$$

For fine structure, <u>or Rotational Raman Spectrum</u>,

$$\bar{\omega}_{raman} = \bar{\omega}_i \pm \left[F(J+2) - F(J)\right]$$

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

★ Note that we are not talking about fine lines within Coarse vibration lines. We are talking about only fine lines on both of Rayleigh line in far-IR end spectra.

$$\Rightarrow \bar{\omega}_{raman} = \bar{\omega}_i \pm B\left[(J+2)(J+3) - J(J+1)\right]$$

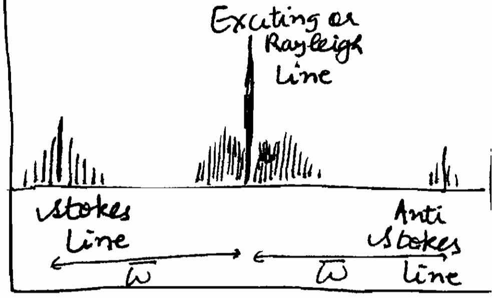
$$= \bar{\omega}_i \pm B\left[4J+6\right]$$

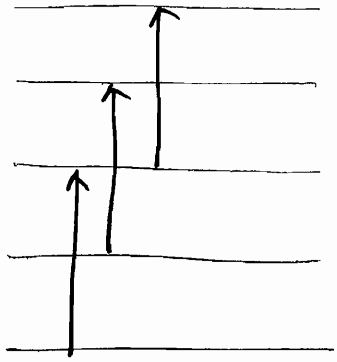
$$\boxed{\bar{\omega}_{raman} = \bar{\omega}_i \pm 4B\left(J + \frac{3}{2}\right)}$$

$$\Rightarrow \bar{\omega}_{raman} = \bar{\omega}_i \pm 6B, \ \bar{\omega}_i \pm 10B, \ \bar{\omega}_i \pm 14B, \ldots$$

From given lines, we can calculate $B \Rightarrow I_{cm} \Rightarrow$ & Bond length

∴ from above two analysis, Raman Spectra comes out to be :

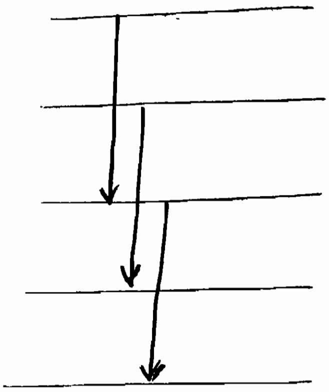




$\Delta J = +2$

"S Branch"

Stoké's lines



$\Delta J = -2$

Anti Stoké's lines

} Both are

★ Homonuclear diatomic molecules do not give vibrational-rotational spectra but give Raman Spectra.
Called Infrared Inactive but Raman Active.

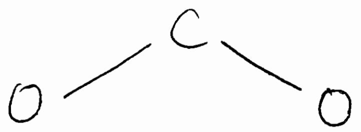
For CO_2 molecule

$O = C = O$

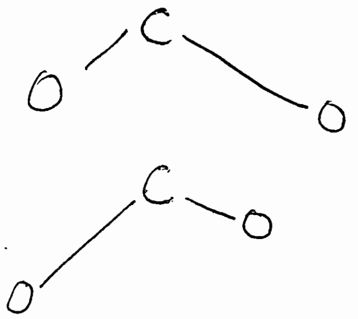
linear mode

Symmetric linear molecule.

Permanant Dipole Moment = 0
⇒ Only Raman Spectra



Bend Mode (Symmetric Or Assymmetric)



No Centre of symmetry
⇒ Dipole Moment
⇒ Infra-red Active ← due to vibration-rot. due to interaction of dipole moment and $\vec{E}$.
as well as
Raman Active ← due to inelastic collision

No Centre of Symmetry } ⇒ Both active

Centre of Symmetry } ⇒ Only Raman Active

Here apart from I_{CM}, r Bond-length, [redacted] type of symmetry is also known from spectra.

→ Mercury Arc was initial source of light. It had drawbacks:

① Its extended source of light ⇒ large quantity of sample is required, leading to wastage of precious materials.

② Some of the light of incident rays, due to extended source could enter spectrometer tube. It will mask weak raman lines.

③ If total energy i.e. (ΔE) between ν' and ν'' = $E_{h\nu}$ incident ⇒ whole incident photon is absorbed completely ⇒ Fluorescent Effect may be caused i.e. if excitation f matches with absorption f. Fluorescent will mask Raman's weak lines. [Since laser light is monochromatic & not of same f as Δv level]

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 grating can be used to record spectra. Also they have wide frequency range.

23 $\quad w_i = \dfrac{1}{514.5 \text{ nm}}$

24 $\quad$ Fine structure cannot be resolved otherwise

In addition, molecules like H_2, D_2, N_2.... the rotational raman lines are alternately weak and strong. In extreme case like O_2, every alternate line is missing. This phenomenon arises from symmetry properties of rotational levels of homonuclear molecules

28 $\quad \dfrac{h^2}{8\pi^2 I} = B = 1.43 \times 10^{-5}$

$$\gamma_0 = 8.4 \times 10^{12} \text{ Hz}$$

$$E(J) = \frac{J^2}{2I} = j(j+1)\frac{h^2}{8\pi^2 I}$$

$$E(v=1) - E(v=0) = h\gamma_0$$

Equating the ②, $\quad j(j+1) = \dfrac{6.62 \times 8.4 \times 100}{1.6 \times 1.43}$

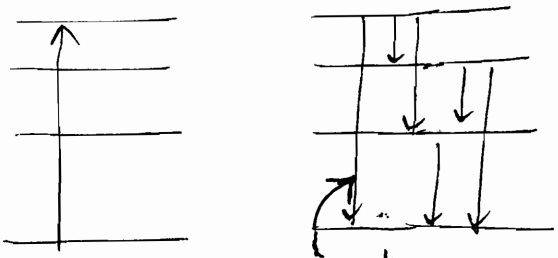
(★) Vibrational Raman Spectra agrees exactly with wave no. of main vibrational rotational spectra in near infra-red spectrum.

while Rotational Raman Spectra separation = 2 [separation of usual microwave spectrum]

(★) Induction or Polarization by incident light cause dipole moment in homonuclear molecules ⇒ rotational, vibrational level occur in them.

⊛ Luminiscence (चमक) < Flurosence / Phosphoroscence

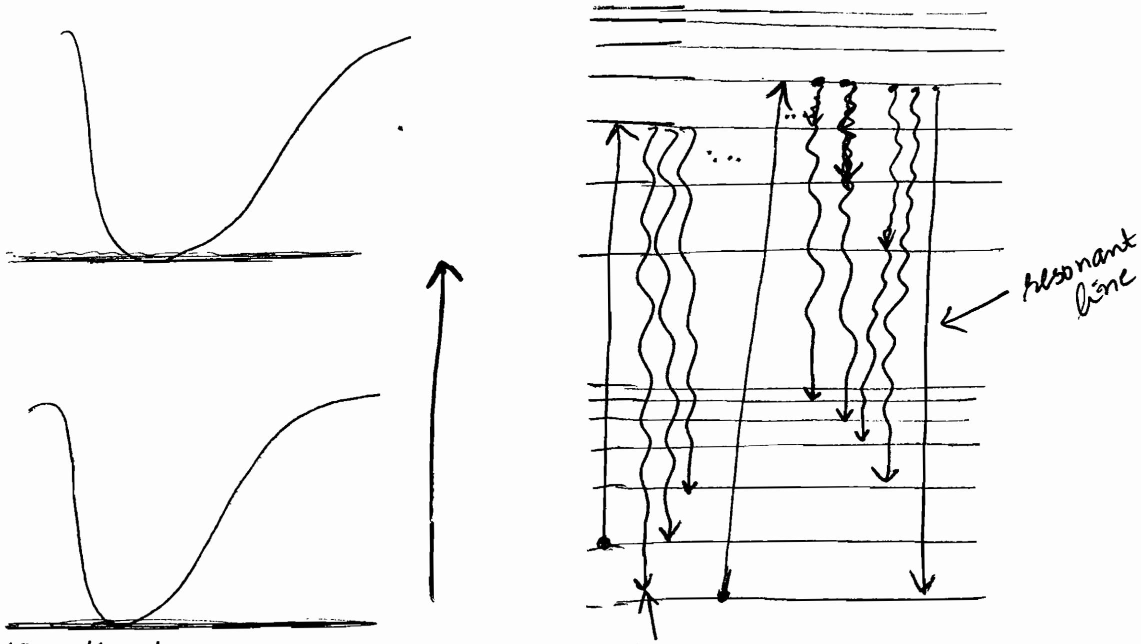
When a molecule is incident upon by a "suitable frequency" i.e. one of the absorption frequencies, molecule may be raised to any excited level (rot / vib / electronic).



→ this frequency is absorbed   → all these frequencies will be emitted

Now molecule has option to come down instantaneously. Its called : Fluroscence. The γ relased are less than incident γ.

In Phosphoroscence, energy is emitted even after source of excitation is removed. It is delayed emission of radiation.

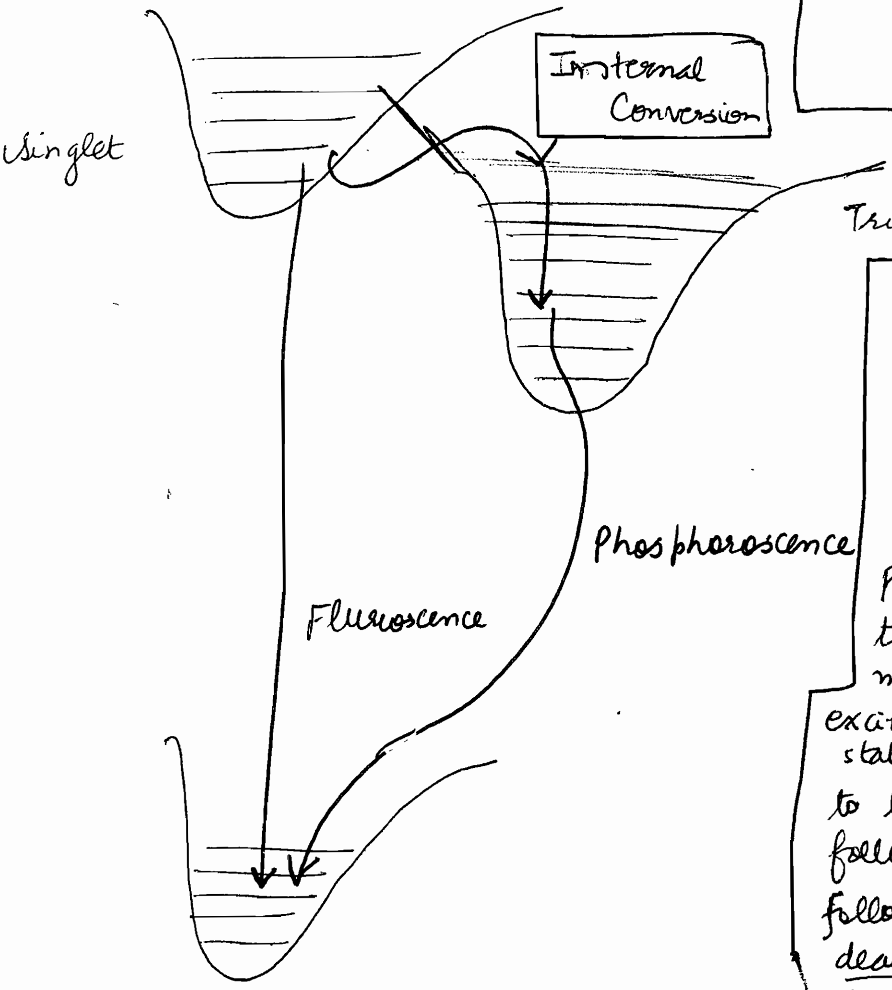


⊙ Intensity distⁿ of the bands will depend upon Frank Condon and Maxwell distⁿ.

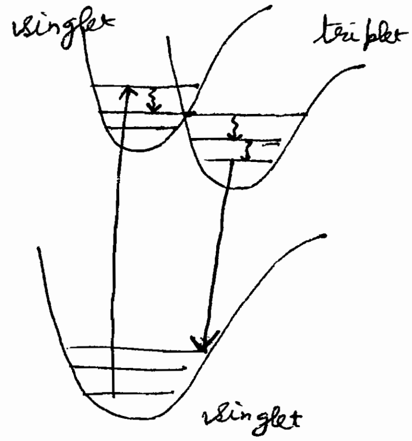
'I' photons that fall will interact with 'I' molecules. These 'I' molecules are raised to higher energy. Incident photon is absorbed.

All frequencies emitted are less than that of resonant line

<u>Singlet, $s = 0$ $r = 1$</u> <u>Triplet, $s = 1$ $r = 3$</u>



(*) Delayed emission caused 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 emissio

Remember selection rule, $\Delta s = 0$

$\sigma - \sigma$ transition : same multiplicity.

It has high Probability ⇒ shorter time.

(*)

Phosphoroscence occurs in violation of selection rule

⇒ low probability ⇒ longer time

⇒ delayed emission.

Molecular Physics (5)

29/02/2012

NMR and EPR/ESR

NMR and EPR are magnetic resonance techniques

↓ Nuclear Magnetic Resonance

↓ Electron Paramagnetic Resonance (EPR) or Electron spin Resonance (ESR)

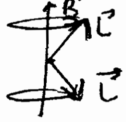
✓ Resonance is matching of frequencies of source and system.

✓ Precession frequency of Nucleus is [redacted] matched with f of oscillating B.

Angular Momentum precesses about field. Energy levels are separated by ΔE.

$+\mu . B$

$-\mu . B$



Remember, we mentioned it in spectroscopy

$\Delta E_{nucleus}$: very small $\approx 10^{-8}$ eV

$h\nu = 10^{-8} \times 10^{-19}$

$\nu \approx 10^{6}$

$\lambda = \frac{hc}{E}$ in Radio Frequency Region

$\Delta E_{electron \; due \; to \; spin} \simeq 10^{-3}$ eV : Microwave Region

* Same technique if used in

RF: NMR

μW: ESR

NMR: nuclear magnetic moment

ESR: e⁻ spin [redacted] Resonance

✓ Its also called EPR because all paramagnetic salts have spin ≠ 0, i.e. have unpaired e^- ⇒ Spin Angular Momentum ≠ 0 ⇒ Larmor Precession ⇒ $\Delta E_{Electronic Spin}$

We know,

$$\vec{\mu}_l = -\frac{e}{2m} g_l \vec{L} \qquad g_l = 1$$

$$\vec{\mu}_s = -\frac{e}{2m} g_s \vec{S} \qquad g_s = 2$$

$$\vec{\mu}_J = -\frac{e}{2m} g_J \vec{J} \qquad g_J = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

⊙ $\vec{\mu}_J$ is component of $\vec{\mu}$ along $\vec{J}$. We are interested in $\vec{\mu}_J$ only as other component averages out to zero.

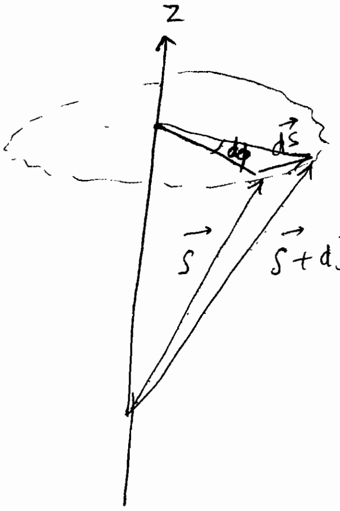
Note that prerequisite of ESR is $S \neq 0$

Atom with unpaired e^- i.e. $S \neq 0$ is kept in steady magnetic field (const $\vec{B_0}$).

$$\Rightarrow \quad \vec{\tau} = \vec{\mu_s} \times \vec{B_0}$$

$\Rightarrow$ $\vec{S}$ will rotate about direction of $\vec{B_0}$ $\Rightarrow$ e^- will precess

$$\Rightarrow \quad \vec{\tau} = \frac{d\vec{S}}{dt} \quad \Rightarrow \quad d\vec{S} \perp \vec{S} \quad \Rightarrow \quad \text{Precession}$$



$$\boxed{\omega_p = \left(\frac{\mu_s B_0}{S}\right)}$$

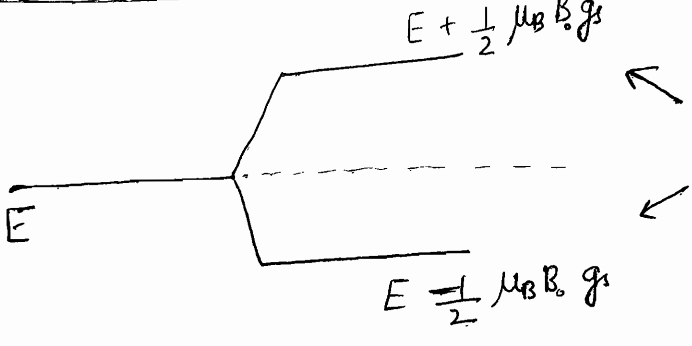
$$\Rightarrow \boxed{\omega_p = \frac{e}{2m_e} g_s B_0}$$

✓ Precisely same derivation for Nucleus Magnetic Moment

Now $\Delta E_{\text{electron spin}}$ will occur due to Potential of τ and Magnetic field.

$$E = \omega_p S_z = \frac{e}{2m_e} g_s B_0 m_s \hbar = \mu_B B_0 g_s m_s$$

For e^- : $m_s = \pm\frac{1}{2}$ $\Rightarrow$ $\boxed{E = \pm\left(\frac{\mu_B B_0 g_s}{2}\right)}$



2 spin states for an electron

$$\underline{\underline{\Delta E = \mu_B B_0 g_s = h\nu_0}}$$ ✓ This ν_0 has no role in NMR/ESR

→ Hence by absorbing frequency ν_0 or emitting frequency ν_0, e⁻ can flip between its spin states.

I am aplying 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 created by 1st field.

Now I apply another oscillating field,

$$\vec{B}_1 = B_1 \sin(2\pi\nu t)$$

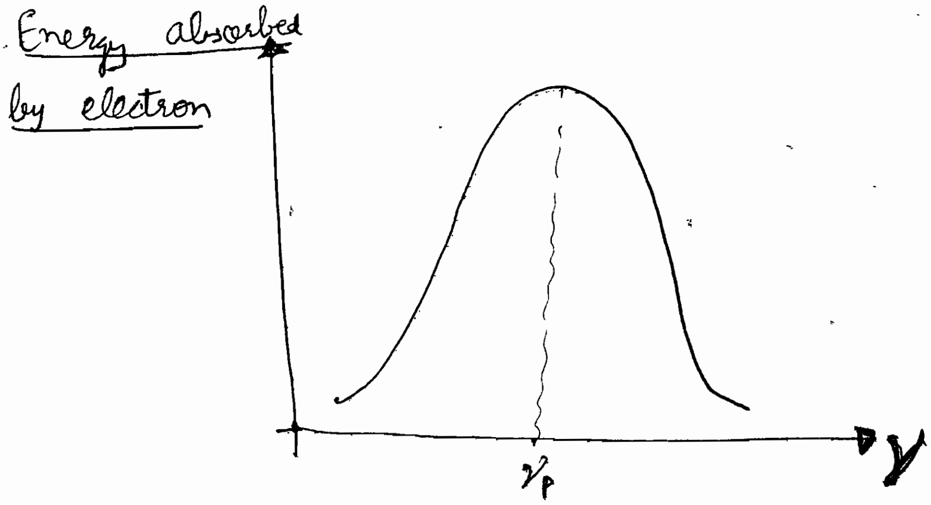
from klystron Oscillator.

This varying field will cause magnetic resonance

When ν of $\vec{B}_1$ becomes equal to $\nu_{\text{Precession}}$, then maximum absorption of energy is Observed.

✓ $\boxed{\nu_0 = \nu_{\text{precession}}}$

$= \nu_2$ for resonance



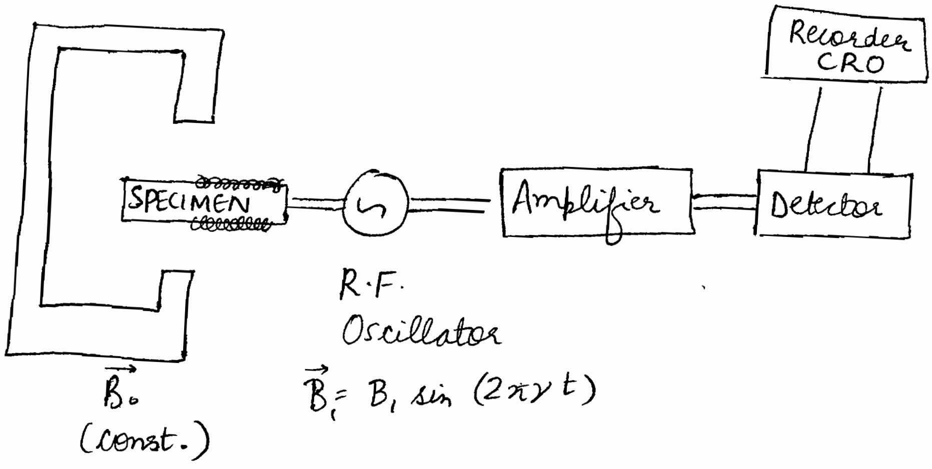
If @ $\nu = \nu_p$, I get maximum energy absorption

$$\Rightarrow \boxed{\nu_p = \frac{e}{4\pi m_e} g_s B_{\text{fixed}}}$$ ✓

$$\Rightarrow \boxed{g_s \text{ is obtained}}$$

ν_{electron} will lie in MicroWave Region ...

$\Delta E \simeq 10^{-3}$ eV



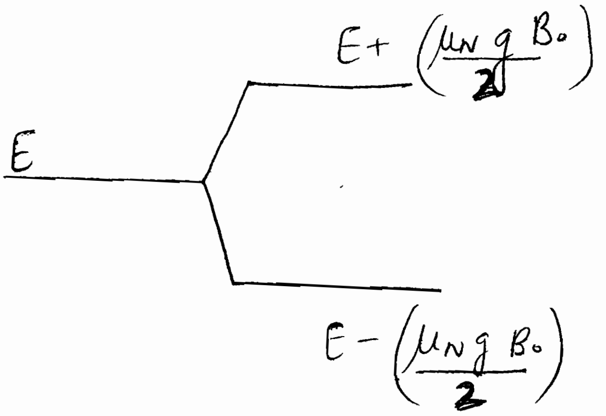
Typical schematic diagram of NMR spectroscopy

(For EPR, change the oscillator to klystron Oscillation)

Ang. Momentum $|\vec{I}| = \sqrt{I(I+1)}\,\hbar$

$$\boxed{\vec{\mu}_{\text{nucleus}} = \frac{e}{2m_p}\, g\, \vec{I}}$$

$$\omega_p = \frac{e}{2m_p}\, g B_0$$



$$\Delta E = \mu_p I_z$$

$$= \underset{\substack{\uparrow \\ \text{Nuclear Bohr Magneton}}}{\left(\frac{e\hbar}{2m_p}\right)} g B_0 m_I$$

$$= \underline{\mu_N g B_0 m_I}$$

which can be $\pm\frac{1}{2}\mu_N g B_0$

(if only single proton)

Similarly,

NMR frequency $\nu = \nu_p$

$$= \frac{e}{4\pi m_p} g B_0$$

⊙ In Chemical analysis and Biological Analysis, NMR and EPR are greatly used as low Energy levels of μwave 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.

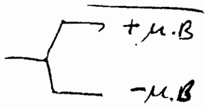
13) $\vec{S} \Rightarrow \vec{\mu_S} \Rightarrow \vec{\tau}$ in $B \Rightarrow \tau \perp S \Rightarrow dS \perp S$

$\Rightarrow$ Precession

22) $$\boxed{\nu_p = \frac{e}{4\pi m_p} \cdot g_p \cdot B_0}$$

$$= \frac{1.6 \times 10^{-19}}{4\pi \times 1.6 \times 10^{-24}} \times g_p \times 1.5$$

✪ $$\nu_p = \frac{\Delta E}{h}$$



$$= \left(\frac{2\mu \cdot B}{h}\right)$$

$$= 2\frac{e\hbar}{2m}\frac{g_I \cdot m_I B}{h}$$

$$= \boxed{\frac{e}{4\pi m_p} g B}$$

✓ अरे भाई $m_{top} - m_{bottom}$ तो 1 ही होगा हमेशा !!

✪ $$\mu_p = \frac{e}{2m} g \vec{I}$$

$$(\mu_p)_z = \frac{e}{2m_p} g I_z = \frac{e\hbar}{2m_p} g m_I$$

$$2.793\,\mu_N = \mu_N\, g\, m_I$$

$m_I = \left(\frac{1}{2}\right)$ (No value of $m_I = \frac{-1}{2}$)

$\Rightarrow g = 2 \times 2.793 = \underline{5.586}$

In water NMR occurs due to Proton

$g_{proton} = 5.586$ (Hence $\mu_p = \frac{e}{2m} \times 5.586 \times$

$= \underline{\underline{\mu_N . 2.793}}$

Chemical shift

$\Rightarrow$ due to shielding : $B = B(1-\sigma)$

Magnetic field encountered by Bare nucleus due to shielding effect of outer electrons

$$\Rightarrow \quad \boxed{\gamma_p = \frac{e}{4\pi m_p} g_p \; B_0(1-\sigma)}$$

We take 2 nucleus A and B

$$B_A = B_0(1-\sigma_A)$$
$$B_B = B_0(1-\sigma_B)$$

B_0 : applied

B_A, B_B : fields at which resonance was observed.

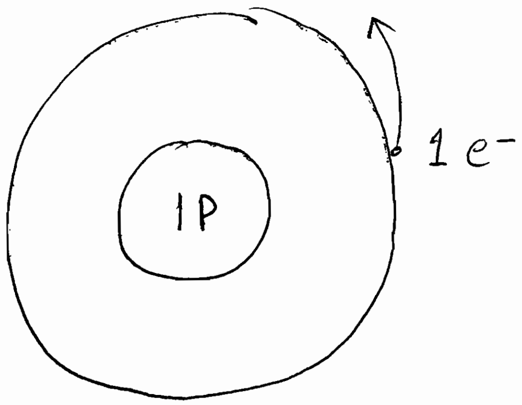
$$\Rightarrow \quad B_A - B_B = -B_0(\sigma_A - \sigma_B)$$

$$\Rightarrow \quad (\sigma_A - \sigma_B) = -\left(\frac{B_A - B_B}{B_0}\right)$$

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.



Neutral H atom

Till now, we have neglected motion of Nucleus

If I use ultra-high resolution spectroscope, I see **hyperfine lines** further than what explained by

$$\left[H = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r} + \alpha(\vec{l}\cdot\vec{s})\right] + \left[\text{lamb shift}\right]$$

It is due to motion of nucleus.

$\vec{J} = \vec{L} + \vec{S}$ ..... Fine Structure

$\vec{I} = \sqrt{I(I+1)}\,\hbar$ ..... Hyperfine structure

$$\Rightarrow \boxed{\vec{F} = \vec{L} + \vec{S} + \vec{I}}$$

$$= (\vec{J} + \vec{I})$$

Total Ang. Momentum of Atom

$$\Rightarrow |J - I| < F < |J + I|$$

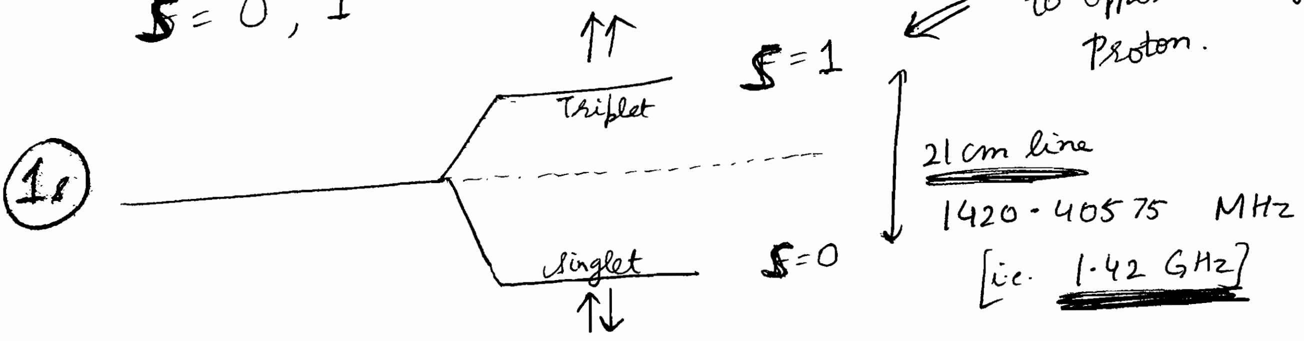
$\Delta F = 0, \pm 1$

Now,
For 1s, 2s : $l = 0$
[closest states]

Hyperfine Structure of Neutral Hydrogen Atom

$\Rightarrow \vec{S} = \vec{S}_e + \vec{S}_p$
(electron) (proton)

$S = 0, 1$



Note that $S = 1$ is higher level due to opposite charge of Proton.

Now selection rule : $\Delta S = 0$

It lies in MICROWAVE Frequency region

Transition Probability $= 2.9 \times 10^{-15}$ per second

$\Rightarrow$ Transition Time $\simeq 10^{14}$ second $\simeq$ 10^7 years

$\boxed{10^7 \text{ seconds} \simeq 1 \text{ year}}$

Hence, importance only in astronomy where such Time Periods are important.

Due to interatomic collisions, Transition time is reduced by a little amount.

- It can provide clear picture of matter power spectrum in period after recombination, by mapping red-shifted 21 cm radiation
- It can provide picture of how universe was re ionized.

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 (very low), this radiation can penetrate (low scattering) the dust clouds 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 been 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 face that both the e- and proton have $(\frac{1}{2})$ spin, so there are 2 possible states, spin parallel (slightly high energy) and spin antiparallel
$\Downarrow$
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 W_e and B ⇒ 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.

eg. Molecules of CO_2 and CS_2 are found to have 2 strong IR bands that are not observed in Raman Spectra

⇒ Centre of Symmetry ⇒ $O=C=O$ $S=C=S$

Molecules H_2O show 3 IR bands that coincide with Raman spectra ⇒

(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 characterize 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.