

ELECTRON SPIN RESONANCE SPECTROSCOPY (ESR)

- ↳ ESR-spectroscopy is an absorption spectroscopy & it involves the absorption of radiation in the microwave region ($10^4 - 10^6 \text{ MHz}$).
- ↳ It is a method for observing the behavior of the electrons within a suitable molecule & for analyzing various phenomena by identifying the electron environment.
- ↳ It is a branch of spectroscopy in which radiation having frequency in microwave region is absorbed by paramagnetic substances, i.e., substances having one or more unpaired electrons to induce transition between magnetic energy levels of electron with unpaired spin.
- ↳ Since, the ESR-active substances are paramagnetic and hence ESR-spectroscopy is also known as electron paramagnetic resonance (EPR) spectroscopy or electron magnetic resonance spectroscopy.
- ↳ The absorption of microwave radiation takes place under the influence of an applied magnetic field.

↳ ESR-spectroscopy is a powerful technique used to study —

i) Free radicals —

eg — Atoms, molecules or ions containing one or more unpaired electrons in solid, liquid or gaseous state/phase

ii) Transition and actinide ions —

(These may have upto five or seven unpaired electrons)

iii) Various point defects in solids.

iv) Systems with more than one unpaired electrons

eg — Triplet state system, biradicals, multiradicals etc.

v) System with conducting electron

eg — Semiconductors and metals.

↳ The basic principle of ESR-spectroscopy is closely related to NMR-spectroscopy but the application and instrumentation are quite different.

Types of substances with unpaired electron —

↳ ESR is useful for paramagnetic substances.

↳ Substances with unpaired electrons are mainly of two types —

↳ Stable paramagnetic substances —

These include stable substances which can be studied very easily by ESR. The examples are simple molecules like NO , O_2 , NO_2 and ions of rare earth elements, and of transition metals and their complexes.

↳ Unstable paramagnetic substances —

This can be produced either as intermediates in chemical reactions or by ~~irradiation~~ irradiation of stable molecules with a beam of nuclear particles or with ultraviolet or X-ray radiation, and the substances produced are also called free radicals or radical ions.

This can be studied by ESR provided the lifetime of such radicals are greater than 10^{-6} second. If the lifetimes are less than 10^{-6} second, then they should be produced at low temperature in solid state called as matrix technique, because this increase their lifetime.

Some examples of ESR-active molecules —

| ESR-active | ESR-inactive |
|--|---|
| $\text{Cu}^{2+} (d^9, 1 \text{ unpaired } e^-)$ | $\text{Cu}^+ (d^{10}, \text{ No unpaired } e^-)$ |
| $\text{Ti}^{3+} (d^1, 1 \text{ " } e^-)$ | $\text{Ti}^{4+} (d^0, \text{ " " "})$ |
| $\text{Mn}^{2+} (d^5, 5 \text{ " } e^-)$ | $\text{Zn}^{2+} (d^{10}, \text{ " " "})$ |
| $\text{H}, \text{O}_2, \text{N}_2, \text{ triplet state}$ | singlet state |
| $\text{Ni}^{2+}, \text{Fe}^{3+}, \text{NO}_2, \text{CO}_3^{2-} \text{ etc.}$ | $\text{H}_2, \text{Na}^+, \text{Cl}^- \text{ etc.}$ |
| (paramagnetic in nature) | (diamagnetic in nature) |

Theory:—

↳ The principle of ESR is similar to NMR except that electron spin is involved in ESR instead of nuclear spin.

↳ The free electron or unpaired electron has a spin ($s = \frac{1}{2}$) and thus spin has an associated magnetic moment (μ_e).

↳ Due to its charge & spin, electron acts as tiny bar magnet & interact with an external magnetic field.

↳ Spin number of electron is, $s = \frac{1}{2}$ and it has two magnetic energy levels or spin angular

momentum quantum numbers values, $m_s = \pm \frac{1}{2}$.

↳ In the absence of a magnetic field, the two values of m_s i.e., $+\frac{1}{2}$ and $-\frac{1}{2}$ will give rise to a doubly degenerate spin energy states.

↳ When a magnetic field is applied, this degeneracy disappears and these two states split into two non-degenerate spin energy states.

↳ The lower energy state corresponds to $m_s = -\frac{1}{2}$ and higher to $m_s = +\frac{1}{2}$.

↳ The low energy state (more stable) has the spin magnetic moment aligned with the applied magnetic and on the other hand, the high energy state (less stable) has its spin magnetic moment aligned against the applied field.

↳ The magnetic moment of electron is thousand times greater than that proton and is given by -

$$\mu_e = -g\beta_s, \quad (\beta = \text{For electron} = 9.273 \times 10^{-24} \text{ JT}^{-1})$$

↳ The -ve sign arises because of negative charge on electron.

↳ The value of μ_e directly proportional to e/m , where, $e = \text{charge of electron}$
 $m = \text{mass of electron}$

$\beta =$ Bohr magneton, $\left(\frac{eh}{4\pi mc}\right)$

$g =$ Spectroscopic splitting factor / g -factor
/ Lande splitting factor.

↳ In the presence of an applied magnetic field (H_0) —

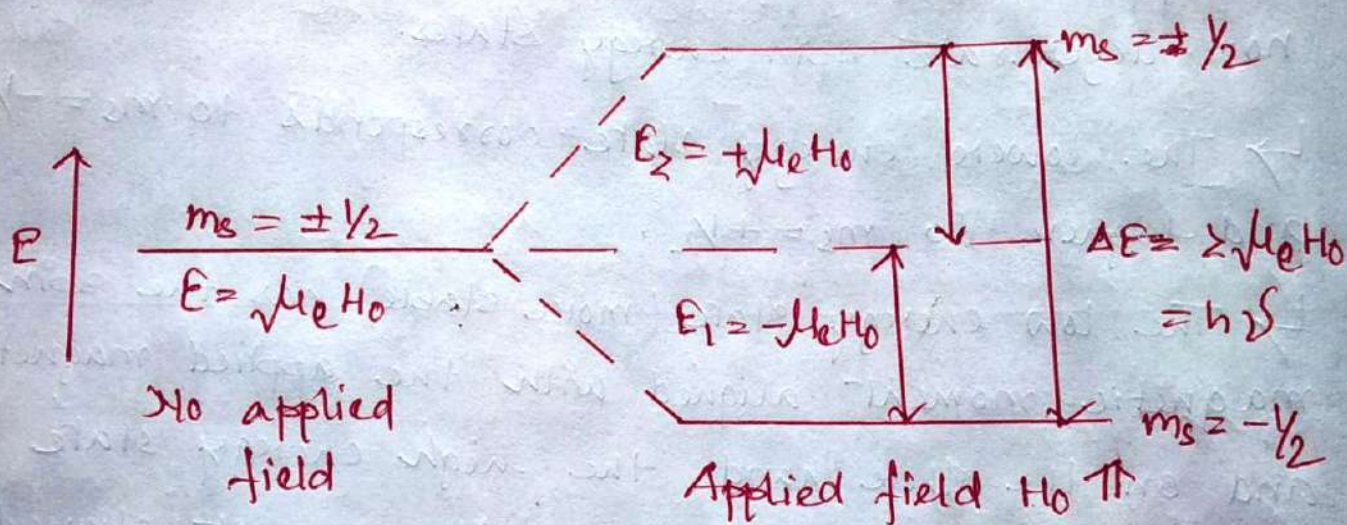


fig 1 — Energy states of an unpaired e^- in an applied magnetic field, H_0 .

↳ In the presence of an applied magnetic field H_0 , the two states will possess energies that are split up from the original state with no applied magnetic field by an amount $-\mu_e H_0$ and $+\mu_e H_0$ for the low energy and high energy states respectively.

$$E = \sqrt{\mu_e H_0} \quad (\text{when, } H_0 = 0)$$

Therefore, in the presence of H_0 —
 $E_1 = -\mu_e H_0$ and $E_2 = +\mu_e H_0$

If, ΔE is the energy difference between these two states —

$$\begin{aligned}\Delta E &= E_2 - E_1 \\ &= \sqrt{\mu_B H_0} - (-\sqrt{\mu_B H_0}) \\ &= 2\sqrt{\mu_B H_0}\end{aligned}$$

Since, in ESR, a transition between the two different electron spin energy states takes place, by the absorption of a quantum of radiation of an appropriate frequency in the microwave region i.e., $\Delta E = h\nu$

$$\text{Therefore, } \boxed{\Delta E = 2\sqrt{\mu_B H_0} = h\nu}$$

Again, $\Delta E = g\beta_B H_0$

$$\therefore \boxed{\Delta E = g\beta_B H_0 = h\nu}$$

Where, $\beta_B = \frac{eh}{4\pi me}$, for e^- , $= 9.273 \times 10^{-24} \text{ JT}^{-1}$
} Bohr magneton

g = Lande splitting factor.

g -factor

$$\boxed{g = \frac{\Delta E}{\beta_B H_0}} \quad \text{OR}$$

$$\boxed{g = \frac{h\nu}{\beta_B H_0}}$$

↳ g value depends on —

i) Orientation of the molecule containing unpaired electron with respect to the applied field.

ii) Physical state of the sample.

↳ It is also known as spectroscopic splitting factor.

↳ For free e^- , $g \approx 2.0023$

Instrumentation —

↳ The major components are —

1) Source —

Klystron tube → It acts as a source of microwave radiation. Microwave radiation is typically produced and amplified by Klystron tube, which is capable of tuning waves and to precise frequency, amplitude and phase. The microwaves are then channeled into resonant cavity by using either waveguide or co-axial tube.

2) Attenuator —

It is used to adjust the level of microwave power incident upon the sample.

3) Waveguide —

It is used to convey the microwave radiations to the sample cavity.

4) Sample cavity—

It is constructed in such a way to maximize the applied magnetic field along sample direction. Most ESR-spectrometers have dual sample cavity, one is for sample and other is for standard material.

5) Electromagnets—

ESR-spectrum is recorded by slowly varying the magnetic field through the resonance condition by sweeping the current supplied to magnet by power supply.

6) Modulation coils—

The variation of magnetic field is produced by supplying a signal to modulation coil oriented with respect to samples.

7) Crystal detector—

The most commonly used detector is a semi-conducting silicon-tungsten crystal detector which acts as microwave rectifier and converts the microwave power into a direct current output.

8) Phase sensitive detector/Auto amplifier—

This amplified signal that contains a lot

of noise.

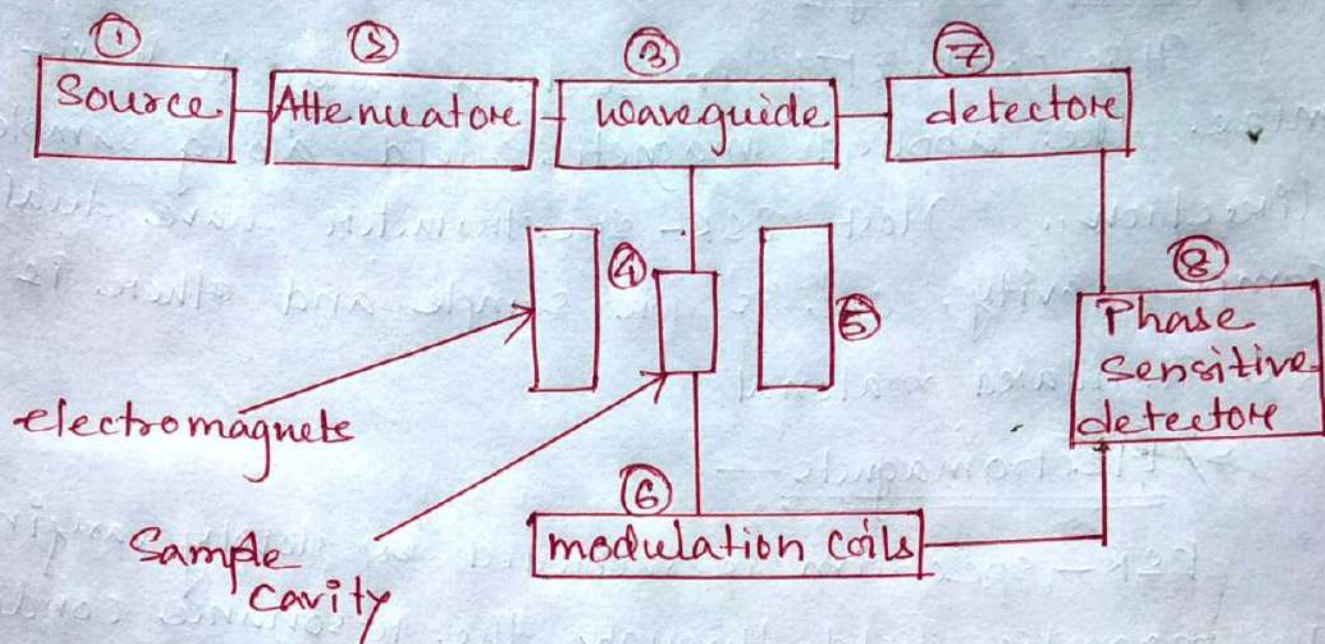


Fig Block diagram of ESR spectrometer

Presentation of spectra

↳ Earlier ESR-spectrum used to be recorded as an absorption intensity against magnetic field. This gives a broad absorption band and has no fine structure. The major disadvantage of the broad signal of ESR-spectrum is that these are more difficult to observe and measure than sharp signals.

↳ For this reason, ESR-spectrum is always obtained as the first derivative of absorption intensity (dI/dH , i.e., slope) is plotted against the magnetic field. This type of plot is more accurate. Also known as dispersion ESR-spectrum

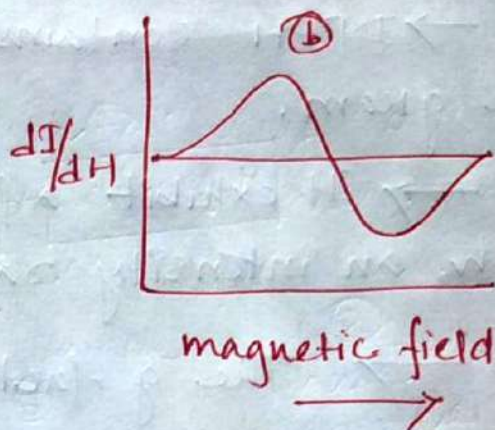
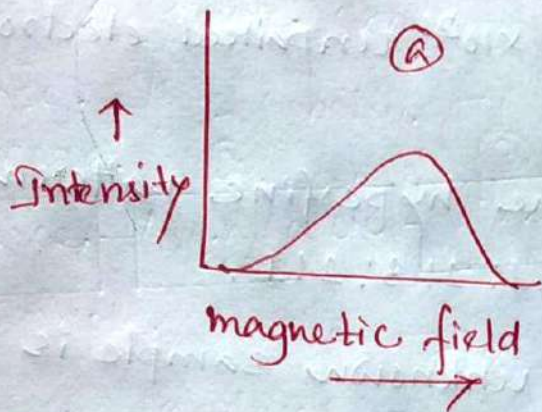
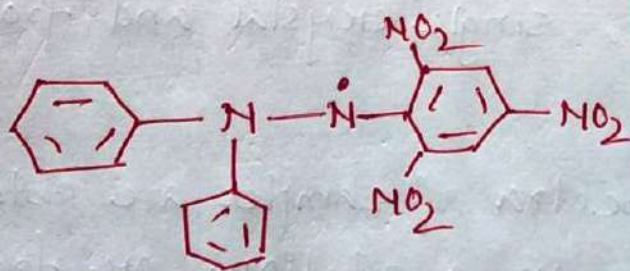


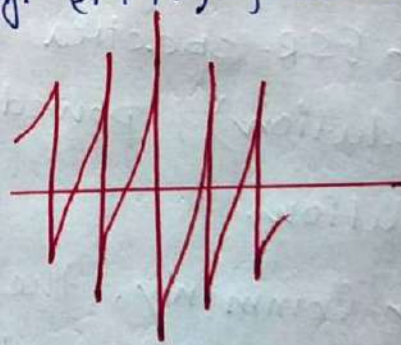
Fig:- (A) An absorption ESR-spectrum and (B) A first derivative or dispersion ESR-spectrum.

↳ The total area covered by either the absorption or derivative curve is proportional to the number of unpaired electrons in unknown sample. Then it compares with standard material having known number of unpaired electrons.

↳ The standard material for ESR-spectroscopy is —
1,1'-diphenyl-2-picrylhydrazyl (DPPH) free radical.



DPPH



1:2:3:2:1

Fig:- Dispersion ESR-spectrum of DPPH

→ DPPH is chemically stable having splitting factor, $g = 2.0036$

→ DPPH contains 1.53×10^{21} unpaired electrons per gram.

→ It exhibits a five line hyperfine pattern with an intensity ratio of 1:2:3:2:1.

→ The g factor of unknown sample is given by —

$$g = g_{\text{ref}} \left(1 - \frac{\Delta H_0}{H} \right)$$

where, $g_{\text{ref}} = 2.0036$, (g-factor of reference)
→ for DPPH
 $\Delta H_0 =$ field separation

$H =$ the resonance frequency.

* (ΔH_0 is +ve, if the unknown sample has its center at a higher field than the reference)

Sampling Procedure —

↳ ESR-spectra can be obtained for gas, liquid (solution), powder, single crystal and frozen solution.

↳ Commonly, the spectra of samples are obtained at room temperature in a solution or frozen solution.

↳ In most cases, water, alcohol and other solvents of high dielectric constant are not suitable for

ESR-studies, since they strongly absorb the microwave power.

↳ However, when there is no alternative to of solvents with high dielectric constant, then these solvents are used only if the sample has strong absorbance and it is contained in a very narrow sample cavity.

↳ If the concentration of paramagnetic species is very high, then broadening of spectral lines may occur.

↳ A quartz sample tube is preferable because glass absorb more of microwave radiation and also exhibit ESR-signal.

↳ It is necessary to remove oxygen from the solvent, otherwise it can lead to broadening of resonance.

Multiplet structures in ESR (Hyperfine Splitting) —

↳ Hyperfine structure results from Hyperfine coupling.

↳ Interaction between electron spin and nuclear spin is known as Hyperfine coupling.

↳ When the unpaired electronic spin interacts with neighboring nucleate spin, then the splitting of

each electron spin states occurs and this splitting is known as hyperfine splitting. Therefore, ESR-signals split into multiplets which are called hyperfine structures.

↳ When an unpaired electronic spin couples with a nucleus with spin I , the absorption signal of the electron is split into a multiplet with $(2I+1)$ lines of equal intensity.

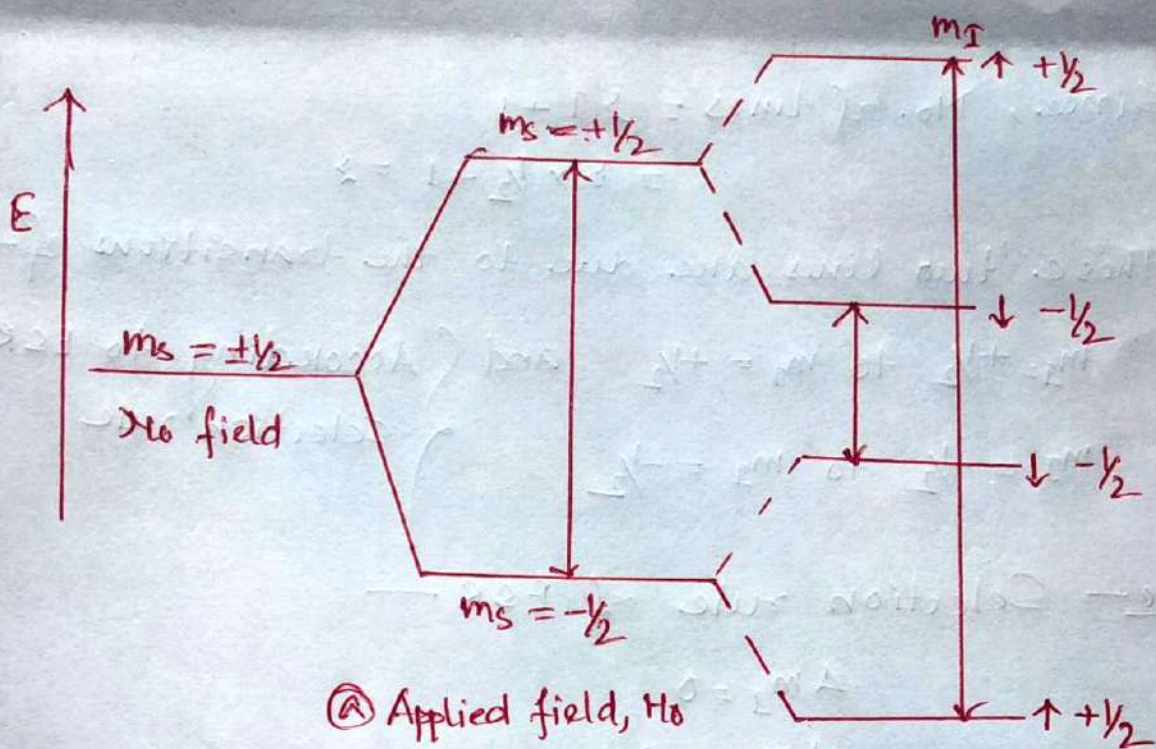
↳ When the absorption signal of an unpaired electron is split by 'n' equivalent nuclei with equal spin ' I ', the number of lines is given by $(2nI+1)$.

↳ Similarly, if the splitting is caused by both, a set of 'n' equivalent nuclei with spin ' I_n ' & a set of 'm' equivalent nuclei with spin ' I_m ', the number of lines is given by — $(2nI_n+1)(2mI_m+1)$, and so on.

ESR of H-atom —

↳ Hydrogen atom has one electron and one proton.

↳ The unpaired electron ($m_s = \pm 1/2$) interacts with nuclear spin ($I = 1/2$), and m_I of hydrogen is $m_I = \pm 1/2$



Ⓐ Applied field, H_0



Ⓑ Effect of applied field and nuclear spins of protons

fig: The splitting of electron spin energy levels of hydrogen atom. Ⓐ On application of magnetic field, Ⓑ Due to effect of nuclear spin on these levels.

↳ The two energy levels of the electron in hydrogen atom is split into two energy levels by the interaction with the nuclear spins of proton, $m_I = \pm 1/2$

where, $m_I =$ nuclear spin angular momentum quantum number.

This corresponds to four different energy levels and ESR-spectrum of hydrogen atom consists of two peaks of equal intensity.

Since, No. of lines = $2I + 1$
 $= 2 \times \frac{1}{2} + 1 = 2$

These two lines are due to the transitions of —

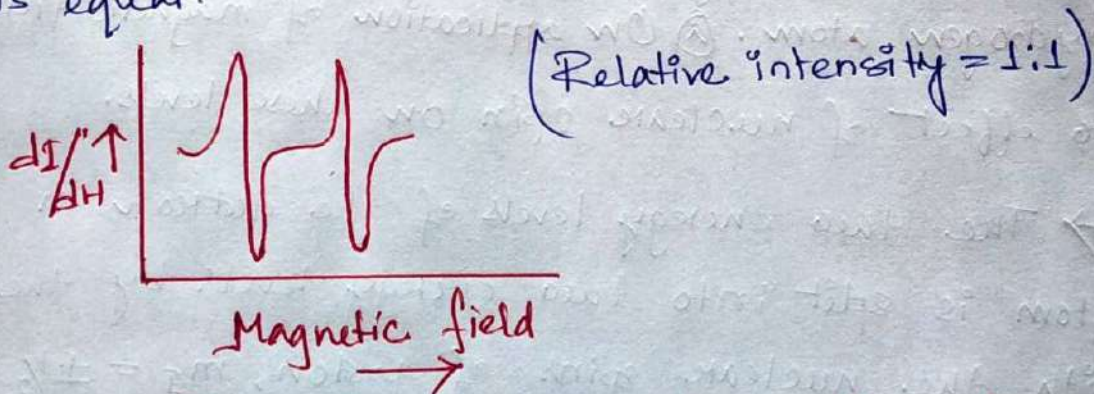
$m_I = +\frac{1}{2}$ to $m_I = -\frac{1}{2}$ and $\left\{ \begin{array}{l} \text{According to ESR} \\ \text{selection rule} \end{array} \right.$
 $m_I = -\frac{1}{2}$ to $m_I = +\frac{1}{2}$

Note — Selection rule of ESR —

$\Delta m_I = 0$

$\Delta m_S = \pm 1$

The two peaks are of equal intensity because the probability of orientations of the nuclear spin of hydrogen atom causing different energy levels is equal.



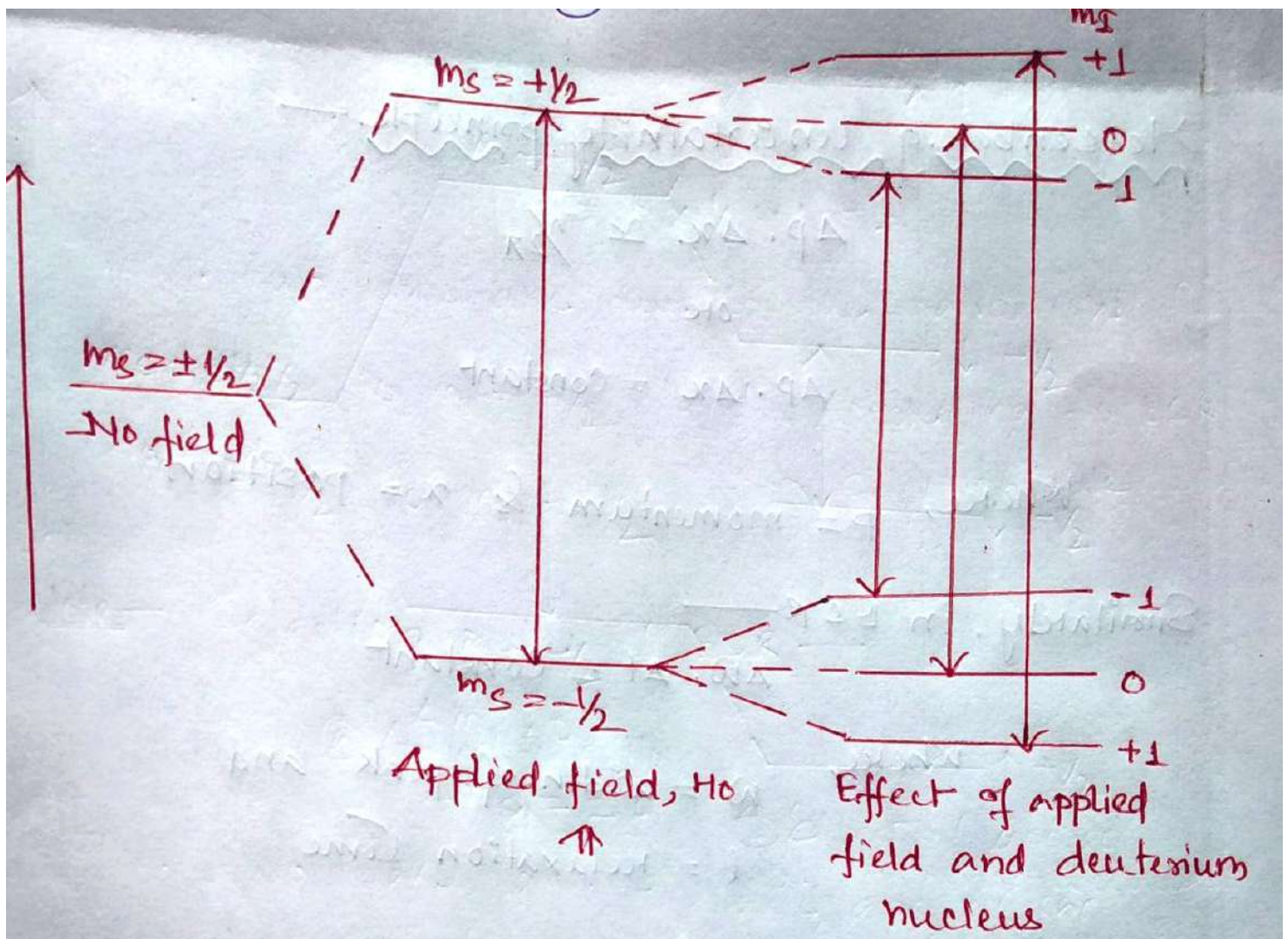
fig! Dispersion ESR-spectrum of H-atom

ESR of Deuterium ($D/{}^2H$) atom —

↳ 'I' value of $D/{}^2H$ is = 1, therefore —

$m_I = +1, 0 \text{ and } -1$

↳ No. of lines — $2I + 1 = 2 \times 1 + 1 = \underline{\underline{3}}$



q! Energy level diagram illustrating coupling between the unpaired electron and deuterium nucleus.

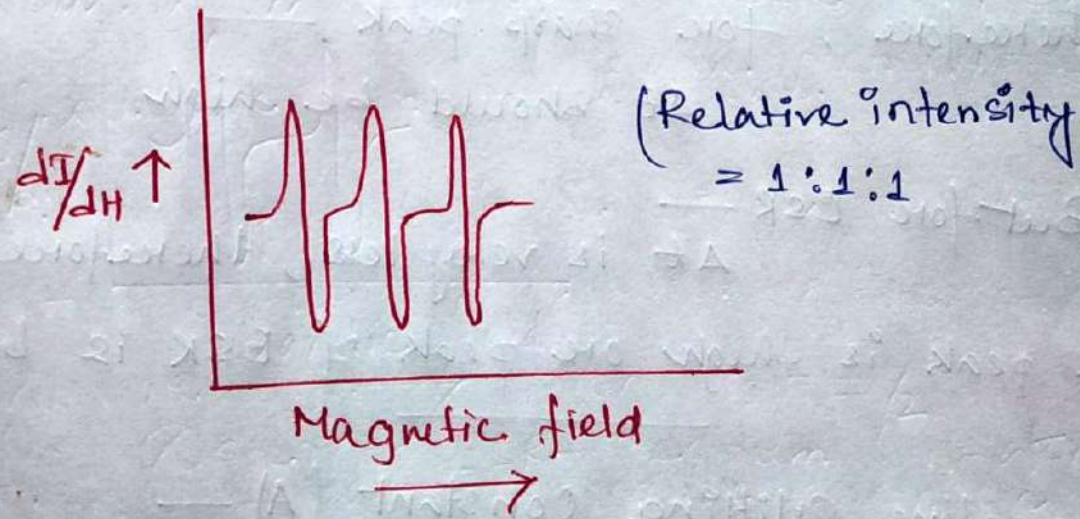


fig: Dispersion ESR-spectrum of D-atom

Heisenberg Uncertainty principle —

$$\Delta p \cdot \Delta x \approx \frac{h}{2\pi}$$

or

$$\Delta p \cdot \Delta x = \text{Constant}$$

Where, p = momentum & x = position

Similarly, in ESR —

$$\Delta \omega \cdot \Delta t = \text{Constant}$$

Where,

ω = width of peak and

t = relaxation time

$$\therefore \Delta \omega \propto \frac{1}{\Delta t}$$

ie., if Δt is high, then $\Delta \omega$ is small

Therefore, for sharp peak —

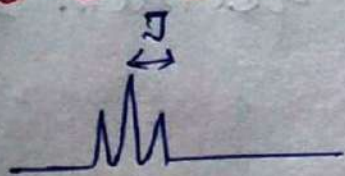
Δt should be high

But for ESR —

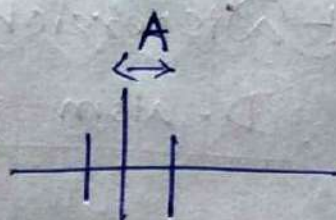
Δt is very less, therefore width

of peak is high one peak of ESR is broad.

Hyperfine splitting constant (A) —



$^1\text{H-NMR}$



ESR

Intensity of signal —

↳ In ESR-spectrum, only one signal is observed.

↳ Further splitting of that signal occurs due to Hyperfine coupling.

↳ For $I > 1/2$ values —

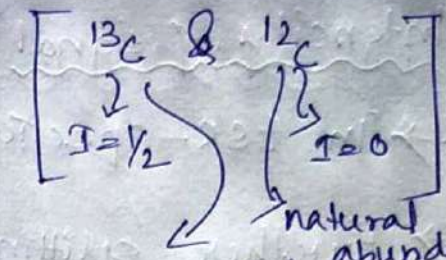
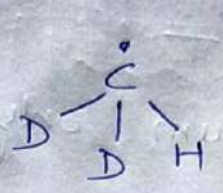
| | $I = 1$ | $I = 3/2$ | $I = 2$ |
|-------|--|---|---|
| $n=1$ | $2nI + 1$ $= 2 \times 1 \times 1 + 1 = 2 + 1$ $= 3$ (triplet) Intensity ratio — $(1:1:1)$ | $2nI + 1$ $= (2 \times 1 \times 3/2 + 1) = 3 + 1$ $= 4$ (quartet) Intensity ratio — $(1:1:1:1)$ | $2nI + 1$ $= (2 \times 1 \times 2 + 1) = 4 + 1$ $= 5$ (quintet) Intensity ratio — $(1:1:1:1:1)$ |
| $n=2$ | $2nI + 1$ $= (2 \times 2 \times 1 + 1)$ $= 5$ (quintet) Intensity ratio — $(1:2:3:2:1)$ | $2nI + 1$ $= (2 \times 2 \times 3/2 + 1)$ $= 7$ (septet) Intensity ratio — $(1:2:3:4:3:2:1)$ | $2nI + 1$ $= (2 \times 2 \times 2 + 1)$ $= 9$ (nonet) Intensity ratio — $(1:2:3:4:5:4:3:2:1)$ |
| $n=3$ | $2nI + 1$ $= (2 \times 3 \times 1 + 1)$ $= 7$ (Septet) Intensity ratio — $(1:3:6:7:6:3:1)$ | | |

↳ For $I = 1/2$,

Intensity ratio follows Pascal's triangle.

↳

eg: D_2CH



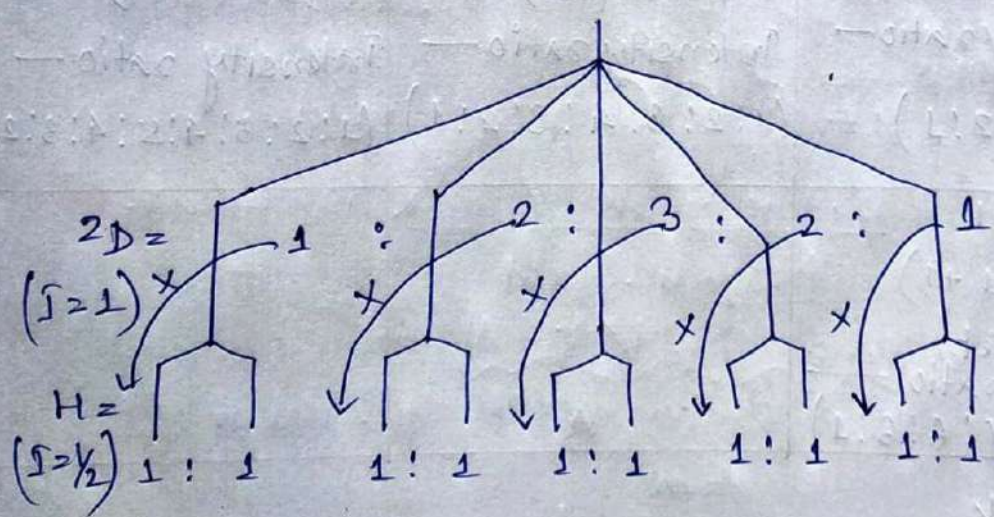
dilute nuclei
(natural abundance $\approx 1\%$)
natural abundance = 98.9%

Since, ${}^{12}C$ has $I=0$, so it is non-magnetic nuclei, so it does not split the spin states of unpaired electron.

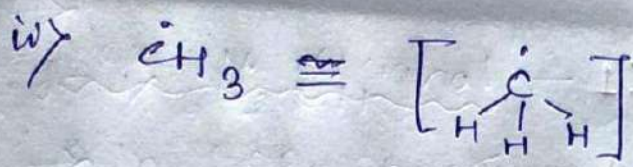
For D , $I_1 = 1$ & For H , $I_2 = 1/2$

Therefore, No. of lines —

$$\begin{aligned} & (2n_1I_1 + 1) (2n_2I_2 + 1) \\ &= (2 \times 2 \times 1 + 1) (2 \times 1 \times 1/2 + 1) \\ &= 5 \times 2 = 10 \text{ lines} \end{aligned}$$



Total intensity ratio = 1:1:2:2:3:3:2:2:1:1



Splitting occurs only due to three protons,

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

For ^{13}C , $I = 0$, so don't participate in splitting

No. of lines —

$$= 2nI + 1$$

$$= 2 \times 3 \times \frac{1}{2} + 1$$

$$= 4 \text{ (quartet)}$$

\therefore Intensity ratio = 1 : 3 : 3 : 1

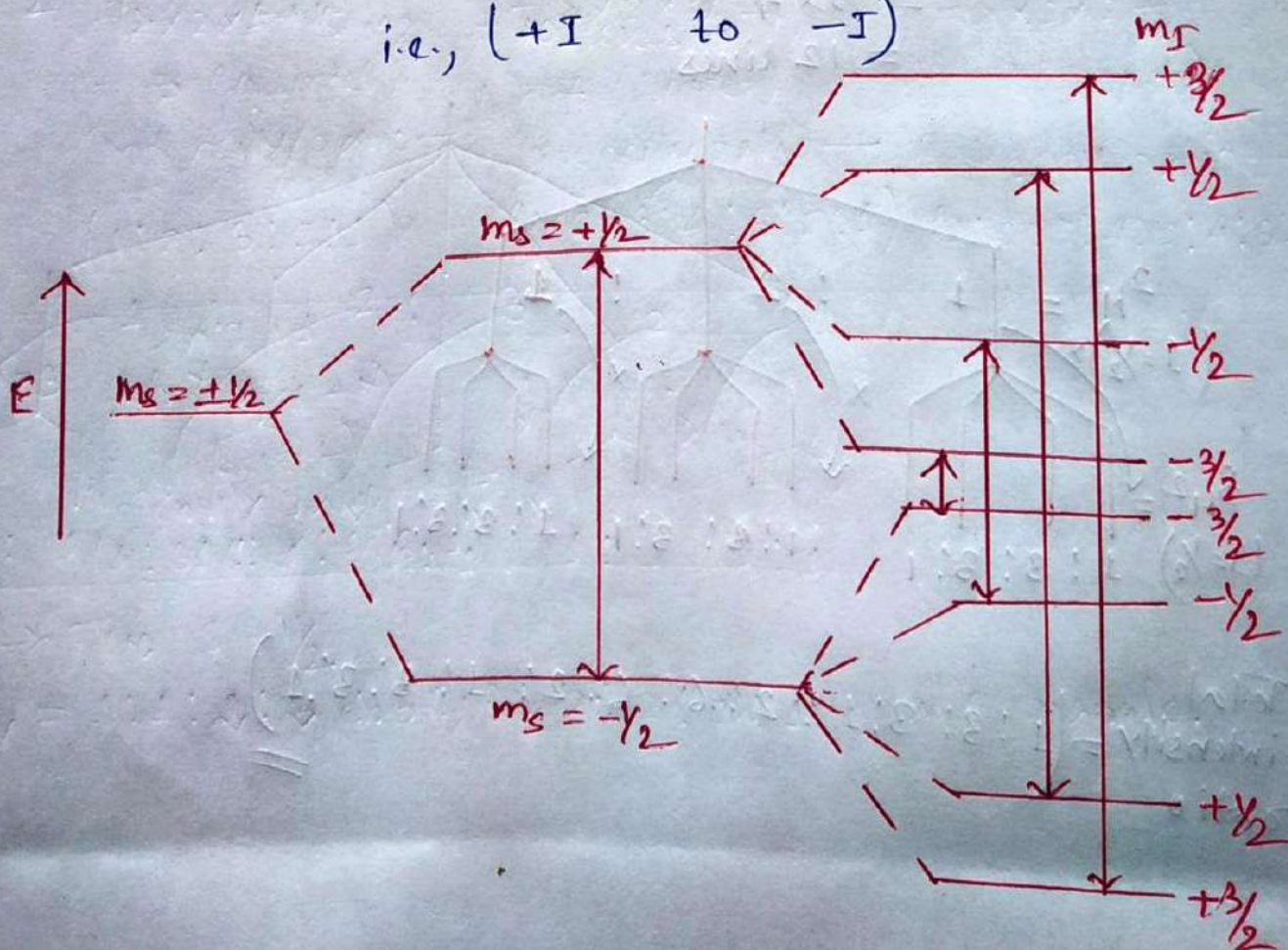
(According to Pascal's triangle, since, $I = \frac{1}{2}$)

Since, for three H-atoms —

$$I = 3 \times \frac{1}{2} = \frac{3}{2}$$

$$\therefore m_I = +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$$

i.e., (+I to -I)



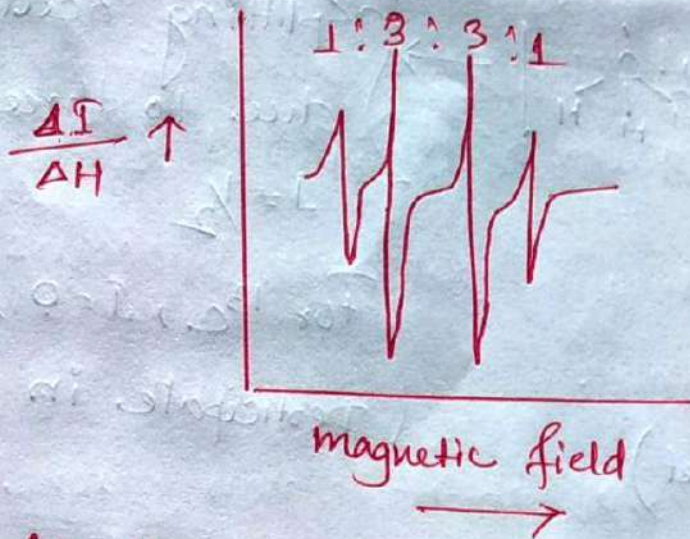
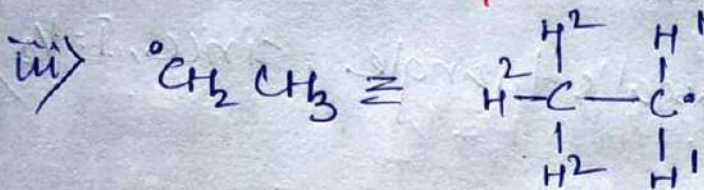
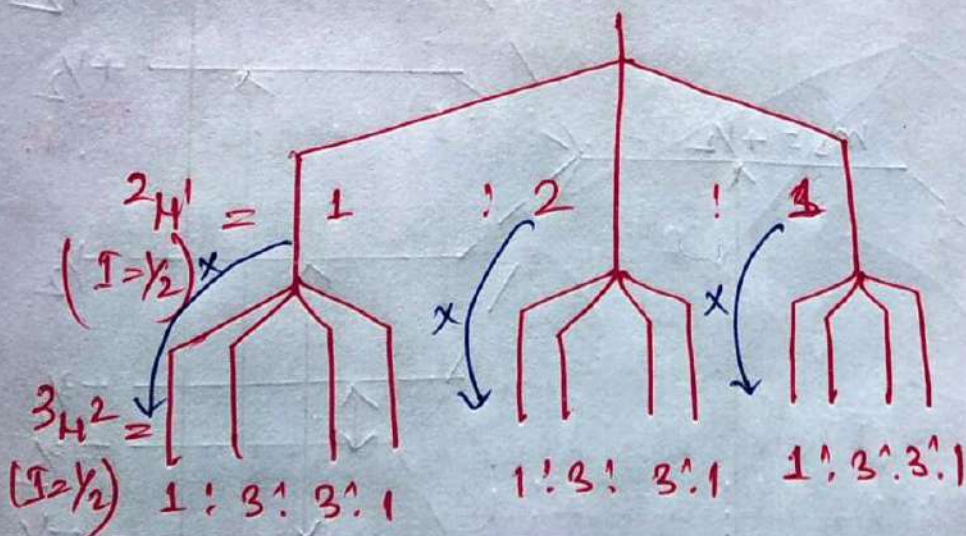


Fig: Dispersion ESR-spectrum of $(\cdot\text{CH}_3)$



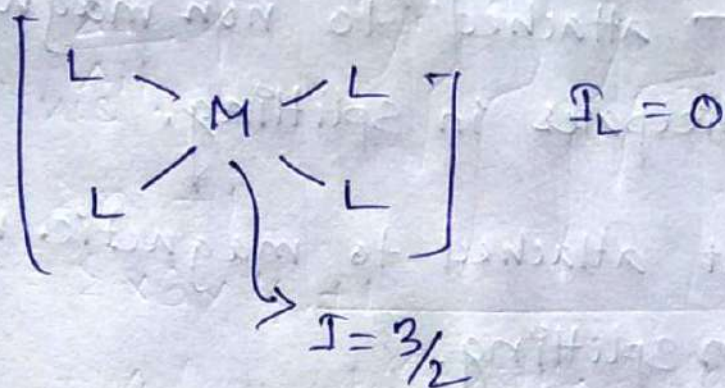
Splitting —

$$\begin{aligned} & (2n_1I_1 + 1)(2n_2I_2 + 1) \\ &= (2 \times 2 \times \frac{1}{2} + 1)(2 \times 3 \times \frac{1}{2} + 1) \\ &= 3 \times 4 \\ &= 12 \text{ lines} \end{aligned}$$



Total intensity ratio = $(1:3:3:1:2:6:6:2:1:3:3:1)$

iv) $[ML_4] =$ square planar complex



\therefore splitting —

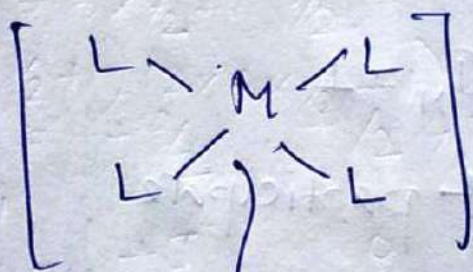
$$\sum n \Gamma + 1$$

$$= 2 \times 1 \times 3/2 + 1$$

$$= 4 \text{ (quartet)}$$

$$\text{Intensity ratio} = (1:1:1:1)$$

v) $[ML_4]$



$$\rightarrow \Gamma = 3/2 \text{ \& } \Gamma_L = 1/2$$

\therefore splitting —

$$(2n_1 \Gamma_1 + 1) (2n_2 \Gamma_2 + 1)$$

$$= (2 \times 1 \times 3/2 + 1) (2 \times 4 \times 1/2 + 1)$$

$$= 4 \times 5$$

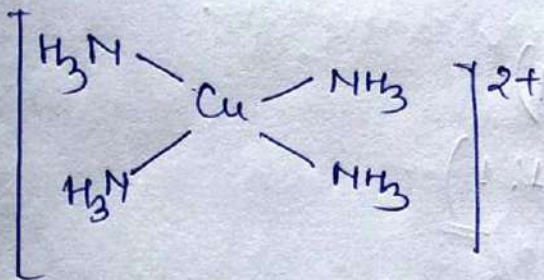
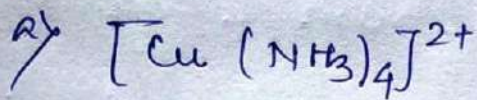
$$= \underline{\underline{20 \text{ lines}}}$$

Osago's Rule — (Applicable for metal complexes)

i) Protons that attached to non-magnetic nuclei ($I=0$), participates in splitting.

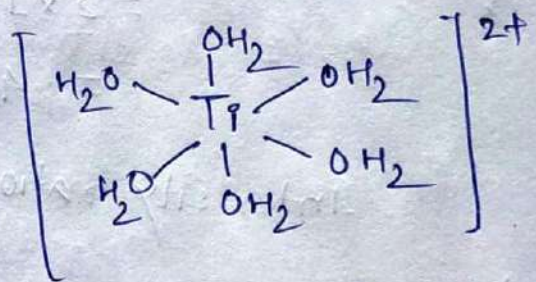
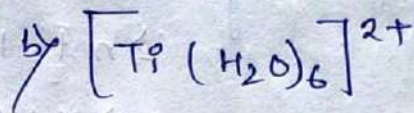
ii) Protons that attached to magnetic nuclei ($I \neq 0$) do not participate in splitting.

eg:—



$$I_{\text{Cu}} = 3/2, \quad I_{\text{N}} = 1$$

\therefore protons do not participate in splitting.



$$I_{\text{Tl}} = 3/2, \quad I_{\text{O}} = 0$$

\therefore protons participate in splitting.

Splitting —

$$\begin{aligned} & (2n_1I_1 + 1)(2n_2I_2 + 1) \\ & = (2 \times 1 \times 3/2 + 1)(2 \times 4 \times 1 \times 1) \\ & = 4 \times 9 \\ & = \underline{\underline{36 \text{ lines}}} \end{aligned}$$

Splitting —

$$\begin{aligned} & (2n_1I_1 + 1)(2n_2I_2 + 1) \\ & = (2 \times 1 \times 3/2 + 1)(2 \times 12 \times 1/2 + 1) \\ & = 4 \times 13 \\ & = \underline{\underline{52 \text{ lines}}} \end{aligned}$$

Kramer's Degeneracy

↳ Showed by the substances containing more than one unpaired electron.

↳ Zero field splitting of electron spin states occurs (i.e., splitting occurs in the absence of magnetic field)

eg:- \rightarrow \geq unpaired e^- ———

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

\therefore For $\geq e^-$ ———

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

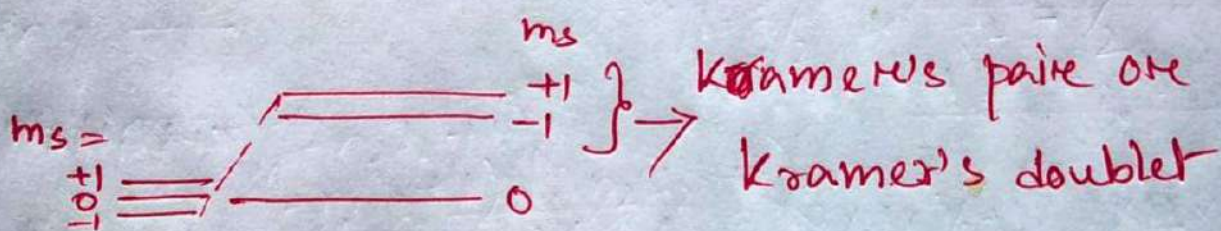
$\therefore m_s = +S$ to $-S$

$$= (1, 0, -1)$$

$$+S \rightarrow -S$$

$$+1, (1-1)=0, (0-1)$$

$$= +1, 0, -1$$



\therefore No. of Kramer's pair = 1

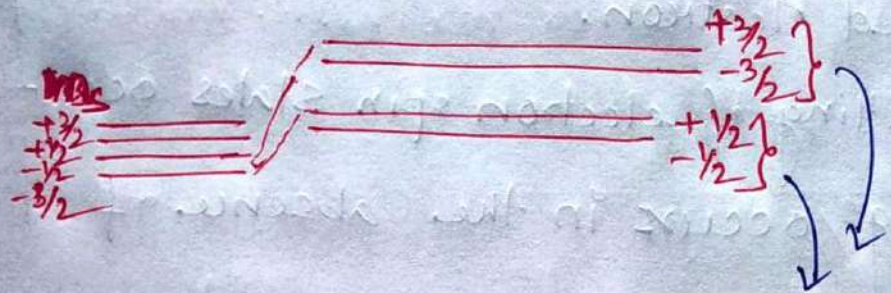
\rightarrow 3 unpaired e^- ———

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

\therefore For 3 e^- ——— $S = 3 \times \frac{1}{2} = \frac{3}{2}$

$$m_s = +s \text{ to } -s$$

$$= +3/2, +1/2, -1/2, -3/2$$



| | |
|---------------------|------|
| $+s$ | $-s$ |
| $+3/2$ | |
| $(+3/2 - 1) = +1/2$ | |
| $(+1/2 - 1) = -1/2$ | |
| $(-1/2 - 1) = -3/2$ | |

Kramer's pair or Kramer's doublet

\therefore No. of Kramer's pair = 2