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CHB-604

NMR SPECTROSCOPY

§ MAGNETIC (SPIN) RESONANCE SPECTROSCOPY

Magnetic resonance spectroscopy is classified into :

ⓐ Nuclear magnetic resonance (NMR) spectroscopy (Spin of Nucleus)

ⓑ Electron spin resonance (ESR) spectroscopy / Electron paramagnetic resonance (EPR) spectroscopy (spin of electron)

NMR spectra : Observed in the radiofrequency region of the electromagnetic spectrum.

ESR spectra : Observed in the microwave region of the electromagnetic spectrum.

- What is difference between Magnetic resonance spectroscopy and IR / Microwave / UV-Visible spectroscopy ?

Answer :→ In Magnetic resonance spectroscopy magnetic field is necessary.

In IR / Microwave / UV-Visible spectroscopy no use of magnetic field and spin.

§ NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

"Nature of Spinning Nucleus"

- All atomic nuclei possess nuclear spin (I) which may be integral (i.e. 1, 2, 3 etc.) or half integral (i.e. $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$ etc.)
- The proton and neutron each has spin $\frac{1}{2}$.
- The angular momentum associated with a nuclear spin is given by,

$$\boxed{\mathbf{I} = \sqrt{I(I+1)} \cdot \frac{h}{2\pi}}$$

- Nucleus also posses nuclear spin and although angular momentum varies from nucleus to nucleus.
- Simplest nucleus proton (^1H) having one proton has spin of half. So, neutron is another particle which is contituent of all other nucleus except ^1H.

- Particle composed of p proton in n neutron then total mass = p+n But the total spin will be vectorial combination of (p+n) spin each of $\frac{1}{2}$ magnitude. There is no law to predict a spin of particular nucleus but some Empirical Rule followed.

2013
2012
2011

TABLE :→ Empirical Rules for Predicting Nuclear Spin

	Number of Protons	Number of Neutrons	Nuclear spin (I)	Example
(i)	EVEN	EVEN	0	$^{4}_{2}He$, $^{12}_{6}C$. $^{16}_{8}O$
(ii)	EVEN	ODD	$\frac{1}{2}$ or $\frac{3}{2}$ or $\frac{5}{2}$	$^{17}_{8}O$ $^{13}_{6}C$
(iii)	ODD	EVEN	$\frac{1}{2}$ or $\frac{3}{2}$ or $\frac{5}{2}$	$\underbrace{^{1}H, ^{15}N, ^{19}F, ^{31}P}_{1/2}, \underbrace{^{11}B}_{3/2}$
(iv)	ODD	ODD	1 or 2 or 3	$\underbrace{^{2}_{1}H, _{7}^{14}N}_{1}, \underbrace{^{10}_{5}B}_{3}$

Note :→ In the only case in which the nucleus has no neutrons i.e. the ^{1}H isotope, "0" is treated as an even number and $I = \frac{1}{2}$.

⊕ A Nucleus with spin I can adopt (2I+1) spin orientations, which are degenerate in the absence of magnetic field. When an external magnetic field is applied, the degeneracy is removed.

e.g. Proton (^{1}H), $I = \frac{1}{2}$

Nuclear spin quantum number, $m_I = +\frac{1}{2}$ & $-\frac{1}{2}$

Number of spin state $= 2I+1$

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

$= 2$.

2011

§ INTERACTION BETWEEN SPIN AND A MAGNETIC FIELD

A charged particle (^1H) spinning about an axis constitutes a circular electric current which in turn produces a magnetic dipole behaves as a tiny bar magnet. The Size of the magnetic dipole i.e. the strength of magnet for a point charge,

$$\mu = \frac{q}{2m} I$$

q = charge of the particle
m = mass of the particle

$$\mu = \frac{q}{2m} \cdot \sqrt{I(I+1)} \cdot \frac{h}{2\pi}$$

$1T = 10^4$ gauss

$$\boxed{\mu = \frac{qh}{4\pi m}\sqrt{I(I+1)}}$$ Am^2 or $(Kg\, S^{-2} T^{-1})\, m^2$ or JT^{-1} (Joules per Tesla)

When remove the fiction that electrons and nuclei are point charges, then

$$\boxed{\mu = \frac{Gqh}{4\pi m}\sqrt{I(I+1)}}$$ JT^{-1}

For electrons, $G = g$ (Lande splitting factor) depends upon quantum state of the $\bar{e}$.

$$\mu = -\frac{gqh}{4\pi m}\sqrt{I(I+1)}$$

$$\boxed{\mu = -g\beta\sqrt{I(I+1)}}$$ JT^{-1}

Where, $\boxed{\beta = \frac{qh}{4\pi m}}$ β is known as 'Bohr Magneton'.

$q = 1.60 \times 10^{-19}$ C (electronic charge)
$m = 9.11 \times 10^{-31}$ kg (mass of electron)

$$\boxed{\beta\ (\text{electron}) = 9.273 \times 10^{-24}\ JT^{-1}}$$

Nuclear dipoles are expressed in terms of a nuclear magneton β_N which is defined in terms of the mass and charge of the proton.

$$\beta_N = \frac{eh}{4\pi m_p}$$

$$\boxed{\beta_N = 5.050 \times 10^{-27}\ JT^{-1}}$$

For a nucleus of mass M and charge pe (p = number of proton),

$$\mu = \frac{Gpe}{2M} \, I$$

$$\mu = \frac{Gpe}{2M} \sqrt{I(I+1)} \cdot \frac{h}{2\pi}$$

$$\mu = \frac{Gp}{M} \sqrt{I(I+1)} \cdot \frac{eh}{4\pi} \cdot \frac{m_p}{m_p}$$

$$\mu = \frac{G m_p p}{M} \cdot \frac{eh}{4\pi m_p} \sqrt{I(I+1)}$$

$$\boxed{\mu = g \, \beta_N \sqrt{I(I+1)}} \quad JT^{-1}$$

Where, $\boxed{g = \frac{G m_p p}{M}}$ g is characteristic of each nucleus

m_p = protonic mass

g has values up to about 6 and is +ve for nearly all known nuclei.

$\boxed{\beta_N = \frac{eh}{4\pi m_p}}$ β_N is known as 'Nuclear Magneton.'

$$\boxed{\mu = \gamma \sqrt{I(I+1)}} \quad JT^{-1}$$

where, 2014 $\boxed{\gamma = g\beta_N}$ γ is known as 'Gyromagnetic ratio'.

'OR'

'Magnetogyric ratio.'

- γ is a constant characteristic i.e. characteristic quantity of each nucleus.
- γ also shows the detective sensitivity of a particular type of nuclei in a NMR experiment.

* The dipole will plainly have components along a reference direction governed by the I_z value,

$\boxed{\mu_z = -g\beta I_z}$ (for electron)

$\boxed{\mu_z = g\beta_N I_z}$ (for nucleus)

For a nucleus, $I = 1$

Angular momentum of the particle $I = \sqrt{1 \times 2} = \sqrt{2}$ Units

TABLE :→ g value, magnetic moment, Gyromagnetic ratios for some nuclei,

Nuclei	spin	g value	magnetic moment	$\frac{\gamma}{10^7}$ $T^{-1}s^{-1}$
^1H	$\frac{1}{2}$	5.5854	2.7928	26.75
^{13}C	$\frac{1}{2}$	1.4042	0.7021	6.728
^{14}N	1	0.40	0.4036	1.934

Unit of γ (Gyromagnetic ratios) = $T^{-1} s^{-1}$

2014

Importances of γ :→

(i) Which nuclei show NMR or not.

(ii) Detection of nuclei which is more easily detect or more difficult.

2014

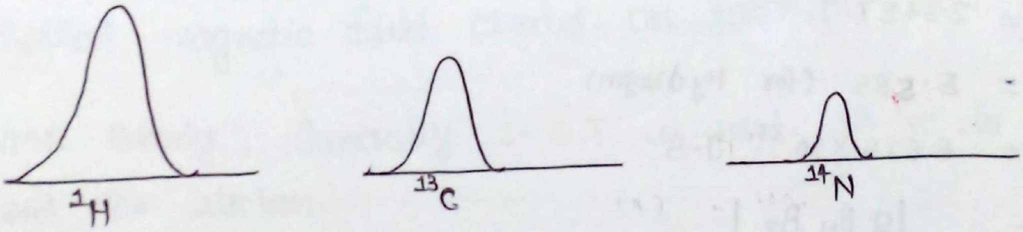
- Larger the γ value, the easier it is to detect the corresponding NMR Signal.

e.g. ^1H, ^{13}C, ^{14}N

$\gamma(^1H) > \gamma(^{13}C) > \gamma(^{14}N)$

Detection of ^{13}C is 4 times difficult than ^1H.

Detection of ^1H is very easy becoz γ value is very high.



The extent of interaction between a magnetic dipole and a field of Strength B_z applied along the z-axis is equal to the product of the two :

$\boxed{\text{Interaction} = \mu_z B_z}$ $B_z = 0$ (no interaction)

Thus, the separation between neighbouring energy levels is, (When I_z differs by unit)

$$\Delta E = |E_{I_z} - E_{(I_z-1)}|$$

$$\Delta E = |g\beta_N I_z B_z - g\beta_N (I_z-1) B_z|$$

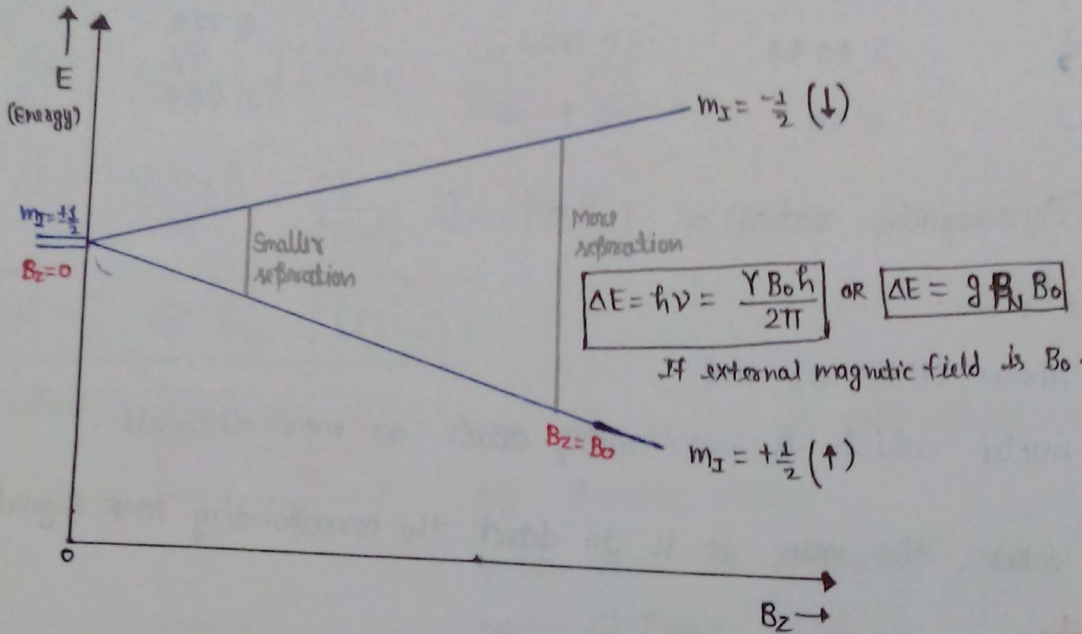
$$\boxed{\Delta E = |g\beta_N B_z|} \text{ Joule}$$

B_z expressed in Tesla.

In Hertz:

$$\boxed{\frac{\Delta E}{h} = \left|\frac{g\beta_N B_z}{h}\right|}\ \text{Hz}$$

Seperation ∝ applied field strength (B_z)



$$\boxed{\Delta E = h\nu = \frac{\gamma B_0 h}{2\pi}} \text{ OR } \boxed{\Delta E = g\beta_N B_0}$$

If external magnetic field is B_0.

* Calculation of approximate frequency to expected:

Case I For Nuclei : (NMR)

$\beta_N = 5.05 \times 10^{-27}\ JT^{-1}$

$B_z = 2.3487\ T$

$g = 5.585$ (for Hydrogen)

$h = 6.626 \times 10^{-34}$ J-S

$$\frac{\Delta E}{h} = \left|\frac{g\beta_N B_z}{h}\right|$$

$$\frac{\Delta E}{h} = \frac{5.585 \times 5.05 \times 10^{-27} \times 2.3487}{6.626 \times 10^{-34}}$$

$$\boxed{\frac{\Delta E}{h} = 100 \times 10^{6}\ Hz}$$ Radiofrequency Region

Case II For Electron : (EPR / ESR)

$\beta = 9.273 \times 10^{-24}\ JT^{-1}$

$g = 2$

$B_z = 0.34\ T$

$h = 6.626 \times 10^{-34}$ J-S

$$\frac{\Delta E}{h} = \left| \frac{g \beta B_Z}{h} \right|$$

$$\frac{\Delta E}{h} = \frac{2 \times 9.273 \times 10^{-24} \times 0.34}{6.626 \times 10^{-34}}$$

$$\boxed{\frac{\Delta E}{h} \approx 9500 \times 10^{6}\ Hz}$$ Microwave region

Principle for NMR and ESR is same but techniques are different, one can not measure EPR/ ESR from NMR and vice-versa.

NMR is more versatile than EPR becoz in EPR used unpaired electron basically radical and NMR only at $L \neq 0$ of nuclei.

⊕ Some example of magnetic field

① Surface of earth, M.F. = 10^{-5} T

② Household wiring, M.F. = 10^{-4} T

③ Small magnet, M.F. = 0.1 T

④ Electromagnet, M.F. = 2 T

⑤ Super conducting magnet, M.F. = 15 T

The highest magnetic field created on earth is 30 T (Steady-state M.F.)

In NMR Steady, Generally 1-5 T is used to nuclei and 0.3 T is used for electron.

§ THE LARMOR PRECESSION

The magnetic dipole moment of a spinning nucleus is,

$$\boxed{\mu = g\beta_N\sqrt{I(I+1)}}\ JT^{-1}$$

According to quantal laws, the vector represented by μ can be oriented only in such a way that its components are integral or half-integral in a reference direction.

Magnetic moment precesses around the direction of magnetic field rather than settle down in the direction of magnetic field, this is called Larmor Precession.

e.g. For a nucleus with spin $\frac{1}{2}$.

$$\mu = g\beta_N\sqrt{\tfrac{3}{2}}$$

and, $\mu_z = \pm\frac{1}{2}g\beta_N$ only.

NOTE :→ When magnetic dipole is placed in external field then it not exactly along external field but some tilted. The tilted angle depend on I (nucleus spin).

Orientation $= 2I+1$

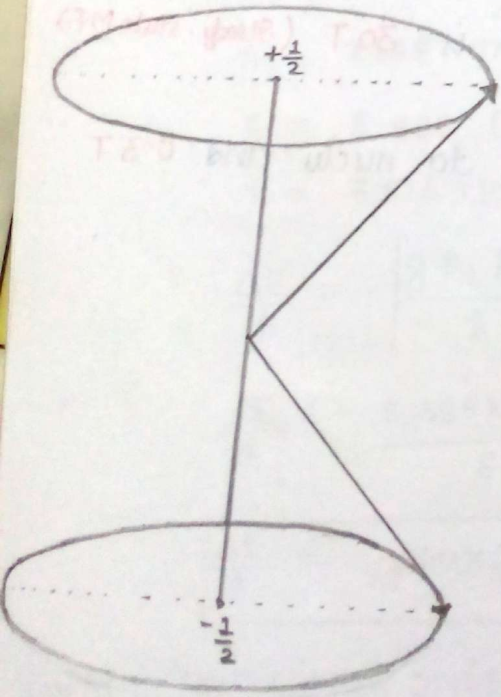


Fig: The two spin orientations allowed to a nucleus with $I=\frac{1}{2}$.

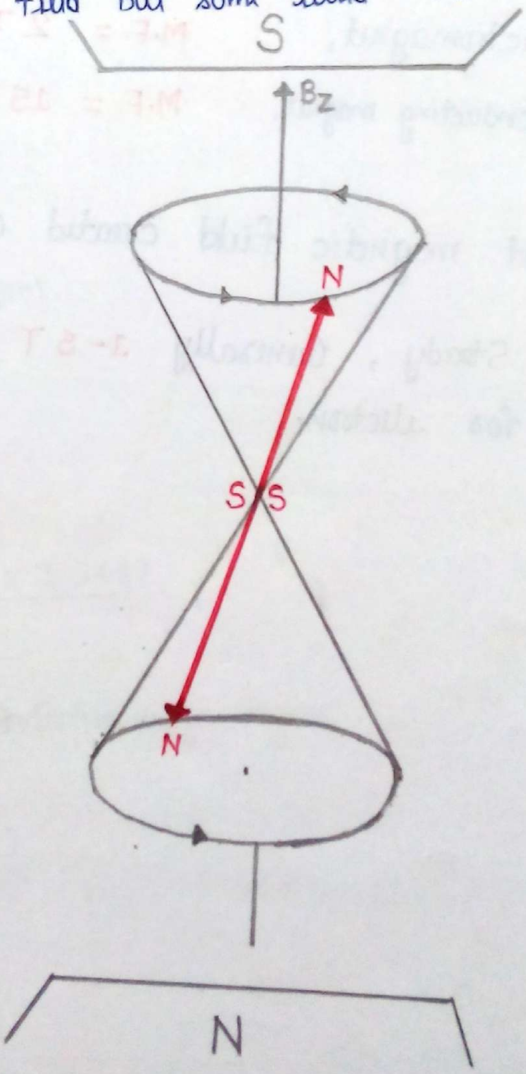


Fig: The Larmor precession of such a nucleus

The precessional frequency or Larmor frequency :→

$$\omega = \frac{\text{magnetic moment}}{\text{angular momentum}} \times B_z \quad \text{rad } s^{-1}$$

$$\omega = \frac{\mu B_z}{2\pi I} \quad \text{Hz}$$

$$\omega = \frac{g\beta_N \sqrt{I(I+1)} \cdot B_z}{2\pi \cdot \sqrt{I(I+1)} \frac{h}{2\pi}} \quad \text{Hz}$$

$$\boxed{\omega = \frac{g\beta_N B_z}{h}} \quad \text{Hz}$$

Larmor frequency

$$\overset{\uparrow}{\boxed{\omega = \gamma B_z}}$$

$$\boxed{\gamma = \frac{\mu}{I(h/2\pi)}} \quad T^{-1} s^{-1}$$

$$\boxed{\omega = 2\pi\nu} \rightarrow \text{NMR frequency}$$

$$\boxed{1 \text{ rad } s^{-1} = \frac{1}{2\pi} \text{ Hz}}$$

Larmor frequency is same as the seperation between two spin energy levels

Significance :→

Particle spins can interact with a beam of electromagnetic radiation.
If the beam has the same frequency of the precessing particle, it can
interact coherently with the particle and energy can be exchanged, this
phenomenon is known as Resonance.

For Nuclei, Resonance is referred as N.M.R. (Nuclear magnetic resonance).

For Electron, Resonance is referred as E.S.R. (Electron spin resonance)
'OR'
E.P.R. (Electron paramagnetic resonance).

Experimentally, this resonance achived by two ways:

① Either apply a fixed magnetic field to a set of identical nuclei so that the nuclei has Larmor frequency of 100 MHz and they swept over a range including 100 MHz, resonance absorption will occur at precisely at 100 Mz.

② On the other hand, we could bath the nuclei in radiation at a fixed frequency of 100 MHz and sweep the applied field over a range until absorption occurs.

§ RELAXATION TIMES

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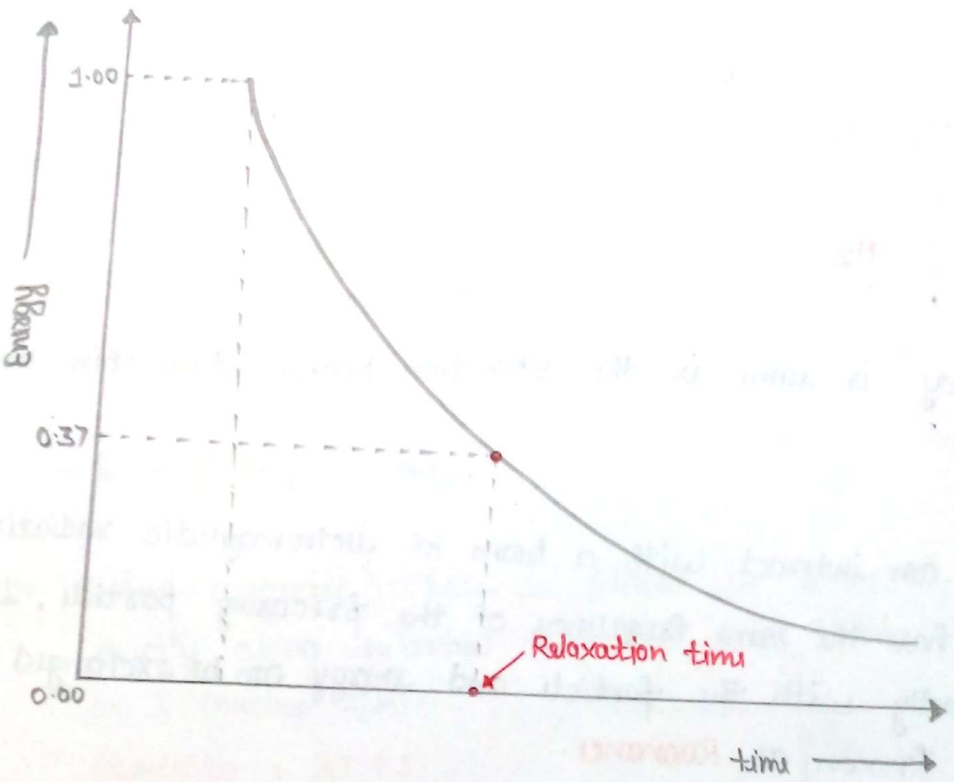
The mechanism by which excess spin energy is shared either with the surroundings or with other nuclei is referred as a relaxation process, the time taken for a fraction $\frac{1}{e} = 0.37$ of the excess energy to be dissipated is called the relaxation time.



2014 Two relaxation process occurs for nuclei:

① The Excess spin energy equilibrates with the surroundings (the lattice) by spin-lattice relaxation having spin relaxation time or longitudinal relaxation time, T_1. Such relaxation comes about by lattice motions (e.g. atomic vibrations in a solid lattice, or molecular tumbling in liquids and gases) having right frequency to interact coherently with nuclear spins.

T_1 (Solids) = 10^{-2} to 10^{4} Second

T_1 (liquids) = 10^{-4} to 10 Second

② There is a sharing of excess spin energy directly between nuclei via spin-spin relaxation or transverse relaxation, the symbol for the time of which is T_2.

T_2 (solids) = 10^{-4} Second

T_2 (liquids) ≈ T_1

Question How T_1 and T_2 affect the line widths of NMR Spectra?

Explanation

$$\boxed{\Delta\nu = \frac{1}{2\pi\Delta t}}$$

Since, T_1 and T_2 reflect the life time of a particular spin state.

Thus, a long relaxation time (both T_1 and T_2 large) means that an excited nuclear spin reverts rather slowly to a lower state i.e. has a long life time,

→ Only a small uncertainty in the excited state energy level that means line widths will be narrow.

e.g. Taking a typical value of one second for the relaxation time of a nucleus in a liquid,

$$\Delta E \approx \frac{h}{2\pi\Delta t} \approx 10^{-34}\ J$$

$$\Delta\nu = \frac{\Delta E}{h} \approx 0.1\ Hz$$

In general, NMR spectrometers are not capable of resolving lines closer than about 0.5 Hz apart, so that a line width of only 0.1 Hz represents a narrow spectral line.

e.g. $\Delta t = 10^{-4}$ sec as for T_2 in a typical solid,

$$\Delta\nu \simeq 1000\,Hz$$

which is clearly a very broad line compared with the resolving power.

Thus, NMR Experiments divided into two main classes:

① Broad line, usually comprising solid samples.

② Sharp line and high-resolution usually of liquids or gases.

§ CHEMICAL SHIFT

2013

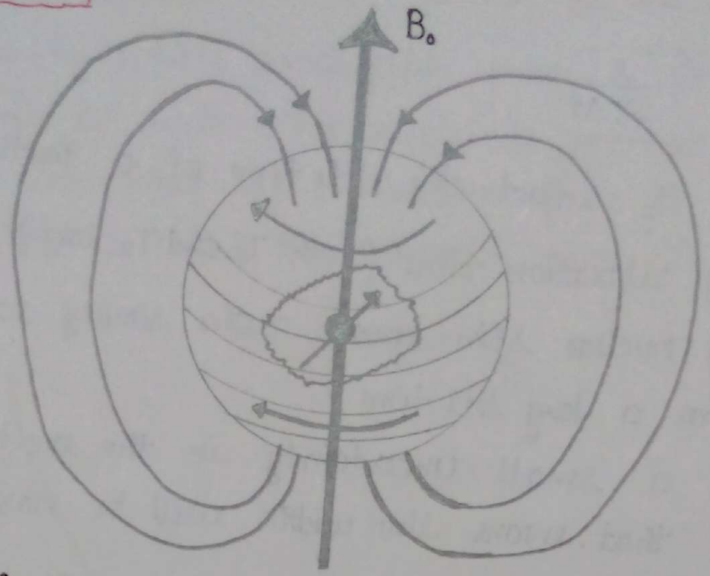


Fig :→ The field, produced by diamagnetic circulation of the electron cloud about a nucleus, opposes the applied field B_0.

Plainly the total field experienced by the nucleus is,

$$B_{effective} = B_{applied} - B_{induced}$$

$$B_{effective} = B_{applied} - \sigma B_{applied} \qquad \because B_{induced} = \sigma B_{applied}$$

$$B_{effective} = B_{applied}(1-\sigma)$$

$$\boxed{B_{effective} = B_0(1-\sigma)}$$

where, B_0 is applied magnetic field.

The electrons effectively shield the nucleus from B_0 so σ is called shielding constant.

$\sigma(^1H) = 10^{-5}$

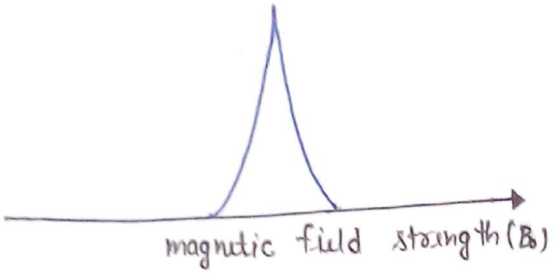
Since, $\Delta\nu = \frac{\Delta E}{h}$ Hz

$\Delta\nu = \frac{\gamma B_z}{h}$ Hz

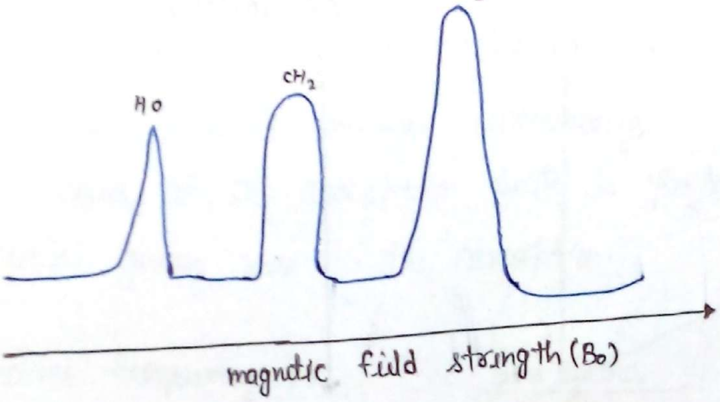
$$\boxed{\Delta\nu = \frac{\gamma(1-\sigma)B_0}{h}} \text{ Hz}$$

Values of σ depends on the electronic or chemical environment around the nucleus. Thus, there are three sets of different proton based on the different local magnetic field.

e.g. $\overset{a}{CH_3}I$ (one peak)

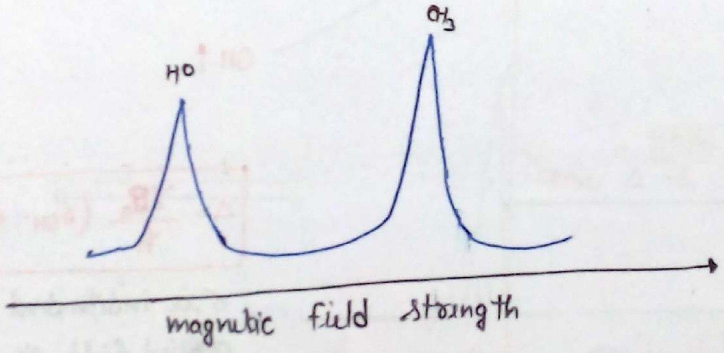


e.g. $\overset{a}{CH_3}-\overset{b}{CH_2}-\overset{c}{OH}$ (three peak)



$$\underset{OH}{\overset{\downarrow}{1}} : \underset{CH_2}{\overset{\downarrow}{2}} : \underset{CH_3}{\overset{\downarrow}{3}}$$ (three peaks)

e.g. $\overset{a}{CH_3}-\overset{b}{OH}$ (two peak)

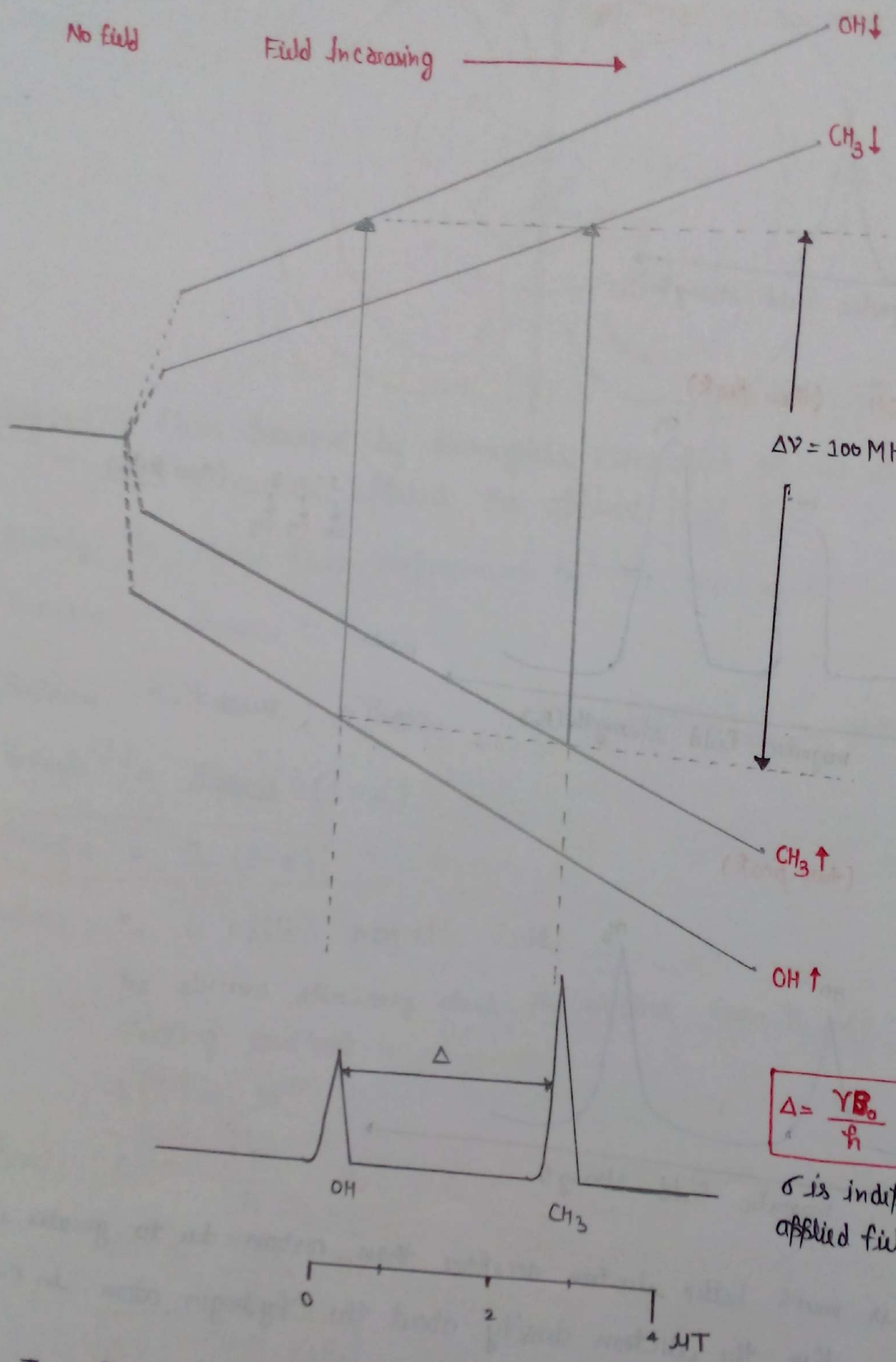


oxygen is much better electron acceptor than carbon due to greater electronegativity of oxygen, then the electron density about the hydrogen atom in C-H bonds should be high than O-H bonds.

$$\sigma_{CH} > \sigma_{OH}$$

$$\therefore \quad B_{CH} = (1-\sigma_{CH})B_0 < B_{OH} = (1-\sigma_{OH})B_{OH}$$

Thus, the field experienced by the Hydrogen nucleus in O-H bonds is greater than at the same nucleus in C-H bonds and for a given applied field, the CH hydrogen nucleus will precess with smaller Larmor frequency than OH



$$\boxed{\Delta = \frac{\gamma B_0}{h}(\sigma_{CH} - \sigma_{OH})}\ \text{Hz}$$

σ is independent of the applied field or frequency.

FIG :- The effect of an applied magnetic field on the energy levels of the methyl and hydroxyl nuclei of methanol (CH_3OH). The applied field is increased rapidly initially until near resonance at 2.3487 T and then the increase is much slower. The N.M.R. Spectrum of methanol is shown at the foot of the figure.

The OH hydrogen nucleus having a smaller shielding constant experiences a greater field, hence its energy levels are more widely spaced than those of the more shielded CH_3 nuclei at any given applied field.

The ratio of the absorption intensities is 1:3 immediately allows us to identify the smaller peak with the single hydrogen nucleus in the OH group, the larger with the CH_3 group.

Since neither carbon nor oxygen have nuclei with spin, they do not contribute to the spectrum.

Two very important facts of N.M.R. Spectroscopy appear in Figure:

(i) Identical nuclei i.e H nuclei give rise to different absorption positions when in different chemical surroundings.

(ii) The area of an absorption peak is proportional to the number of equivalent nuclei giving rise to the absorption.

Resonance frequency :→

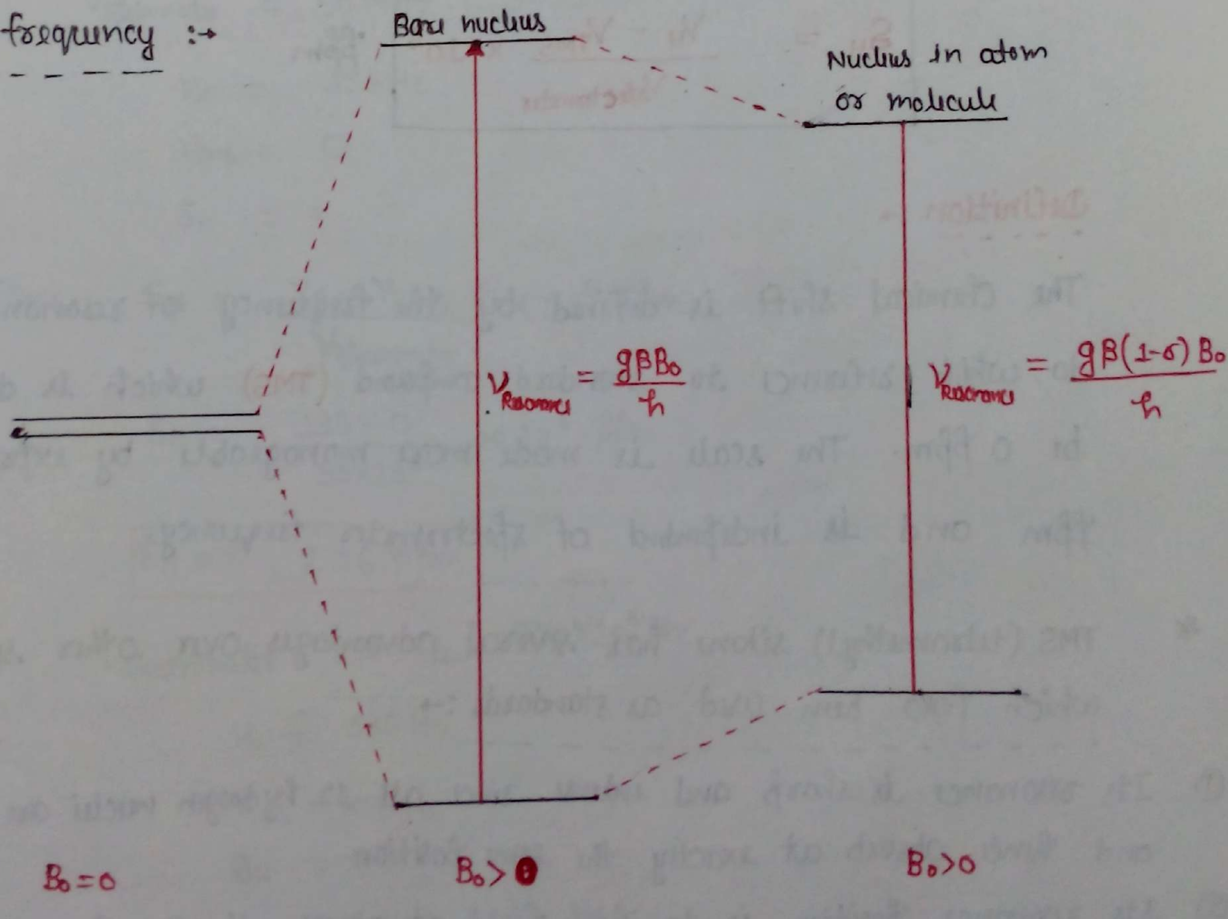


FIG: Effect of electron shielding on the nuclear magnetic Resonance condition. The resonance frequency for a nucleus in an atom or molecule is lower than that for a bare nucleus i.e. for an isolated proton.

In general, σ (Shielding constant) is a small number about 10^{-5} for proton, whose magnitude depends on the electronic structure around the nucleus.

Resonance frequency.

$$\boxed{\nu_H = \frac{g\beta_H(1-\sigma_H)B_0}{h}}$$

$$\nu_H \propto B_0$$

We are interested not in the absolute shifts of the NMR peaks from that expected for a bare proton but in the relative positions of the peak.

To avoid this complicasy and standardized the resonance frequency relative to a reference compound, Tetramethyl silane [TMS, $(CH_3)_4Si$], ν_H is divided by frequency in spectrometer.

$$\text{Chemical shift} = \frac{\text{Resonance frequency of nucleus (H) relative to TMS}}{\text{Spectrometer frequency}} \times 10^6$$

$$\boxed{\delta_H = \frac{\nu_H - \nu_{TMS}}{\nu_{spectrometer}} \times 10^6} \text{ ppm}$$

Definition :→

The Chemical shift is defined by the frequency of resonance express to with reference to standard compound (TMS) which is defined to be 0 ppm. The scale is made more manageable by expressing in ppm and is independent of spectrometer frequency.

* TMS (tetramethyl) silane has several advantages over other substances which have been used as standards :→

① Its resonance is sharp and intense since all 12 hydrogen nuclei are equivalent and hence absorb at exactly the same position.

② Its resonance position is to high field at almost all other hydrogen resonances in organic molecules & hence can be easily recognized. (σ_{TMS} is large)

③ It is a low B.P. liquid (27°C) so can be readily removed from most samples after use.

④ It is chemically inert i.e. non-reacting.

CHEMICAL SHIFT ≡ Upfield (more shielded) OR Downfield (less shielded)

{Example} The NMR signal of H spectrum of CH_3I recorded at 130 Hz, 195 Hz and 585 Hz from the TMS peak using a spectrometer operating at 60 MHz, 90 MHz and 270 MHz respectively. calculate its chemical shift in ppm relative to TMS.

{Solution} (i) $\nu_{spectrometer} = 60\ MHz = 60 \times 10^6\ Hz$

$\nu_H = 130\ Hz$

$\nu_{TMS} = 0$

$\delta_H = ?$

Since, $$\delta_H = \frac{\nu_H - \nu_{TMS}}{\nu_{spectrometer}} \times 10^6\ ppm$$

$$\delta_H = \frac{130 - 0}{60 \times 10^6} \times 10^6\ ppm$$

$$\boxed{\delta_H = 2.16\ ppm}$$

(ii) $\nu_{spectrometer} = 90\ MHz = 90 \times 10^6\ Hz$

$\nu_H = 195\ Hz$

$\nu_{TMS} = 0$

$\delta_H = ?$

Since, $$\delta_H = \frac{\nu_H - \nu_{TMS}}{\nu_{spectrometer}} \times 10^6\ ppm$$

$$\delta_H = \frac{195 - 0}{90 \times 10^6} \times 10^6\ ppm$$

$$\boxed{\delta_H = 2.16\ ppm}$$

(iii) $\nu_{spectrometer} = 270\ MHz = 270 \times 10^6\ Hz$

$\nu_H = 585\ Hz$

$\nu_{TMS} = 0$

$\delta_H = ?$

Since, $$\delta_H = \frac{\nu_H - \nu_{TMS}}{\nu_{spectrometer}} \times 10^6\ ppm$$

$$\delta_H = \frac{585 - 0}{270 \times 10^6} \times 10^6\ ppm$$

$$\boxed{\delta_H = 2.16\ ppm}$$

Question The NMR signal of H spectrum of Benzene is appear at 7.3 ppm from TMS peak using a spectrometer operating at 200 MHz. calculate the frequency in Hz.

Solution

$$\boxed{\delta_H = \frac{\nu_H - \nu_{TMS}}{\nu_{spectrometer}} \times 10^6} \text{ ppm}$$

Given, $\delta_H = 7.3$ ppm

$\nu_{TMS} = 0$

$\nu_{spectrometer} = 200 \text{ MHz} = 200 \times 10^6 \text{ Hz}$

$\nu_H = ?$

$$7.3 = \frac{\nu_H - 0}{200 \times 10^6} \times 10^6$$

$$\nu_H = 200 \times 7.3$$

$$\boxed{\nu_H = 1460 \text{ Hz}}$$

- When using a spectrometer operating at 400 MHz.

Given. $\delta_H = 7.3$ ppm

$\nu_{TMS} = 0$

$\nu_{spectrometer} = 400 \text{ MHz} = 400 \times 10^6 \text{ Hz}$

$\nu_H = ?$

$$7.3 = \frac{\nu_H - 0}{400 \times 10^6} \times 10^6$$

$$\nu_H = 400 \times 7.3$$

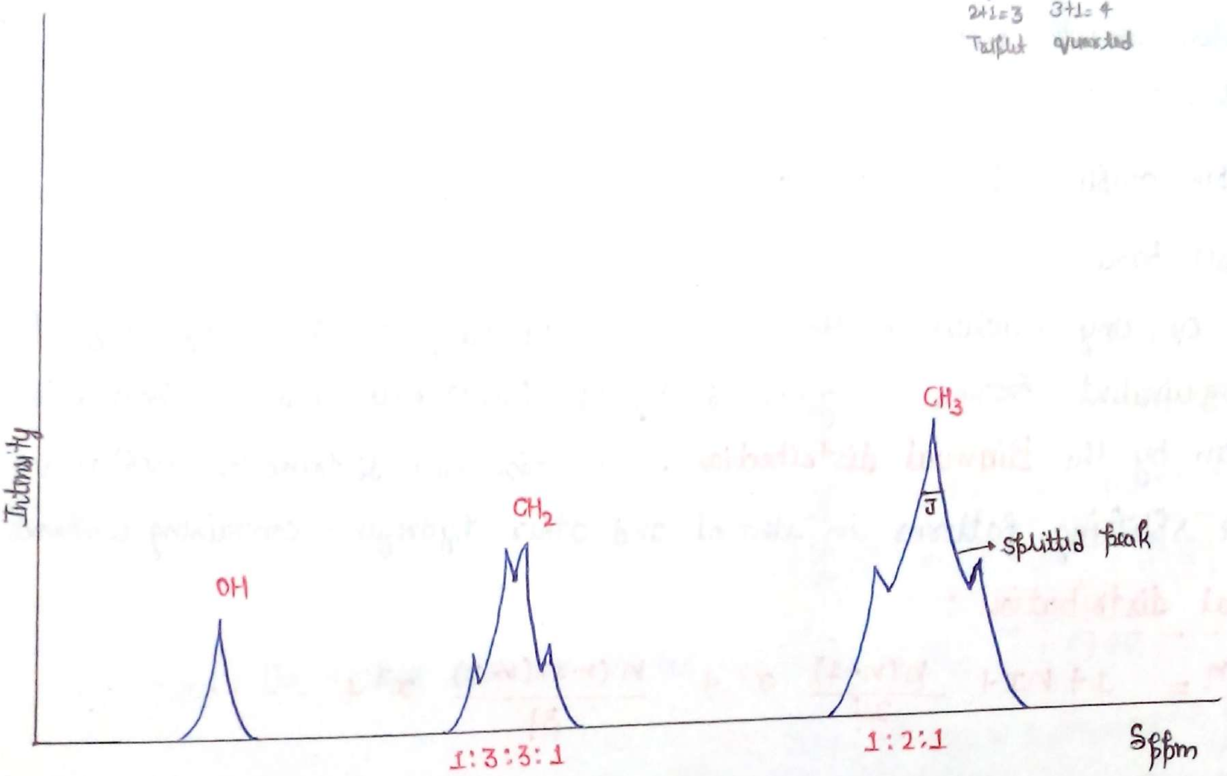
$$\boxed{\nu_H = 2920 \text{ Hz}}$$

$(\nu_H - \nu_{TMS})$ difference increasing with better machine i.e. spectrometer i.e. peak separation increases.

Separation between two peaks is directly proportional to spectrometer frequency therefore field NMR (1000 MHz NMR machine) is important for study of protein solution.

§ SPIN - SPIN SPLITTING OR SPIN- SPIN COUPLING

e.g. At high resolution, the spectrum of ethanol, $\underset{\substack{\downarrow\\2+1=3\\\text{Triplet}}}{CH_3}-\underset{\substack{\downarrow\\3+1=4\\\text{quartet}}}{CH_2}-OH.$



The $-CH_2$ and $-CH_3$ peaks actually consist of four and three splitted peaks, respectively with relative intensities of 1:3:3:1 and 1:2:1. The spacing between each group of splitting peak is independent of the spectrometer.

Each nucleus with $I \neq 0$ has a nuclear magnetic moment and this nucleus can affect the magnetic field experienced by a neighboring nucleus, slightly changing the frequency at which the neighbouring nucleus will undergo NMR absorption.

In the liquid or gas phase where rapid molecular rotation occurs, the direct nuclear spin-spin interaction called direct interaction, averages to zero.

An additional, indirect interaction between the nuclear spins that is transmitted through the bonding electrons. This interaction is unaffected by molecular rotation and causes splitting of the NMR peaks.

The separation between the lines (splitting peak) in each group gives the spin-spin coupling constant (J), whose magnitude is determined by the extent of this magnetic interaction.

The following points are worth noting about spin-spin coupling :

① Nuclei must be magnetically nonequivalent to produce spin-spin coupling.

eg. The protons in the methyl group in ethanol are magnetically equivalent, so they do not interact with each other.

② Spin-Spin coupling is observed only for two nuclei separated by no more than three bonds.

③ For ^1H or any nucleus with $I = \frac{1}{2}$, the splitting of a line by a group of n equivalent protons is governed by the (n+1) rule and the intensities are given by the Binomial distribution. The binomial distribution explains the NMR splitting patterns in ethanol and other hydrogen-containing compounds.

Binomial distribution :

$$(1+x)^n = 1 + nx + \frac{n(n-1)}{2!}x^2 + \frac{n(n-1)(n-2)}{3!}x^3 + \cdots\cdots$$

For CH_2, $n = 2$, $n+1 = 3$ (splitting)

$$(1+x)^2 = 1 + 2x + 1x^2$$

1 : 2 : 1 (Intensity)

For CH_3, $n = 3$, $n+1 = 4$ (splitting)

$$(1+x)^3 = 1 + 3x + 3x^2 + 1x^3$$

1 : 3 : 3 : 1 (Intensity)

* PASCAL'S TRIANGLE

TABLE : The Coefficients of the Binomial Distribution

n	Intensity Ratio	Multiplicity
0	1	Singlet
1	1 1	Doublet
2	1 2 1	Triplet
3	1 3 3 1	Quartet
4	1 4 6 4 1	Quintet
5	1 5 10 10 5 1	Sextet

Example Calculate the nuclear spin angular momentum and the magnetic moment for a proton.

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

$g = 5.585$ (for proton)

$\beta_N = 5.05 \times 10^{-27}\ J\,T^{-1}$

Solution The nuclear spin angular momentum $\mathbf{I} = \sqrt{I(I+1)}\,\frac{h}{2\pi}$

$$\mathbf{I} = \sqrt{\tfrac{1}{2}\left(\tfrac{1}{2}+1\right)}\ \frac{6.626 \times 10^{-34}}{2 \times 3.14}$$

$$\mathbf{I} = \sqrt{\tfrac{1}{2} \times \tfrac{3}{2}} \times 1.055 \times 10^{-34}$$

$$\mathbf{I} = 0.866 \times 1.055 \times 10^{-34}$$

$$\boxed{\mathbf{I} = 9.14 \times 10^{-35}\ J\text{-}S}$$

The nuclear magnetic moment, $\mu = g\,\beta_N \sqrt{I(I+1)}$

$$\mu = 5.585 \times 5.05 \times 10^{-27} \sqrt{\tfrac{1}{2}\left(\tfrac{1}{2}+1\right)}$$

$$\mu = 5.585 \times 5.05 \times 10^{-27} \times 0.866$$

$$\boxed{\mu = 2.44 \times 10^{-26}\ J\,T^{-1}}$$

Example In a spectrometer operating at 1T, the NMR frequency of ^{19}F is 40.06 MHz. Calculate the magnetogyric ratio of ^{19}F.

Solution Given, $B_z = 1T$

$\nu = 40.06\ MHz = 40.06 \times 10^{6}\ Hz$

$\gamma = ?$

$$\gamma = \frac{\omega}{B_z}$$

$$\gamma = \frac{2\pi\nu}{B_z}$$

$$\gamma = \frac{2 \times 3.14 \times 40.06 \times 10^{6}}{1}$$

$$\boxed{\gamma = 2.517 \times 10^{8}\ T^{-1} S^{-1}}$$

Example The magnetic moment of ^{31}P is equal to 1.1305 nuclear magnetons, i.e. 1.1305 β_N. Calculate its magnetogyric ratio and the g-factor.

Given, $\beta_N = 5.05\times10^{-27}\ JT^{-1}$

Nuclear spin of ^{31}P is $\frac{1}{2}$.

Solution

$$\gamma = \frac{\mu}{I\cdot\frac{h}{2\pi}}$$

$$\gamma = \frac{1.1305\times5.05\times10^{-27}}{\frac{1}{2}\cdot\frac{6.626\times10^{-34}}{2\times3.14}}$$

$$\boxed{\gamma = 1.083\times10^{8}\ T^{-1}S^{-1}}$$

$$\because \quad \mu = g\beta_N I \qquad \boxed{\text{For } ^{31}P,\ \mu = 1.1305\ \beta_N}$$

$$1.1305\ \cancel{\beta_N} = g\ \cancel{\beta_N}\times\frac{1}{2}$$

$$\boxed{g = 2.261}$$

Example Calculate the NMR frequency in MHz of the proton (^1H) in a magnetic field of intensity in a magnetic field of Intensity 1.4092T,

Given that, $g = 5.585$

$\beta_N = 5.05\times10^{-27}\ JT^{-1}$

Solution

$$\nu = \frac{g\beta_N B_z}{h}$$

$$\nu = \frac{5.585\times5.05\times10^{-27}\times1.4092}{6.626\times10^{-34}}$$

$$\nu = 60\times10^{6}\ Sec^{-1}$$

$$\nu = 60\times10^{6}\ Hz$$

$$\boxed{\nu = 60\ MHz}$$

Example Calculate the magnetic field strength required to observe the NMR frequency for fluorine (^{19}F) at 60 MHz.

Given. $g = 5.257$ (for ^{19}F)

$\beta_N = 5.05 \times 10^{-27}\ J\,T^{-1}$

Solution

$$\nu = \frac{g\,\beta_N\,B_z}{h}$$

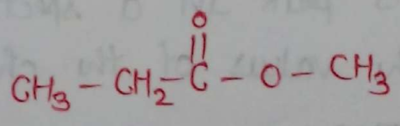
$$B_z = \frac{h\nu}{g\,\beta_N}$$

$$B_z = \frac{6.626\times10^{-34} \times 60\times10^{6}}{5.257\times 5.05\times10^{-27}}$$

$$\boxed{B_z = 1.4973}$$

Example Predict the proton-NMR spectrum of ethyl acetate.

Answer Ethyl acetate :



$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_3$

There is no splitting due to spin-spin interaction of the protons in either of the two methyl groups or in the methylene group.

The CH_2 protons split the CH_3 peak into three lines i.e triplet.
The CH_3 protons split the CH_2 peak into four lines i.e. quartet.

CH_3 : triplet , $\textcircled{n=2}$, $n+1=3$

$(1+x)^2 = 1+2x+x^2$

Intensities → 1:2:1

CH_2 : Quartet , $\textcircled{n=3}$, $n+1=4$

$(1+x)^3 = 1+3x+3x^2+x^3$

Intensities → 1:3:3:1

Example Which of the following nuclei do not show nuclear magnetic resonance:

^{1}H, ^{2}H, ^{12}C, ^{13}C, ^{14}N, ^{15}N, ^{16}O, ^{19}F, ^{31}P, ^{32}S ?

Answer Nuclei that contain odd no. of protons and/or neutron show NMR Spectra.

NMR active → They have half - Integral spin.

Nuclei that contain even no. of protons and/or neutron do not show NMR Spectra.

NMR Inactive → They have Integral spin (in particular zero spin).

NMR Active : ^{1}H (1p, 0n), ^{2}H (1p, 1n), ^{13}C (6p, 7n), ^{14}N (7p, 7n), ^{15}N (7p, 8n)
^{19}F (9p, 10n),

NMR Inactive : ^{12}C (6p, 6n), ^{16}O (8p, 8n), ^{32}S (16p, 16n.

Example A compound shows a proton - NMR peak at 240 Hz down-field from the TMS peak in a spectrometer operating at 60 MHz. What are the values of the chemical shifts δ and τ in ppm relative to TMS?

Solution

$$\delta = \frac{\nu - \nu_{TMS}}{\nu_{spectrometer}} \times 10^{6} \text{ ppm}$$

$$\delta = \frac{240 - 0}{60 \times 10^{6}} \times 10^{6} \text{ ppm}$$

$$\boxed{\delta = 6 \text{ ppm}}$$

$$\because \quad \delta + \tau = 10$$

$$6 + \tau = 10$$

$$\therefore \quad \boxed{\tau = 4 \text{ ppm}}$$