NMR

Nuclear Magnetic Resonance Spectroscopy is an absorption spectroscopy in which sample absorbs electromagnetic radiation in the radio-frequency region ranges from (3 MHz to 30,000 MHZ).

It involves nuclear magnetic resonance which depends on the magnetic property of atomic nuclei.

~~Magnetic Nuclei~~: More than 100 isotopes are so far known which have NMR activity, but the most common nuclei are ^{1}H (Proton) and this is called as Proton Magnetic Resonance & ^{13}C, i.e. called as Carbon magnetic resonance.

Theory :⇒ Proton & Neutrons both have spin quantum number ½ and depending on how these particle pair up in the nucleus, the resultant nucleus may or may not have a net non-zero nuclear spin number.

If the spin of all the particles get paired up the net spin number of the nucleus will be zero. These nucleus are known as non-magnetic nuclei.

All the non-magnetic nuclei are NMR inactive.

⇒ When there is one net unpaired nutron or proton will be present in the nucleus, the nuclear spin will be half. similarly as the number of unpaired nuclear particle increases in the nucleus there will be net non-zero spin quantum number. This type of nucleus is known as magnetic nuclei. All the magnetic nuclei are NMR active.

⇒ The isotopes with either odd mass number or odd atomic number possess a nuclear spin and only such isotopes can exhibit a nuclear magnetic resonance.

Table – spin number of some Isotopes.

Mass Number	Atomic No.	Spin Number	Example
Odd	odd or even	1/2, 3/2, 5/2 } Half integer	$^1H_1$, ^{13}C, ^{15}N, ^{19}F, ^{31}P, ^{11}B, ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br, ^{127}I, ^{17}O
Even	Even	No spin	
Even	odd	1, 3 } Integer	^{14}N, ^2H or (D), ^{10}B

Calculation for I = $^1H_1$ = Nut + Proton , Nuclear spin = spin for P + spin for N

= 1 + 0 ∴ " " = 1/2

= 1 unpaired

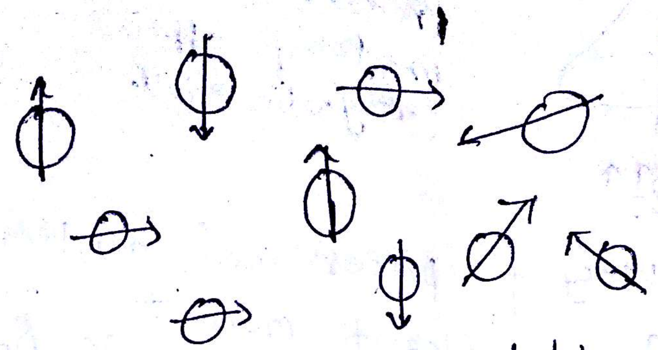
$^{19}F_9$ = Nu + P

19 = Nu + 9 (4 are paired and 1 unpaired) ∴ Nuclear spin = 1/2

Nu = 10 = 5 pair

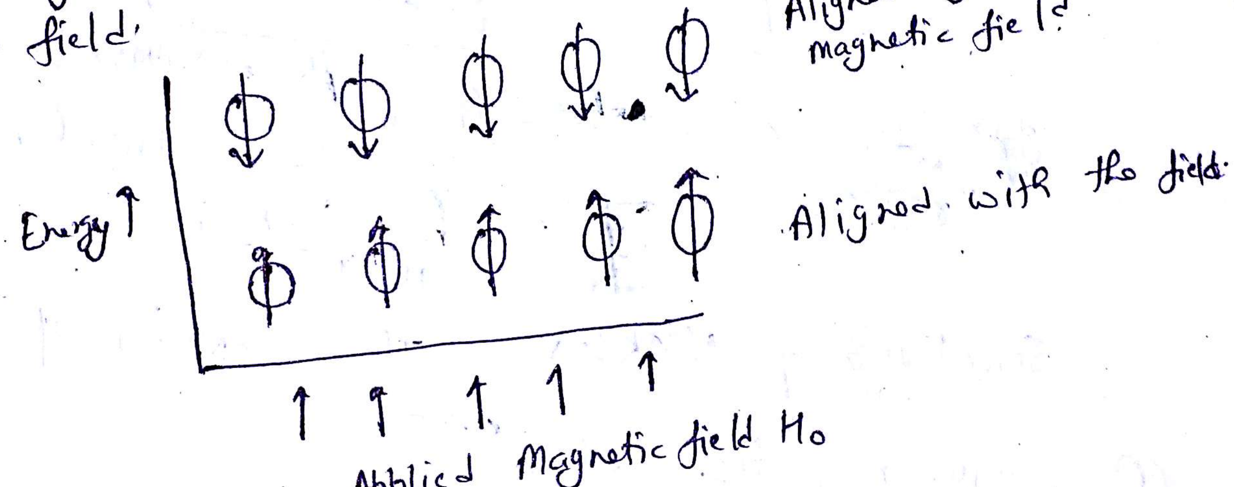
4. Behaviour of Magnetic Nuclei in the Magnetic field : ⇒

Orientation of nuclear magnetic ~~dipole~~ nuclei in the absence of an external magnetic field.



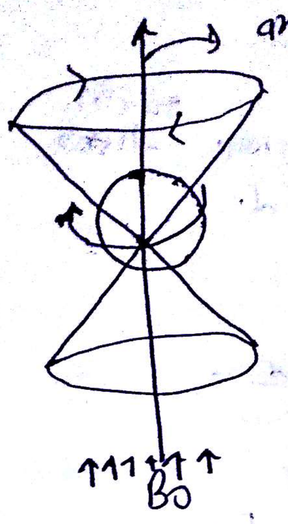
They are randomly oriented.

When an external magnetic fied is applied they will align parallel or antiparallel to the applied magnetic field.



⇒ A nucleus with a magnetic moment can be treated as a tiny bar magnet.

⇒ If this bar magnet is placed in an external magnetic field, the magent starts precesses in the direction of applied magnetic field. This motion is known as precessional motion or gyroscopic motion.



The frequency of precessional motion

$$\nu = \frac{\text{Magnetic moment}}{\text{Angular moment}} \times B_0 \ \text{rad sec}^{-1}$$

$$\boxed{\nu = \frac{\gamma B_0}{2\pi} \ Hz}$$

gyro-magnetic ratio ← note $\gamma = \frac{\mu_0}{I}$ → magnetic moment / Angular moment

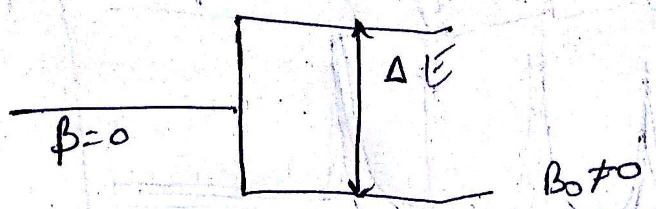
$$I = \frac{h}{2\pi}\sqrt{I(I+1)}$$

Sensitivity of NMR: ⇒ The sensitivity of NMR depends on –

1. Gyromagnetic ratio
2. Applied magnetic field
3. Natural Abundance of the Magnetic Nuclei.

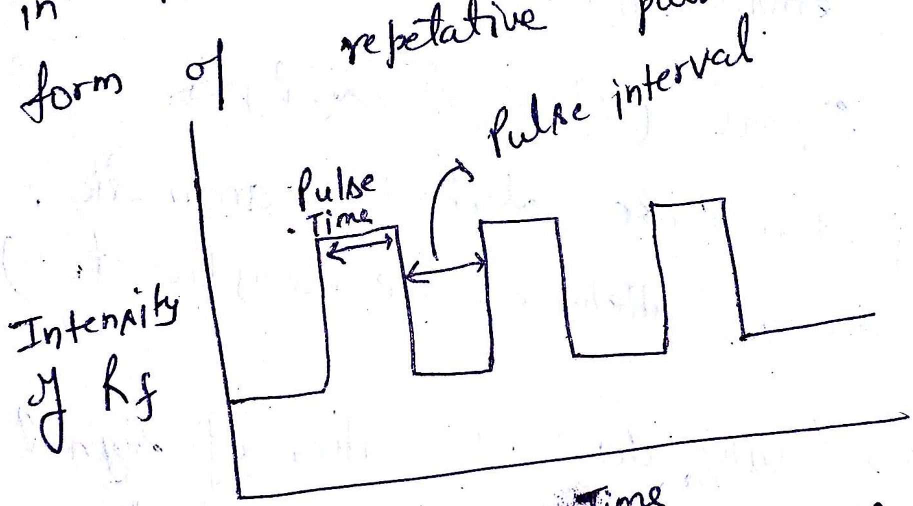
Recording of NMR signal :-

frequency sweep method ⇒ constant magnetic field & Rf turning.

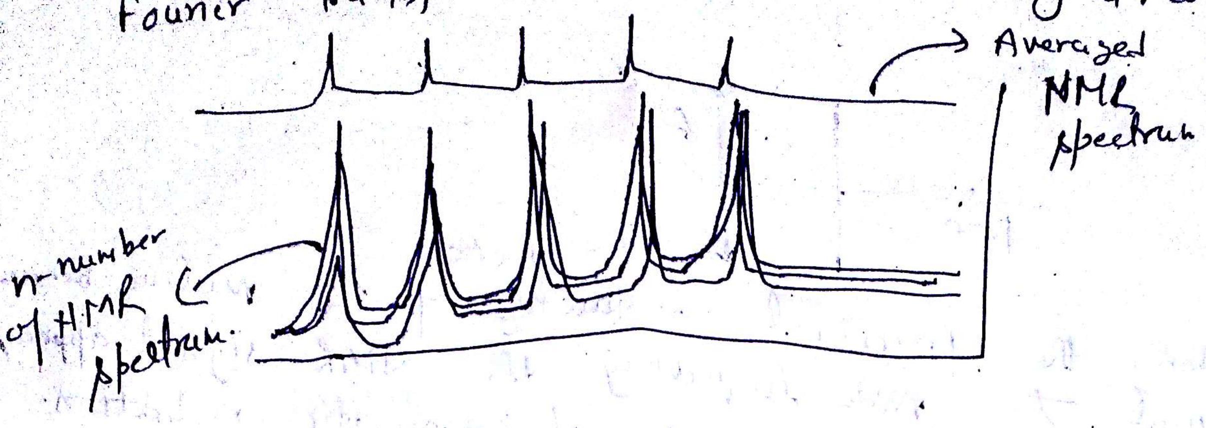


When the precessional frequency of the nucleus becomes equal to radio frequency the NMR signal appears with the absorption of electromagnetic radiation.

Since the population difference in two energy level is very less. So the radiofrequency in NMR recording is always applied in the form of repetative pulse.



with in the pulse Time all the nucleus transits from lower to higher energy level producing the NMR signal while in the pulse interval the relaxation of excited nucleus takes place resulting the population difference again. By repeating the number of pulse we can record n number of NMR spectrum and averaged NMR spectrum can be obtained by fourier transform calculation using a computer



Parameters of NMR :=)

(1) Number of Signal => Number of types of proton in different chemical environment.

(2) Position of Signal (chemical shift) => Types of proton (like aliphatic, aromatic, olefinic, hydroxy, aldehydic, carboxylic etc.)

(3) Area of Signals (Integration) => Area of signal tells about the ratio of number of proton related to different signals.

(4) Splitting of Signal := Number of neighbouring magnetic nuclei

(5) Splitting constant := Gives idea about the relative stereochemistry and identity of neighbouring magnetic nuclei.

Chemically

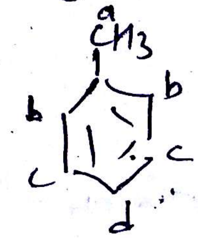
All the chemically equivalent proton gives the same signal in the NMR spectrum.

eg

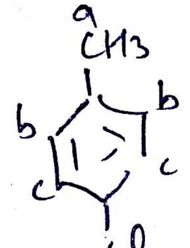
$\overset{a}{CH_3}-\overset{b}{CH_2}-Cl$ — Two signal

$\overset{a}{CH_3}-\overset{b}{CH_2}-O-\overset{b}{CH_2}-\overset{a}{CH_3}$ $\longrightarrow$ Two signal

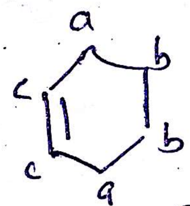
$\overset{c}{CH_3}-\overset{b}{CH_2}-O-\overset{a}{CH_3}$ $\longrightarrow$ Three signal



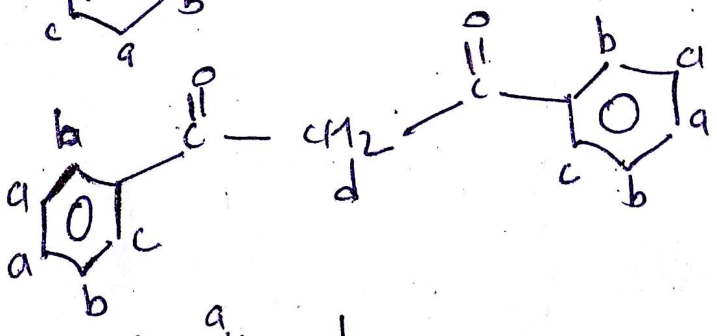
$\longrightarrow$ four signal



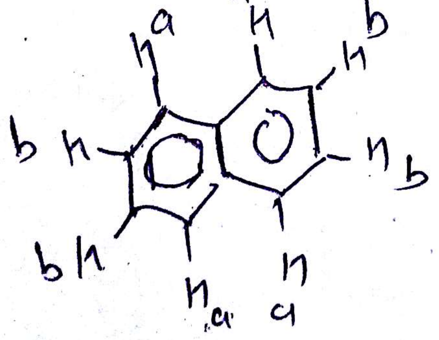
$\longrightarrow$ Three signal



$\longrightarrow$ Three signal



— four signal

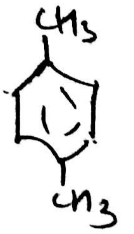


— Two signal

ans $CH_3-CH_2-CH_2-Cl$ $CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3$

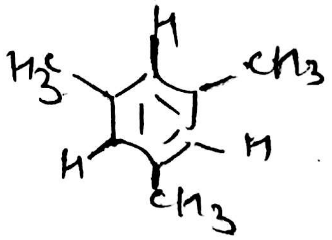
$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

ans p-xylene & two isomer of $C_2H_4Cl_2$



$H_3C-CH-Cl_2$

& $Cl-CH_2-CH_2-Cl$

ans Mesitylene – 

ethyl succinate — $CH_2-COO\,CH_2-CH_3$