NMR Spectroscopy

Q) What is nmr - Spectroscopy ?

* A spectroscopic tool that exploite the magnetic properties of certain nuclei to decipher the structure & properties dynamics of molecules.

It is most versityle toole in the hands of organic chemists It provides lots of information regarding structure of molecules, so it helps in

* Also used for studying the interaction between molecules.

It is find that vary wide range of applications that beauty of thee particular technique.

Importance of NMR Spectroscopy:-

* The number of different types of the NMR active nuclei being probed in a molecule.

ex

Suppose i looking for a molecule, then how many types of proton in a molecule there.

* The relative number (Signal integration) of each type of the active nuclei.

* The chemical environment (chemical shift) of each type of the nucleus and

Different types of protons over there what kinds of chemical environment there in either they are electro positive environment or electronegative environment all those things can be decided from the spectrum.

* The interaction (coupling), if any between different types of neighboring nuclei.

another things is that if you two different kinds of proton and nucleii which are NMR active if they are coupling & interacting with eachother that also onto the spectrum.

* This gives a reach source of information in the organic chemistry.

Basis for NMR

- Zeeman observed that certain isotopes when placed in an external magnetic field give rise to multiple spin states
- This splitting of energy levels in an external magnetic field is called Zeeman effect and forms the basis for NMR.
- The Zeeman effecte for a nucleus depends on its spin quantum number.

Nuclei that are NMR active?

* The type of nuclei active in NMR is determined by their spin.
* The spin of the nuclei in turn is determined by their composition (Number of protons and neutrons).
* The nuclei can be divided into three groups on the basis of their spin quantum Nos.

Group 1: Nuclei with both Z & N even (⇒ A is even)
⇒ All proton spins & the neutron spins are paired
⇒ Net nuclear spin is No, I = 0
⇒ Invisible to NMR

Z = atomic number
N = No of neutrons
A = mass number

All the nuclear are paired and protons are paired then net quantum no will be zero it is invisible to NMR spectrum.
Spherical non-spinning nuclei, I = 0
^{12}C, ^{16}O, ^{18}O & ^{32}S which are not active in NMR

Group 2: Nuclei with both Z and N odd (–A is even).
⇒ Such nuclei have odd number of unpaired protons & odd number of unpaired neutrons (the two pair up individually)

⇒ As consequences the net magnetic spin will be non zero.
⇒ Such nuclei detected by the NMR, however not the main nuclei.

Group-3 Nuclei with even Z & odd N or vice versa (⇒ A is odd)

⇒ Such nuclei may have even number of proton spins (all paired up) and odd number of unpaired neutrons spin & vice versa

⇒ Net nuclear magnetic spin would be odd integral multiple of $\frac{1}{2}$.

⇒ Detectable and useful in NMR.

Spherical spinning nuclei $I = \frac{1}{2}$ are the most imp. eg ^1H, ^{13}C, ^{15}N & ^{19}F

Nuclear Composition and Nuclear spin quantum number

no of protons	Num of neutrons	Spin quantum Number I
Even	Even	0
odd	odd	Integer (1, 2, 3)
Even	odd	Half integer ($\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$)
Odd	Even	Half integer ($\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$)

What happenes to the nuclei when spin quantum

no is half ?

A spinning spherical nucleus has an associated angular momentum that is given by the symbols (I) this angular momentum give the magnitude of nuclear spin angular momentum

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

I = nuclear spin quantum no

I is the magnitude of spin angular momentum.

A spinning charged nucleus also has an associated magnetic moment, μ. The magnetic moment, μ of a spinning nucleus proportional to its spin angular momentum (I)

$$\mu = \frac{g_N e}{2m_p} I$$

where g_N is the g-factor, a characteristic of the nucleus.
e is the charge on a proton
m_p is the mass of the proton
→ $\mu = \gamma I$ is called gyromagnetic ratio

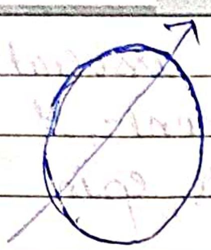
$$\gamma = \frac{g_N e}{2m_p}$$

Magnitude of magnetic moment, μ
Substituting the value of I

$$\Rightarrow |\mu| = \gamma\sqrt{I(I+1)}\,\hbar$$

→ Since the nucleus is having a +ve charge on that particle μ & I both of point in the same direction.
Alternatively we can written as ⇒ $g_N \mu_N \sqrt{I(I+1)}$

$\mu_N = \frac{e\hbar}{2m_p}$ is called Nuclear magneton the unit for expressing magnetic dipole moments of nuclei.



$|\mu| = g_N \sqrt{I(I+1)}\ \mu_N$

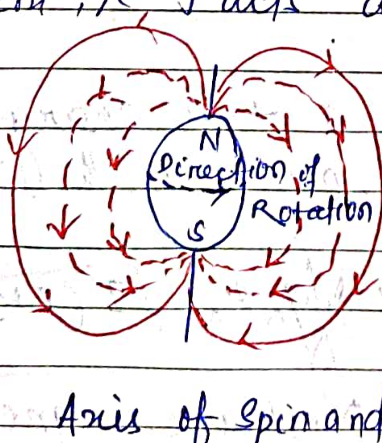
$\mu_N = 5.0507 \times 10^{-27}\ JT^{-1}$ is the unit for magnetic field

Now lets go further where we have come what is NMR / whats the importance of NMR then we talk about what kinds nuclei are going to be useful for me.

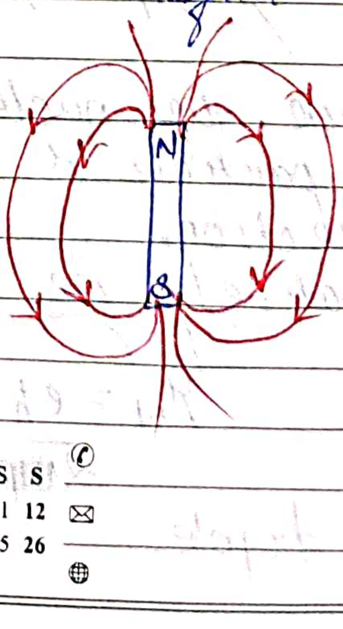
The nuclei are useful for me that which have $I = \frac{1}{2}$ and having spherical shape nuclei have an associated with angular momentum with magnetic momentum.

As we talk about spectroscopy we have to talk about the Energy level for the transition of Electron.

\# A spinning spherical nucleus having a magnetic moment, μ acts as a tiny bar magnet



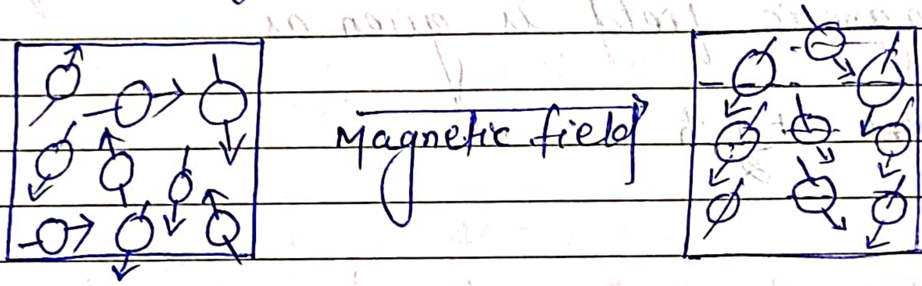
magnetic lines of force



Axis of Spin and of the magnetic moment

If you look at a spinning nucleus the magnetic moment associated with it (as it similar to the bar magnet we can say that spinning nucleus behave like as a Bar magnet.

The nuclei in the sample move in all direction (means they move randomly but in the presence of applied magnetic field the nuclear spins allign themselves



In the absence of field all orientations possible but in presence of magnetic field the arranged them selves in a two ways (i) alligned themselves with the magnetic field (ii) Opposed the magnetic field (against)

* Two orientations aligned with the field or against it

Thus the spin of nucleus can be quantised
* The nuclear spin magnet is a quantum particle
→ Unlike a small bar magnet it may take up only certain allowed orientations.

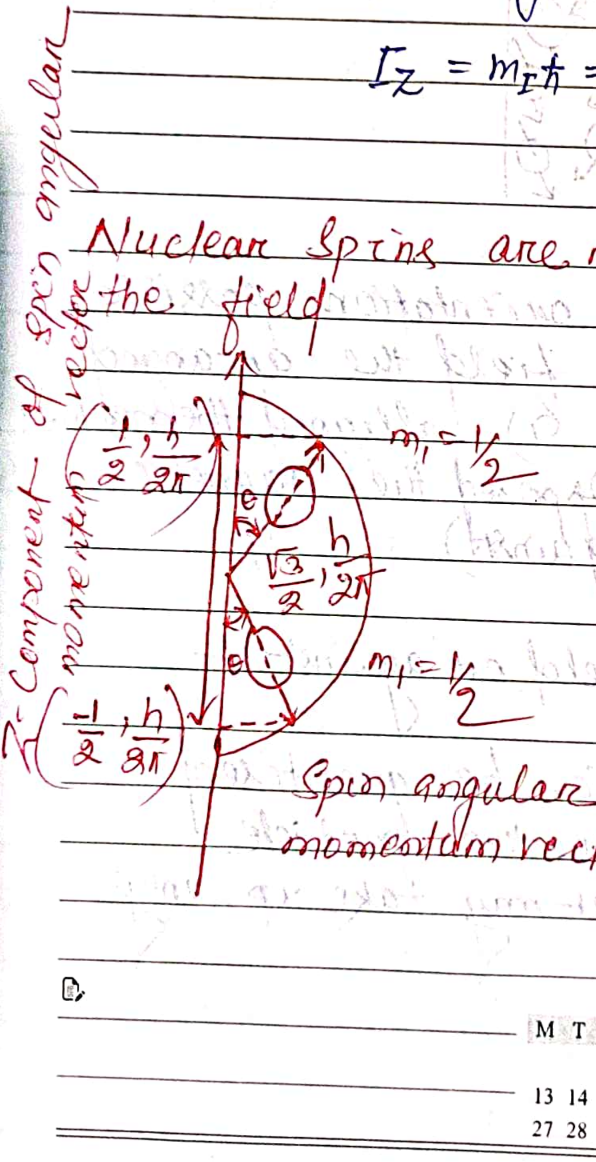
→ A nucleus with spin quantum number, I when placed in an external magnetic field, can assume $(2I+1)$ orientations.

→ Thus, for $I = \frac{1}{2}$, there are two orientations
$$[(2I+1) = (2 \times \tfrac{1}{2} + 1) = 1 + 1 = 2$$

→ The z - component of spin angular momentum I_z is quantized & its value in the direction of the applied magnetic field is given as

$$I_z = m_I \hbar = \pm \frac{1}{2} \hbar$$

Nuclear Spins are not truly aligned with or against the field



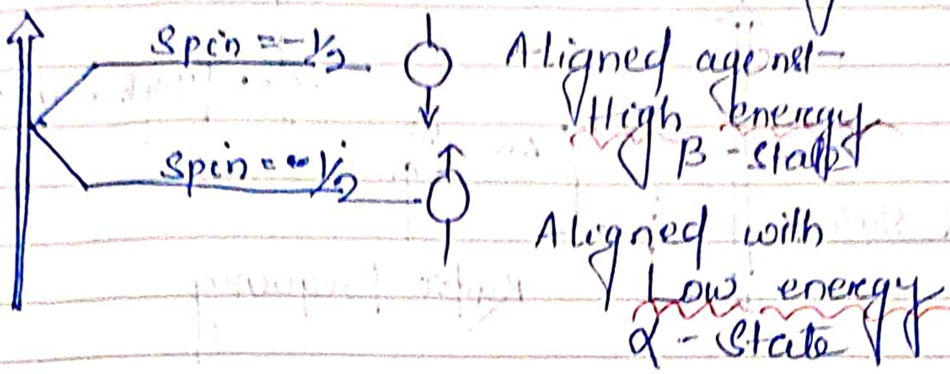
for $I = \frac{1}{2}$ $|\mu| = \gamma \frac{\sqrt{3}}{2} \hbar$

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

$m_I = +\frac{1}{2}$ & $-\frac{1}{2}$

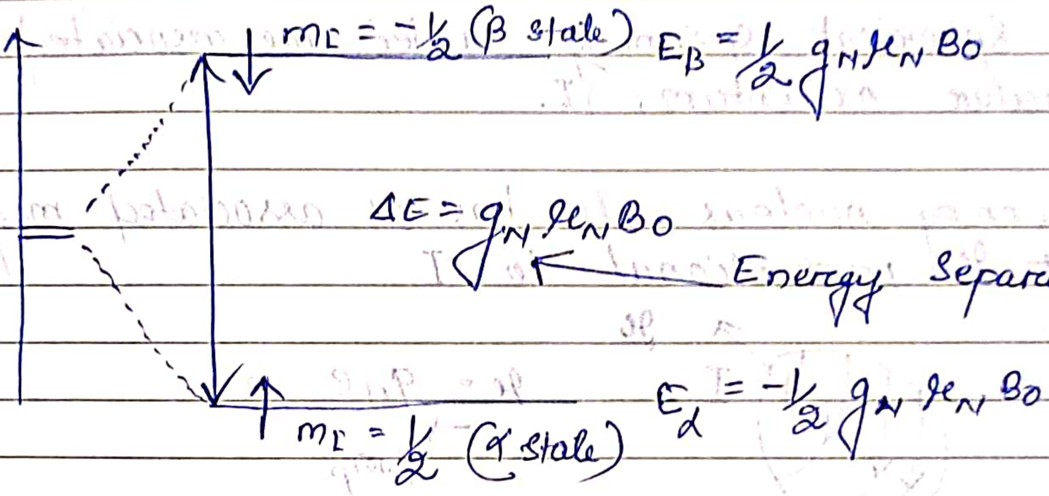
$I_z = \frac{1}{2}\hbar$ & $-\frac{1}{2}\hbar$

Different orientations of the nuclear magnetic moment for the nuclei are associated with different energies.



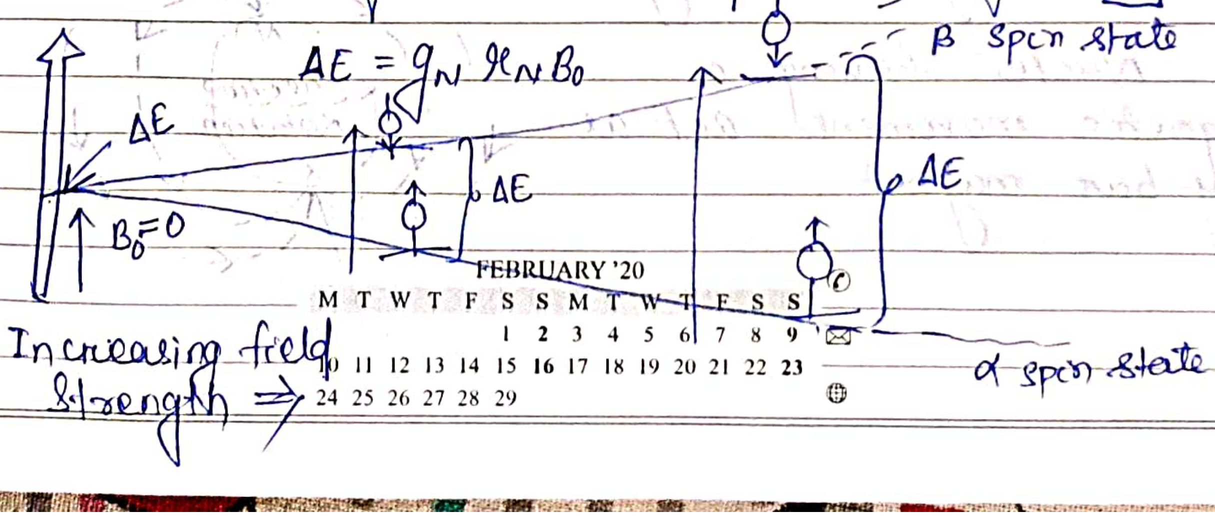
The energies depend on μ_z and B_0

$$E = \mu_z \cdot B_0 = \pm \frac{1}{2} g_N \mu_N B_0$$

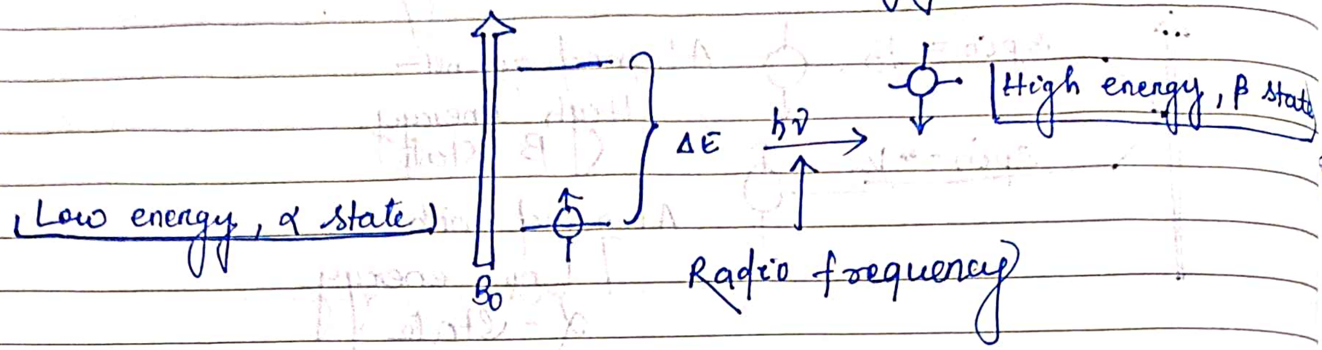


The energy difference of the two levels depend on applied field, B_0

$$\boxed{\Delta E} = \left(\frac{1}{2} g_N \mu_N B_0 - \left(-\frac{1}{2} g_N \mu_N B_0\right)\right) = g_N \mu_N \boxed{B_0}$$



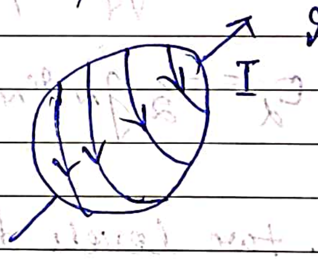
EM radiation in the radiofrequency region can cause transition amongst these energy levels



→ The nuclei with spin quantum number $I = \frac{1}{2}$ (^{1}H, ^{13}C, ^{15}N & ^{19}F) are active in NMR

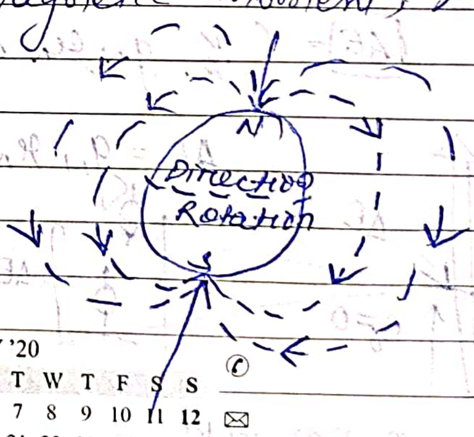
→ These spherical, spinning nuclei are associated with an angular momentum, I.

→ The spinning nucleus also has an associated magnetic moment, μ proportional to I



$$\mu = \frac{g_N e}{2m_p} I$$

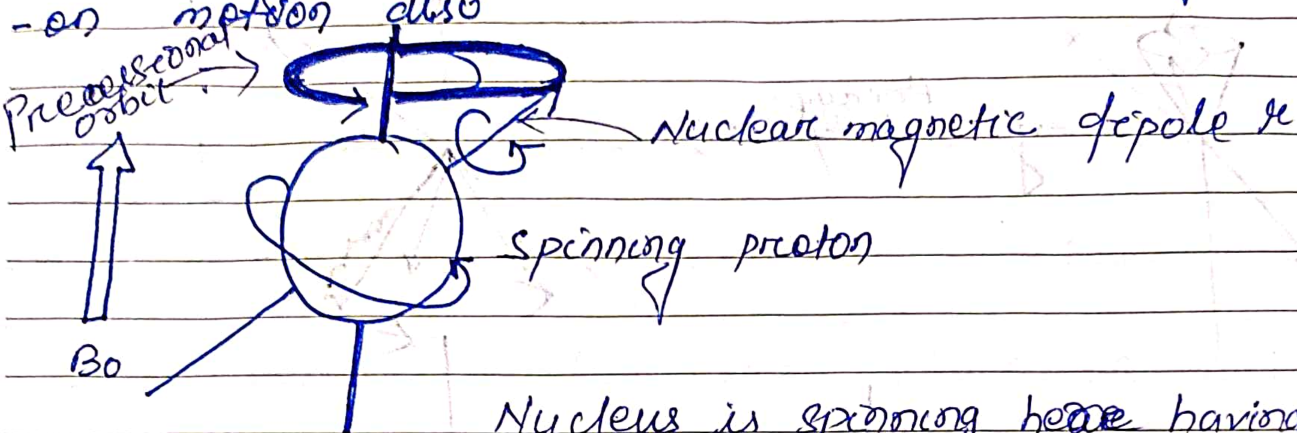
12 Sunday → Such nuclei with magnetic moment, μ act as tiny bar magnets.



exp Nuclei having a magnetic movement act as teeny bar magnet

Precessional motion of Nucleus.

In the magnetic field the nuclear spin undergoes a precessi-on motion also



Nucleus is spinning hence having magnetic moment also precessing as well

→ The magnetic moment vector at an angle w.r.t Bo, experiences a torque.

→ This causes it to precess about the direction of the magnetice field.

→ Called laremour precession

→ The laremour Precessional frequency is directional proportional to the strength of the external magnetic field (B_0)

$$\omega \propto B_0 \qquad \omega = \gamma B_0$$

The normal frequency, ν & the precessional frequency ω are related as

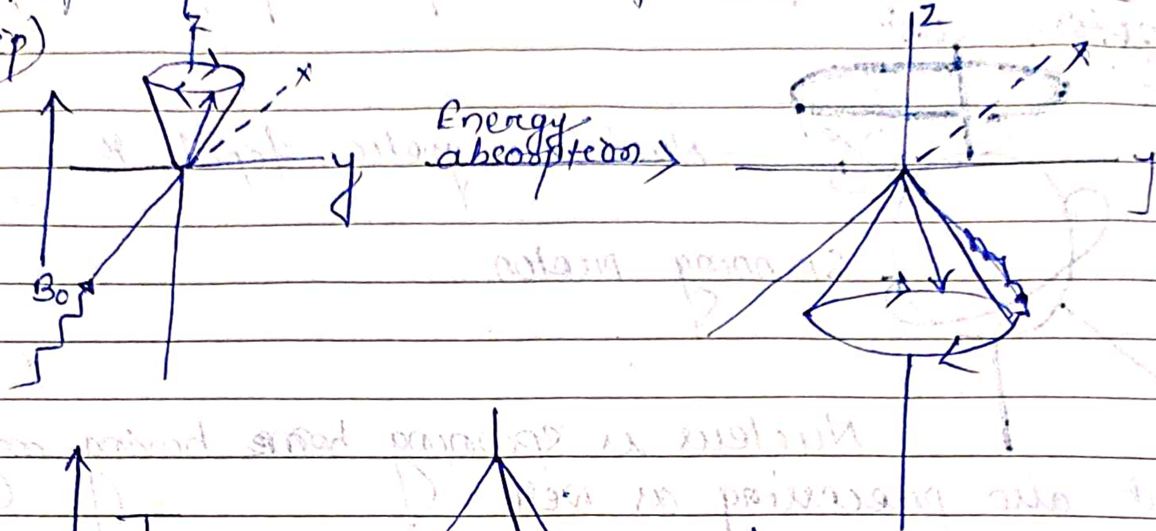
$$\omega = 2\pi\nu = \gamma B_0$$

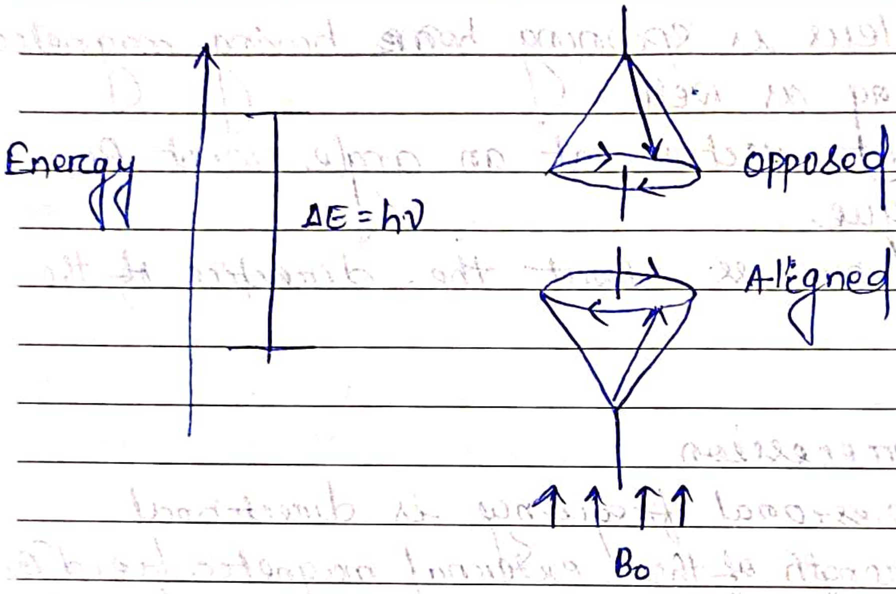
$$\nu = \frac{\gamma B_0}{2\pi} = \frac{B_0}{2\pi}\frac{\mu}{I}$$

$$\nu = \frac{g_N \mu_N B_0}{h}$$

→ Recall it is the same as the frequency of radiation required to cause a transition between nuclear spin states.

⇒ This provides a mechanisms for the transition (Spin flip)





That we will provide Radio frequency it absorbe with the nuclei of spin flip takes place.

We got two energy levels their certain collections of nucleus spins are their, will be distributed amongs this level accoding to Boltzman law

* The nuclear spins distributed in the two energy levels according to Boltzmann law

Boltzmann law $\frac{n_2 \text{ (upper)}}{n_1 \text{ (lower)}} = e^{(-\Delta E/KT)}$

→ ΔE is the energy difference between the energy levels

→ k is the Boltzmann constant $(= 1.380658 \times 10^{-23}\ J/K)$

The population difference between the levels is very small

→ The ratio (n_2/n_1) for protons is a magnetic field of 1.5 T at room temperature (300K)

The energy difference

$$\Delta E = g_N \mu_N B_0$$

$$= 5.585 \times (5.05 \times 10^{-27}\ JT^{-1}) \times 1.5\ T$$

$$\Delta E = 4.23 \times 10^{-26}\ J$$

ΔE value is very small & if you go further to work out since ΔE is very small

Since $\Delta E/KT$ is very small

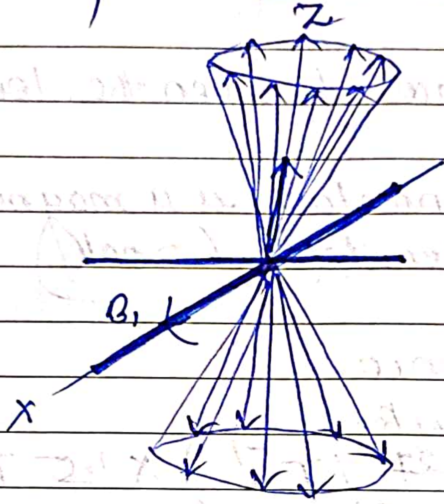
$$e^{(-\Delta E/KT)} \approx (1 - \Delta E/KT)$$

$$= 0.9999$$

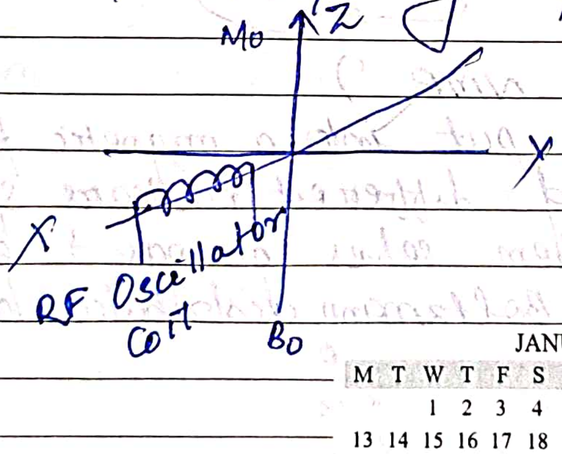
What is resonance in NMR?

I have taken a sample put into a magnetic field when put into magnetic field different nuclears spins they distribute among them selves amongs the energy level their according to Boltzmann distribution law.

As a consiquences of it what happed is that more no of spins alligned with the magnetic field & less spins which will be opposed the field. Since there are more no spins alligned with the ~~field~~ field net magnetisation in the direction field them.

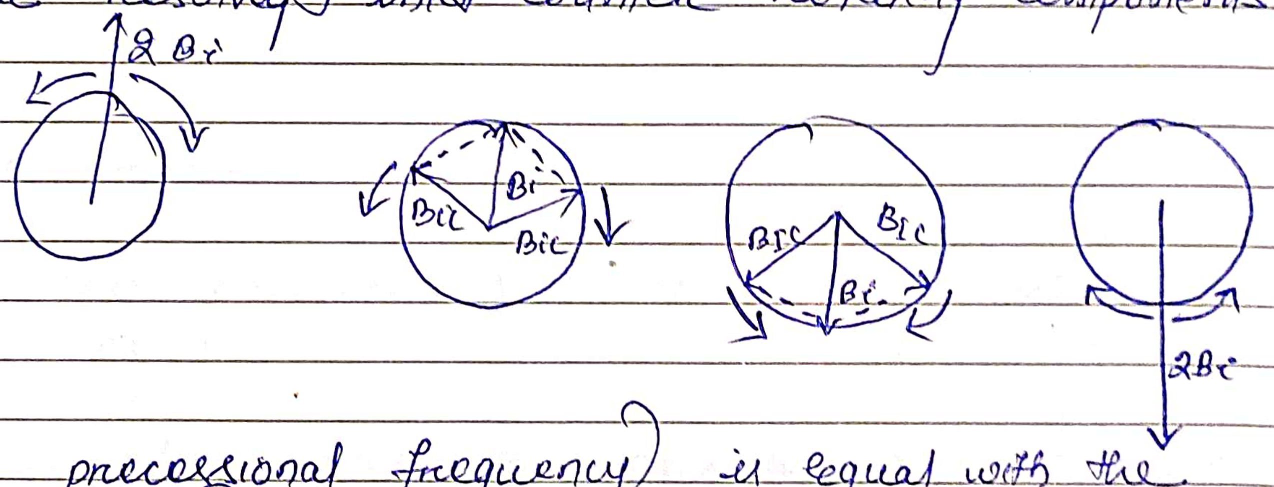


That is the consequences of distribution of nuclears spins amongst the various energy level. But our issuse is we want to kind of excute transitions their inorder to do a transition their we need to supply energy, that energy is supplied interms of radiofrequency wave. That radio frequency applied the



x-axis, our nucleus spins are alligned the net magnetisation M_0 in direction of B_0 & I applying a radio frequency along the x-axis there. Radio frequency basically em radiation (that there is a electrical component & there is a magnetic component) out of two componest only magnetic component which is of interest there. So oscilating magnetic field which is comeing there, the oscillating field has to come & interact with kind of a spin magnetisation alligned with field over there.

* The oscillating magnetic field of the radiofrequency can be resolved into counter rotating components.



When precessional frequency is equal with the radio-frequency then two becomes resonate there is energy absorption.

Resonance means that stage at which the frequency of the applied radion frequency and the precessional frequency match exactly that stage is called resonance.

If continuously radio (frequency) was given to a time will come population of both the stage is equal that is refers to as saturation of excited state and there will be no absorption.

* The nuclear spins relax to maintain the population difference.

There are two mechanisms of relaxation

→ Spin lattice relaxation

→ Spin-spin relaxation

19 Sunday

Question of NMR ?
Short Question

1) Which types of nuclei show magnetic properties for the purpose of NMR spectroscopy ?

2) Define chemical shift ?

3) Why T.M.S used as a standard reference ?

4) What is anisotropic effect ?

5) Define spin-spin coupling ?

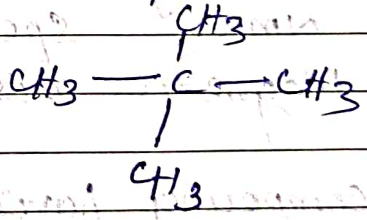
6) What is coupling constant j ?

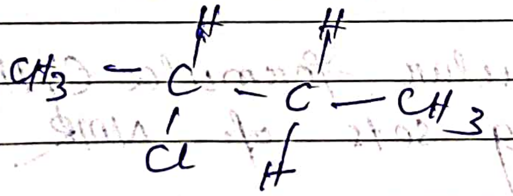
7) Define precessional frequency ?

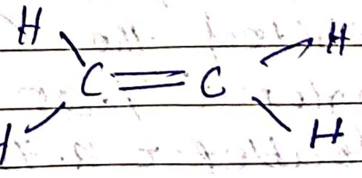
8) Write two characteristics of a solvent used in N.MR spectroscopy ?

9) Indicate the number of signals you expect for the compounds given below ?

(i) $CH_3-CH_2-CH_2-CH_3$

(ii) 

(iii) 

(iv) 

Long Question :-

1) Describe the theory of nmr spectroscopy. what information can be obtained from the nmr absorption peaks?

2) What is meant by the term chemical shift? Name the various factors on which the value of chemical shift depends?

3) Short Notes on
(a) Name some important solvents in nmR spectroscopy. what are the important characteristics of solvent used in this technique.
(b) Why TMS used as a standard referen

4) Write Notes on
(a) Equivalent and non equivalent protons?
(b) Shielding and Deshielding of protons?

5) (a) What do you understand by the term in relation to NMR spectroscopy?
(i) magnetic anisotropy (ii) Spin - Spin Splitting

6) A compound having molecular formula $C_9H_{11}Br$ exhibited the following sets of NMR data.
(i) Singlet τ 7.25 5H
(ii) Doublet τ 2.75 2H
(iii) Multiplet τ 3.40 1H
(iv) Doublet τ 1.45 3H

Q7) Write important applications and limitations of NMR Spectroscopy?

MCQ FOR NMR Spectroscopy

1) IN NMR if the atom contain two near by proton then these will produce?
(i) Doublet (ii) Triplett (iii) Quartet
(iv) All of these

2) IN NMR if the atom contain three near by proton then these will produce?
(i) Doublet
(ii) Triplets
(iii) Quartet
(iv) All of these

3) Transition metal in NMR spectroscopy is
(i) Ferromagnetic
(ii) Paramagnetic
(iii) Diamagnetic
(iv) All of these

4) Which of the following has the lowest chemical shift value?
(A) CH_3I
(B) CH_3Br
(C) CH_3F
(D) CH_3Cl

5) The distance between the centers of the peaks of doublet is called as ?
(a) Coupling constant
(b) Spin constant
(c) Spin - spin coupling
(d) chemical shift

6) H_2, CH_4, C_2H_6 and C_6H_6 exhibit which PMR spectra ?
(a) Singlet
(b) Doublet
(c) Triplet
(d) Quintet

7) The nuclei that doesn't give NMR signal is
(a) 15N
(b) 11B
(c) 19F
(D) 31P

8) Signal splitting in NMR arises from
(A) Shielding effect
(B) Spin - Spin decoupling
(C) Spin - Spin Coupling
(D) Deshielding effect

9) Which of the following solvent is not used in NMR ?
(A) D_2O (B) $CHCl_3$
(C) CCl_4 (D) $CDCl_3$

10) Select the nuclei that can produce NMR signal

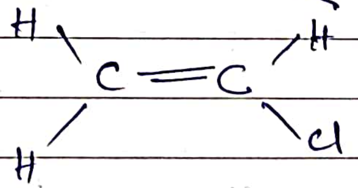
(a) $^{1}_{1}H$ (b) $^{11}_{5}B$

(c) $^{19}_{9}F$ (d) $^{14}_{7}N$

(A) A, D
(B) B, D
(C) A, C
(D) B, C

11) More the sheelding effect
(A) Lower the chemical shift
(B) No change in chemical shift
(C) Higher the chemical shift
(D) More the peak splitting

(12) The number of NMR signals possible for vinyl chloride in 1H NMR is



(A) 1
(B) 2
(C) 3
(D) 4

13) Enantiotropic protons are
(A) Chemically equivalent
(B) Magnetically equivalent
(C) Both A & B
(D) Does not give NMR Signal

14) In proton NMR spectroscopy, Hydrogen bonding results in
(A) Shielding effect
(B) Deshielding effect
(C) peak splitting
(D) All of the above

15) Which of the following main component of mass spectroscopy deal with resolving the ions into their characteristics mass components according to their mass-to-charge ratio?
(A) Ion Source
(B) Analyzer
(C) Detector system
26 Sunday (D) Analyzer tube

16) Who discovered the mass spectrometer
(A) Francis Aston
(B) J.J Thomson
(C) Ernest O. lawrence
(D) Walter kaufmann

17) In which state of matter mass spectroscopy is being performed?

(A) solid (B) liquid (C) Gaseous (D) plasma

(18) What are the main criteria on which mass spectrometer used for?
(A) Composition in sample
(B) Relative mass of atoms
(C) Concentration of elements in the sample
(D) properties of sample

19) Separation of ions in mass spectrometer take place on the basis of which of the following?
(A) Mass
(B) Charge
(C) molecular weight
(D) mass to charge Ratio

20) What is use of mass spectroscopy?
(A) Determination of molecule weight
(B) Elucidating the chemical structure of molecules
(C) A & B
(D) None of the Above

M	T	W	T	F	S	S	M	T	W	T	F	S	S
					1	2	3	4	5	6	7	8	9
10	11	12	13	14	15	16	17	18	19	20	21	22	23
24	25	26	27	28	29								

13) Q1) Mass spectra is also called
(A) Positive ion spectra
(B) Line spectra
(C) A & B
(D) None of the above

14 Q2) Highest m/z peak in mass spectrum is called as
(A) Base peak
(B) Fragment peak
(C) isotopic peak
(D) parent peak

15 Q3) Mass spectrometer requires
(A) High temperature
(B) High cooling
(C) High vaccum
(D) High pressure

Q4) Which ratio measured by mass detector?
(A) Z/m
(B) e/m
(C) m/e
(D) m/z