NMR   Mitali Dewan / B. Sc Chem(H) / SEM IV / CC-19

NMR- Spectroscopy.

* NMR spectroscopy deals with what?

Ans. NMR spectroscopy deals with nuclei.

* NMR spectroscopy deals with what type of nuclei?

Ans. It deals with those nuclei which behave as tiny magnets.

* which nuclei do behave as tiny magnets?

Ans. Those nuclei which possess mechanical spin or angular momentum behave as tiny magnets. Since such a nucleus contains a +ve charge and if it spins around its axis it would produce a magnetic field. The total angular momentum would depend on the spin no. (I) which may have values 0, ½, 1, 3/2, 5/2, 2, 3 .... etc. depending on the particular nucleus. The numerical value of spin no. I is related to the mass no. & atomic no. of the nucleus. From this relation nuclei can be divided into three (3) type –

Type	Mass no.	At. no.	Spin no.	Examples
Type-1	odd	even or odd	½, 3/2, 5/2 etc.	$_1H^1$, $_6C^{13}$, $_7N^{15}$, $_9F^{19}$, $_{14}Si^{29}$, $_{15}P^{31}$, $_{47}Ag^{107}$, $_{50}Sn^{119}$, $_{80}Hg^{199}$ (all have $I = 1/2$) $_{17}Cl^{35}$, $_{17}Cl^{37}$, $_5B^{11}$ ($I = 3/2$) $_8O^{17}$, $_{53}I^{127}$ ($I = 5/2$)
Type-2	even	odd	1, 2, 3 etc.	$_1H^2$, $_7N^{14}$ ($I = 1$) $_5B^{10}$ ($I = 3$)
Type-3	even	even	0	$_6C^{12}$, $_8O^{16}$ ($I = 0$)

protons of organic compound.

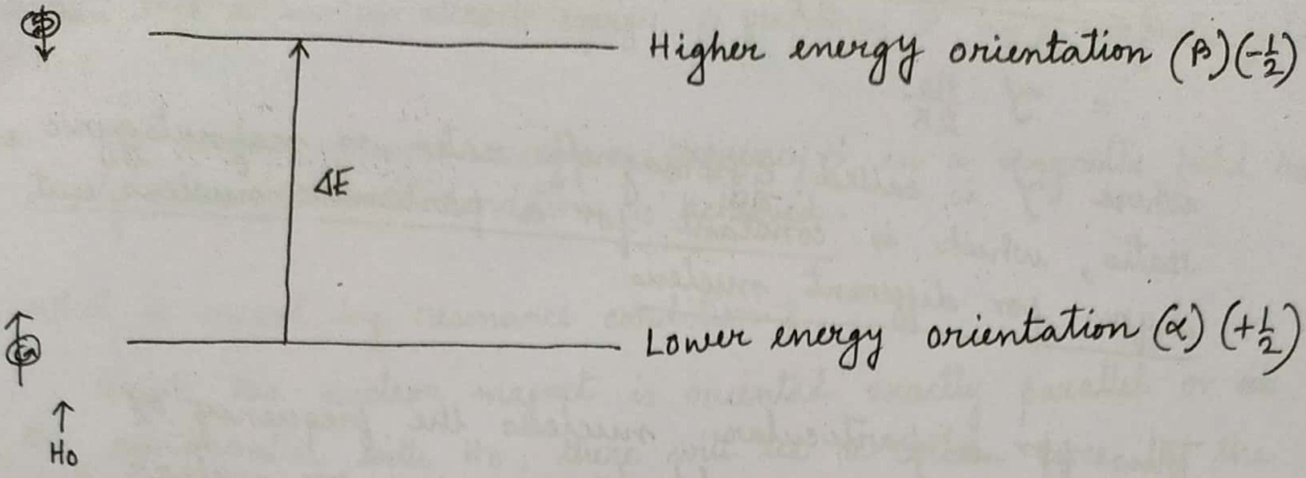
Nuclei of type 1 and type 2 having $I \neq 0$ behave as tiny magnets and can be studied by NMR spectroscopy, while nuclei of type-3 having $I = 0$ do not come under preview of NMR spectroscopy. Since their nuclei do not possess mechanical spin.

* Why is it necessary for a nucleus to behave as a tiny magnet to be studied by this spectroscopy?

Ans: This is because when such a tiny nuclear magnet is placed in a uniformed external magnetic field it takes up any one of the possible orientation given by the no. $(2I+1)$ (where I is spin no. of the nucleus) each orientation being characterised by a definite energy level. This provides a situation where it is possible induce nuclear transition from a lower to higher energy orientation by the absorption of energy of appropriate frequency and corresponding to this absorption of energy one gets a signal.

Thus for ${}_1H^1$ (or any other nucleus having $I = 1/2$) the no. of such possible orientation that the nuclear magnet can assume when placed in a uniformed magnetic field $= 2 \times \frac{1}{2} + 1 = 2$

One is lower energy and the other is a higher energy orientation as shown below.



It is now possible to induce a transition of the nucleus from the lower energy state to the higher energy state by absorption of energy of appropriate frequency and corresponding to this absorption of energy ($\Delta E = h\nu$) one gets a NMR signal for the nucleus.

* what is the nature of the frequency of energy that is necessary to induce such a nuclear transition and how is it related to the strength of the applied magnetic field H_0 ?

Ans. This is given by the following relation —

$$\Delta E = h\nu = \frac{\mu \beta_N H_0}{I}$$

where μ = magnetic moment of the nucleus

β_N = constant called Bohr magneton

h = Planck's constant

I = Spin no. of the nucleus

H_0 = Strength of the applied magnetic field

$$\therefore \ \nu = \frac{\mu \beta_N 2\pi}{h I} \times \frac{H_0}{2\pi}$$

$$= \gamma \cdot \frac{H_0}{2\pi}$$

where γ is called Gyromagnetic ratio as magnatogyric ratio, which is constant for a particular nucleus but differs for different nucleus.

Thus for a particular nucleus the frequency of energy (ν) which would be necessary for nuclear transition, is directly proportional to the strength of the applied magnetic field H_0 i,e $\nu \propto H_0$

For a magnetic field strength of 7·1 tesla (H_0) ν is 300 MHz /sec. i,e 300×10^6 Hz/sec. i,e the frequency of energy necessary to induce such nuclear transition falls in the radio-frequency region.

A radio frequency oscillator having capacity matching with the applied magnetic field may serve as the source of energy.

H_0 (Tesla)	1·4	2·1	2·3	5·1	5·8	7·1	9·2	11·5
$^1H_1$	60 MHz	90 MHz	100 MHz	220 MHz	250 MHz	300 MHz	400 MHz	500 MHz
^{13}C	15·1 MHz	22·6 MHz	25·2 MHz	55 MHz	62·9 MHz	75·5 MHz	100·8 MHz	126 MHz

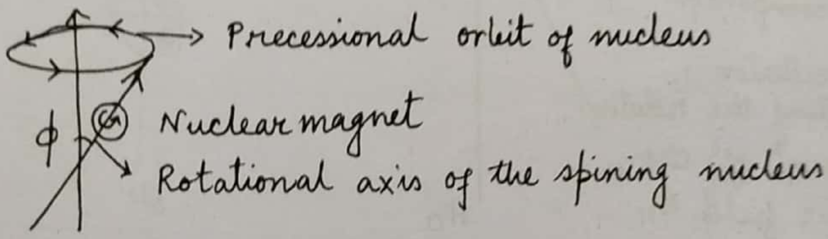
1 Tesla = 10^4 gauss

* When does a nucleus absorb energy of frequency ν in a magnetic field H_0?

Ans: The nucleus absorbs energy of frequency ν in a magnetic field H_0 only when resonance condition is achieved.

* What is meant by resonance condition?

Unless the nuclear magnet is oriented exactly parallel or ~~at~~ the antiparallel with H_0, there will be a certain force by the external magnetic field to orient it but ~~because~~ as the nucleus is spining, the effect is that, its rotational axis draws out a circle perpendicular to the applied magnetic field as shown in fig.



This motion of the nucleus is called precession. The nucleus thus has a precessional frequency. The common example of this type of gyroscopic motion is a common top which precess when spin with an initial axis of rotation different from earth gravitational force.

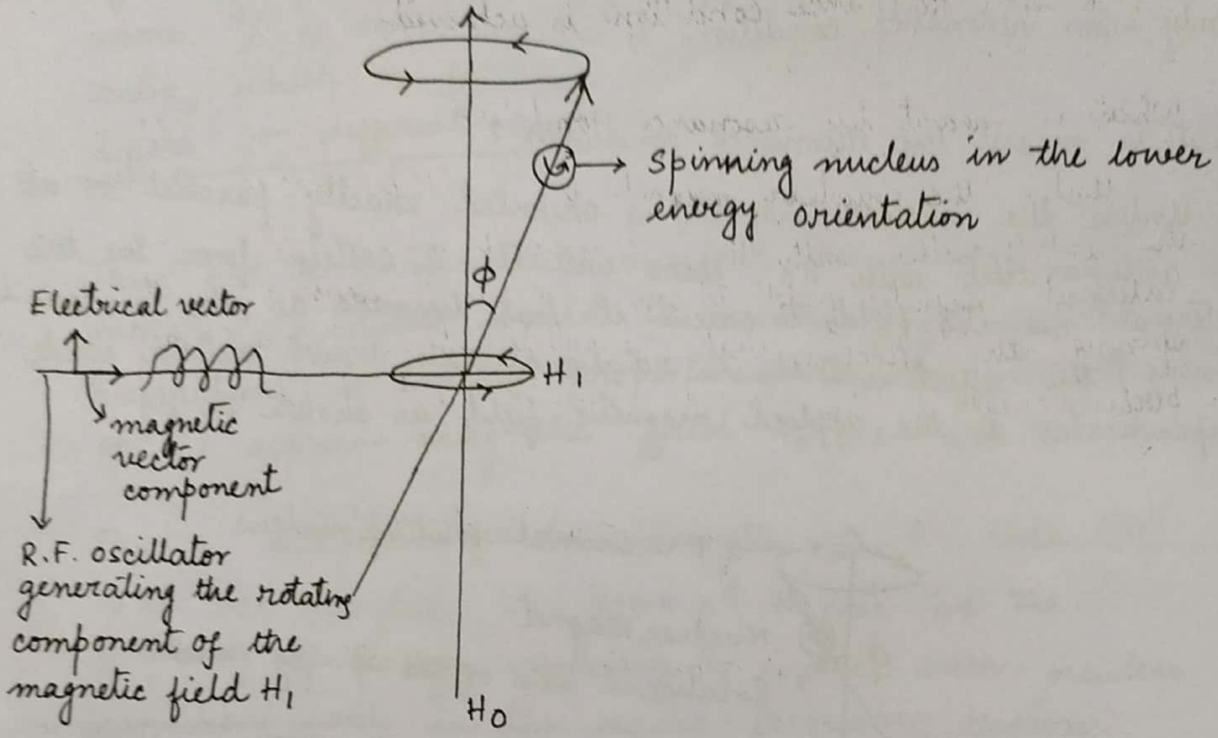
* What is the nature of precessional frequency of the spining nuclear magnet and the relation between precessional frequency and the applied magnetic field?

Ans. The precessional frequency ν of the nuclear magnet is directly proportional to the strength of the applied magnetic field and exactly equal to the frequency of the electromagnetic radiation supplied by radiofrequency oscillators.

$$\nu = \gamma \cdot \frac{H_0}{2\pi}$$

protons of organic compound.

For example, a proton exposed to an external magnetic field of 7.1 tesla will precess about 300 million times per second so that $\nu = 300$ MHz/sec.



* Resonance condition

The act of turning over the nucleus from one orientation to the other corresponds to the change in the angle ϕ (fig above), this can be brought about by the application of secondary magnetic field H_1 in a direction perpendicular to the main magnetic field. Further if this new field H_1 is to be continuously effective on the precessing nuclear magnet, it must rotate in a plane perpendicular to the direction of H_0 in the same phase with the precessing nucleus. This secondary magnetic field which is not applied from out side is infact the magnetic vector component of the electromagnetic radiation supplied by the r.f oscillator.

when the frequency of the rotating magnetic field H_1 becomes exactly equal to the precessional frequency of the nucleus, the precessing nucleus and the rotating magnetic field are said to be in resonance and absorption of energy by the nucleus can occur to give the NMR signal.

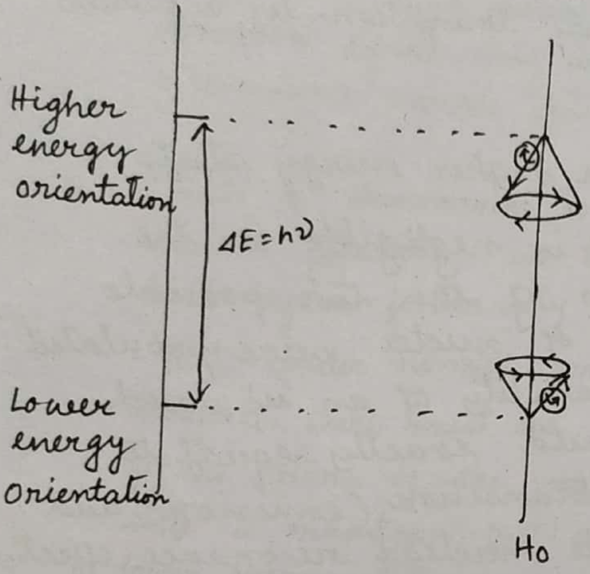


Fig : Representation of Nuclear transition in resonance condition

* what is necessary condition that ensures net absorption of energy by the nuclear magnet ?

Ans. The necessary condition that ensures net absorption of energy by the nuclear magnet is i) the maintanance of small but [illegible]finite excess of nuclei always in the lower energy state, ii) Resonance condition .

protons of organic compound.

* How is this maintained?

Ans. Let us explain the NMR phenomena in the light of theory of electromagnetic radiation which states—

i) the probability of an upward transition by absorption of energy from the magnetic field is exactly equal to the probability of downward transition by a process stimulated by the field.

ii) Spontaneous transition from higher energy state to the lower energy state is negligible in the radiofrequency region. Thus if the two possible spin states in a collection of nuclei were populated exactly equally, the probability of an upward transition (absorption) would exactly equal to That of a downward transition (emission) and there will be no observable nuclear resonance effect. Since the net absorption of energy is becoming zero.

But under ordinary condition, in a magnetic field there is a very slight excess of nuclei in the lower energy state. The nuclei take up a Boltzmann Distribution —

The Boltzmann factor being about 0.001%. It is this very small but finite excess of nuclei in the lower energy state that gives rise to net absorption of energy in the radiofrequency region.