I. D. C. Part III rd.
Chem. (Hons.); Paper V
Unit - 4

NMR — Spectroscopy — Phy. Chem. (1)

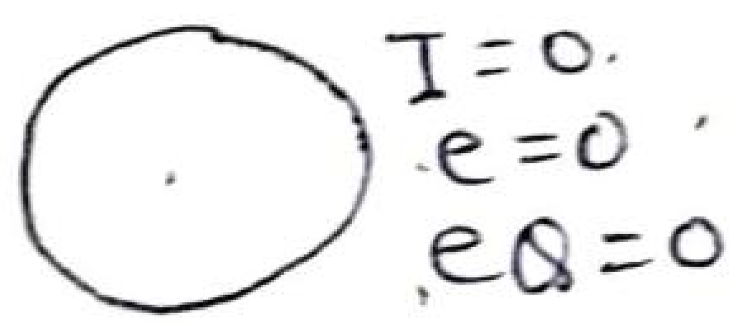
Nuclear Magnetic Resonance spectroscopy

The properties necessary to understanding of NMR spectroscopy are -)

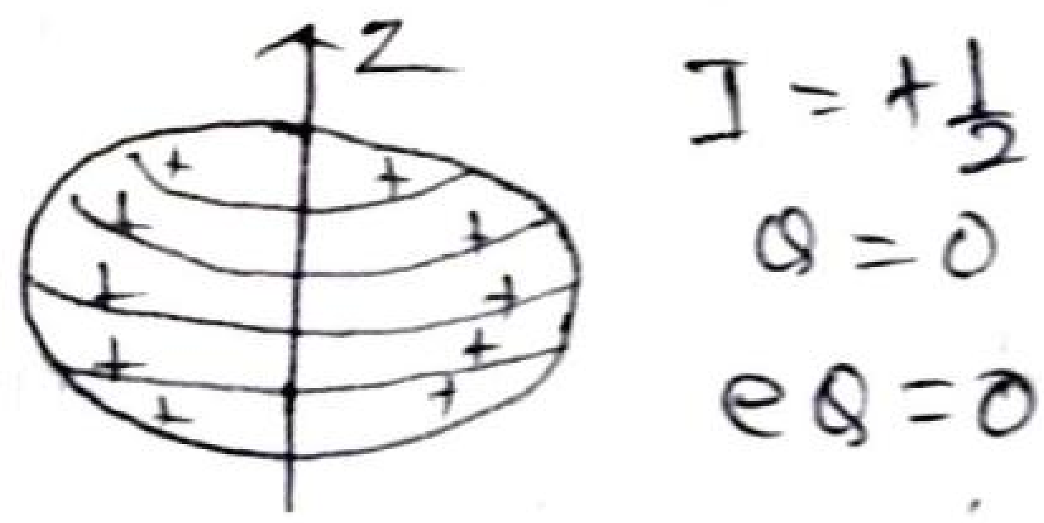
(i) Net spin of a nucleus (p+n)
(ii) Distribution of +ve charge

If nuclear spin (I) is zero, there is no net spin of the nuclear charge and also its $eQ = 0$,
Where, e = unit of electrostatic charge, and
Q = measure of deviation of charge distribution from spherical symmetry.

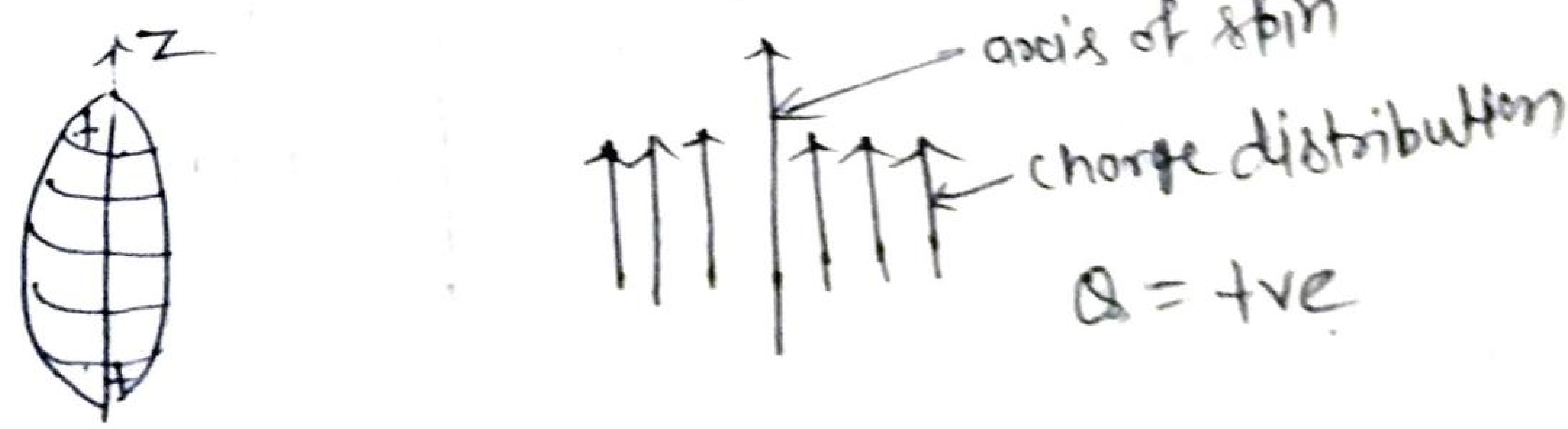
(i) For $I = 0$, e is zero and hence 'eQ' $= 0$



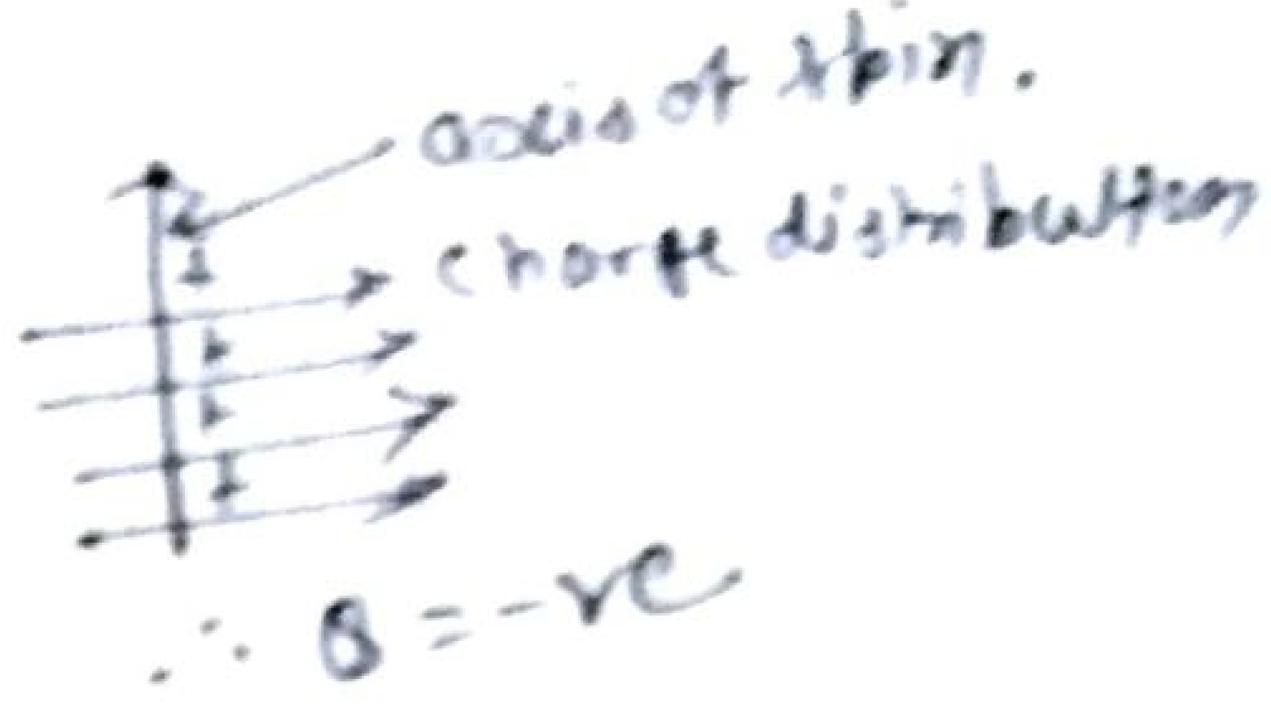
(ii) When $I = \frac{1}{2}$, there is net spin in the nucleus, as the +ve charge distribution is spherical, so. $Q = 0$ and hence $eQ = 0$



(iii) If $I \geq 1$, there is again net spin is zero of the nuclear charge but +ve charge distribution is non spherical, if +ve charge distribution is elongated along the axis of spin Q is +ve and hence $eQ > 0$

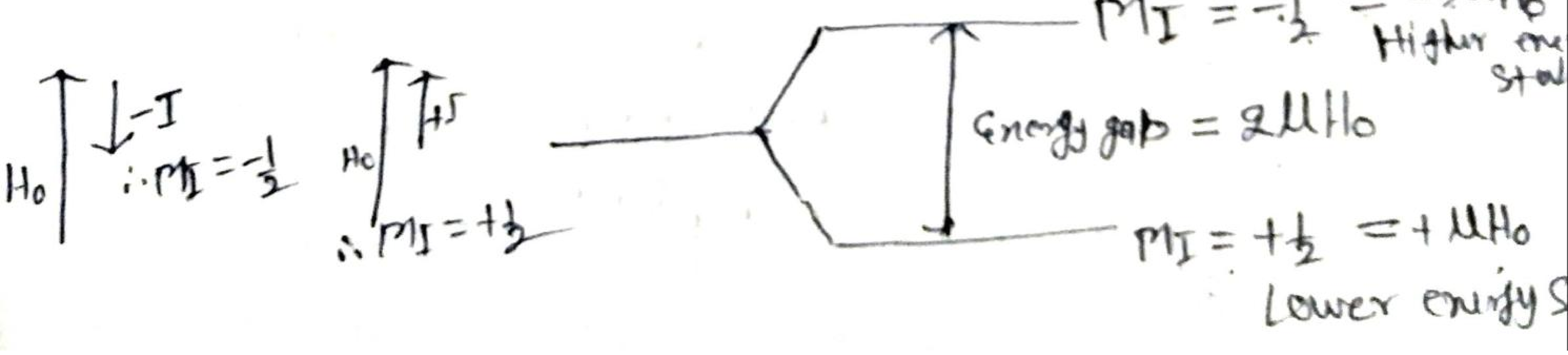


(iv) If the +ve charge distribution is flattened about the prime axis i.e., ⊥ to the prime axis (Q) is -ve and hence $eQ < 0$



If $I = 0$, there is no question of NMR spectra of such nuclei. If $I = 1$ or $I > 1$, spectra is some what complex and only special cases are consider. So most of the NMR spectra concerned with the nuclei having $I = \frac{1}{2}$ like ^{1}H, ^{13}C, ^{19}F, ^{31}P etc.

When $I = \frac{1}{2}$, there can be two allowed orientations of the nuclear magnetic moment vector in the external mag. field. One is $M_I = +\frac{1}{2}$ and other is $M_I = -\frac{1}{2}$. In the absence of external mag. field the two mag. moment vectors are degenerate, but as soon as external mag. field is imposed, the degeneracy is lost and it splits into two parts $M_I = \pm\frac{1}{2}$ is in lower energy as it is produced by the spinning of nucleus in the direction of applied mag. field, the other is $M_I = -\frac{1}{2}$, which represents the higher energy level produced by the spinning of the nucleus in the opposite direction of applied mag. field.



If μ = mag. moment of the nucleus, and (2)

H_0 = strength of the applied mag. field.

The energy gap b/w the levels is given by

$$\Delta E = -\mu H_0 - (+\mu H_0) = |-2\mu H_0| = 2\mu H_0 \quad \text{--- (1)}$$

As, μ for a particular nucleus is constant, the value of ΔE depends on the strength of the applied mag. field strength H_0. We also know that $\Delta E = h\nu$

from eq.^{n} (1) $h\nu = 2\mu H_0$

$$\therefore \nu = \frac{2\mu H_0}{h} \quad \text{--- (2)}$$

This shows ν is proportional to H_0 ($\nu \propto H_0$)

Now, if an emt. radiation of radio frequency range is passed through the sample of nuclei populated in lower state may absorb the energy whose ν is matching to eq^n (2) and it is excited in the higher state. This is called <u>Fliping of spin</u> or filiping of protons. When, $\nu = \frac{2\mu H_0}{h}$ the nucleus is said to be in resonance with applied emt radiations.

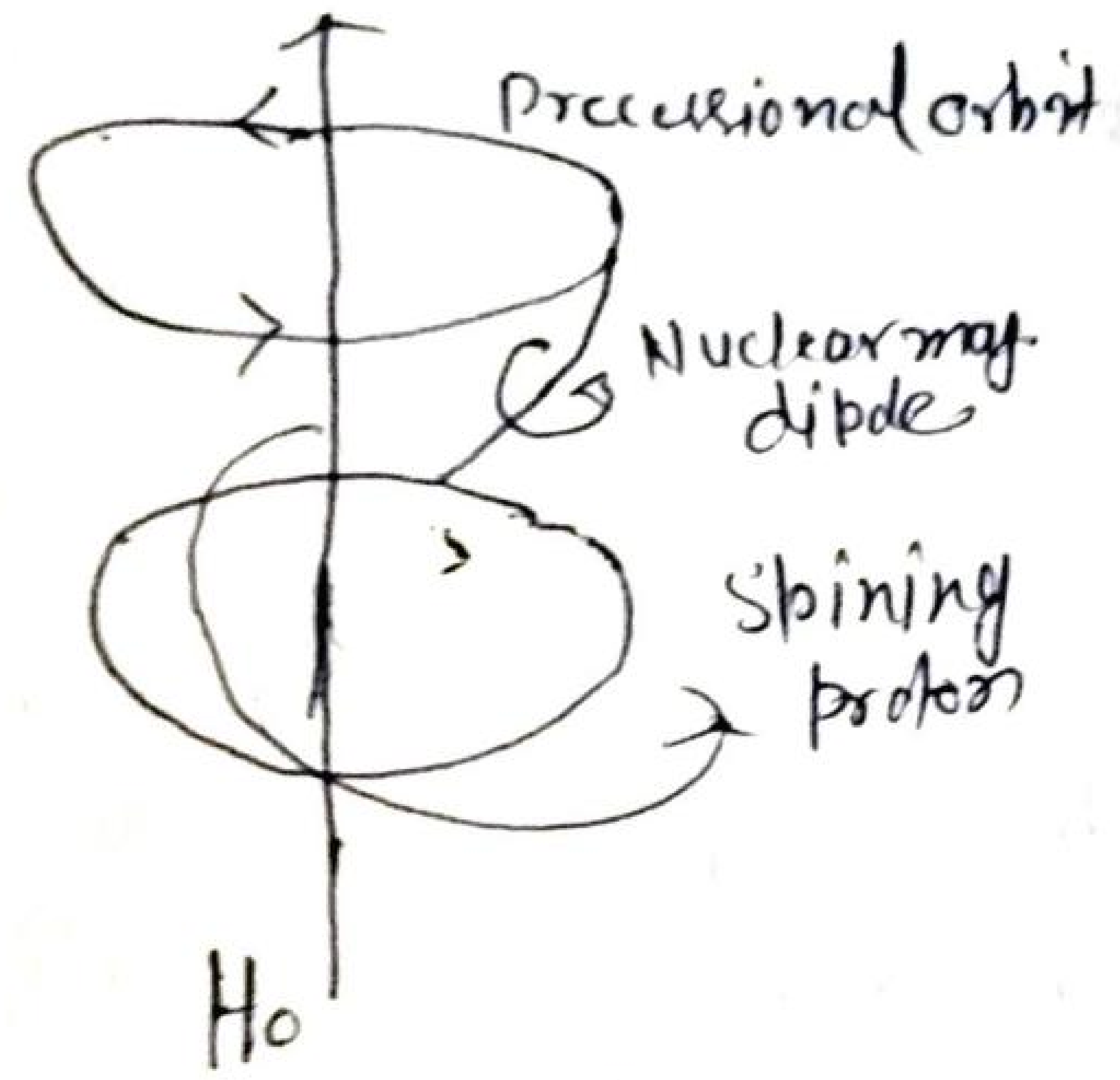
since ΔE is not very large compared to 'KT' i.e., thermal energy, the thermal agitation reduces the excess nuclei in lower energy state and thus the two states become equally populated at normal temperature. A/c to Boltzmann's distribution law

$$\frac{N_e}{N_g} = 1.000006 = e^{-\Delta E/KT}$$

so, when the state of resonance is reached the fliping of the nuclei from $M_I = +\frac{1}{2}$ to $M_I = -\frac{1}{2}$ is equally probable and possible for fliping of nuclei from $M_I = -\frac{1}{2}$ to $M_I = +\frac{1}{2}$ and subsequently no spectra is expected.

Q. How does interaction b/w nuclear mag. moment and external mag. field occur?

Ans.: A nucleus having nuclear spin $\frac{1}{2}$ (or more) may be assumed as a bar magnet which spins on its own axis. When it is placed in an external mag. field, the interaction b/w the moment of the nuclear bar magnet and the external mag. field produces torque. This torque causes the nuclear mag. moment vector to precess about the applied mag. field vector (H_0). The phenomenon is called Larmor precession.



Proton precessing in mag. field Ho

The angular frequency of this Larmor precession is called Larmor frequency, ω. rad. sec. It depends on the strength of ~~mag field~~ the applied mag. field H_0, as

$$\omega = \gamma \cdot H_0$$

where γ is magnetic gyric ratio or Gyromagnetic ratio (or constant)

$$\gamma = \frac{2\pi\mu}{hI}$$

Here μ = mag. moment of the spining bar magnet
I = spin Q. No. of the bar magnet nucleus
h = plank's const

So, at first to the nuclei of spin $I = \frac{1}{2}$ (or more), at first a strong mag. field is applied externally to cause the nuclei to precess about it.

Now emr radiation is applied which is comparable to ΔE and hence radiofrequency range. When the frequency of applied emr radiation is just equal to the of Larmor frequency of the nucleus, it comes into resonance with the applied emr radiation.

Under this condition the nuclei may absorb energy from the radiation and flip into the higher energy state or a nucleus in higher energy state may emit the energy and flip back to the lower state as both the states are almost equally populated at room temperature so, a mag. field of stronger strength is applied so that a little more nuclei may be in ground level, and hence under the condition of resonance, the fliping of protons occur from the lower to higher state producing signal in detectors i.e., n.m.r. spectrum.

[~~we know that~~ A/c to fundamental NMR equation which correlates ang. frequencies with mag. field, we say that

$$\omega = 2\pi\nu = \gamma H_0$$].

we know that $\omega = 2\pi\nu$ and $\Delta E = h\nu$

So, $\Delta E \propto \omega$ (frequency of Larmor precession)

So, resonance state is reached only when $\omega = 2\pi\nu$

where ν = radio frequency (r.f)

This condition may be reached in two different ways :-

(I) Applied mag. field is kept const. and thus Larmor frequency of nuclei is fixed and now the applied r.f. is scaned untill the matching occurs i.e., $\omega = 2\pi\nu$

(II) In other way, the radiofrequency is fixed and the strength of applied mag. field i.e., H_0 is varied untill the matching occur i.e., $\omega = 2\pi\nu = 2\pi\left(\frac{2\mu H_0}{h}\right)$

The most n.m.r. instrument follows the 2nd process.

In both the process, when matching occur the fliping of protons start producing signal i.e, n.m.r. spectra

... non radioactive transition ...

However, after initial flipping again both the states are equally populated. Under this state the sample is called saturated.

However, the state of saturation is avoided in the instruments by proper mechanism. In the instruments; that arrangement is made in such a way that, the excited nuclei may return to the ground state no by emitting energy directly, rather by some other mechanism. This happens by two mechanisms

(i) spin-spin relaxation and
(ii) spin-lattice relaxation

~~Precessi~~ Precessional Frequency (ω) :→

It may be defined as the number of revolutions per second made by the mag. moment vector of the nucleus around the external field Ho.

or

It may be defined as the ~~precessional~~ frequency of the spinning bar magnet (nucleus) equal to the frequency of emf. radiation in mega cycle per second necessary to induce a transition from one spin state to another.