Nuclear Magnetic Resonance :

It is a branch of spectroscopy in which radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule. The magnetic energy levels are created by keeping the nuclei in a magnetic field.

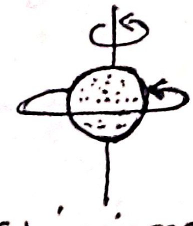
The phenomenon of nuclear magnetic resonance (NMR) was first enunciated by American physicist, Felix Bloch of the stanford University and Edward Purcell of Harvard University in 1946, for which they shared Nobel Prize in 1952.

Principles of NMR spectroscopy:

The nucleus of hydrogen atom (proton) behaves as a spinning bar magnet because it possesses both electric and magnetic spin. The nucleus of H atom generates a magnetic field Fig(1).

NMR involves the interaction between an oscillating magnetic field of electro magnetic radiation and the magnetic energy of the H nucleus when these are placed in an external static magnetic field.

fig(1)



Spinning charge in nucleus generates magnetic dipole

Consider a spinning top. It performs a slower waltz like motion which the spinning axis of the top moves slowly around the vertical axis. This is precessional motion and the top is said to be precessing around the vertical axis of earth's gravitational field. The precession arises from the interaction of spin with earth's gravity acting vertically downwards.

Theory

quantum description of NMR.

According to the quantum theory, a spinning nucleus can only have values for the spin angular momentum

$$\text{spin angular momentum} = [I(I+1)]^{1/2} \frac{h}{2\pi}$$

where I - spin quantum number

h - planck's constant.

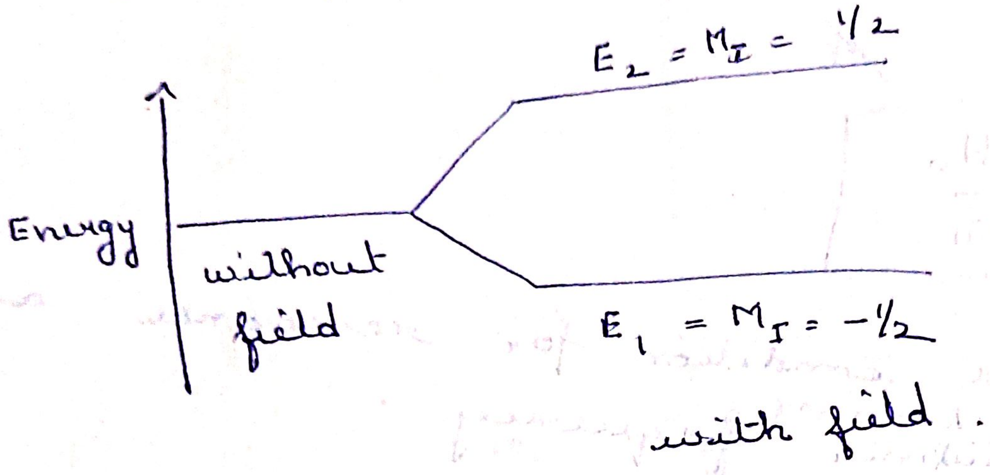
The magnetic moment of the nucleus μ is

$$\mu = \gamma \times \text{spin angular momentum}.$$

$$\mu = \gamma [(I+1)I]^{1/2} \frac{h}{2\pi}$$

γ - gyromagnetic ratio.

If the nucleus is introduced into the magnetic field H_0, the two energy levels become separate corresponding to $m_I = -1/2$ (antiparallel to the direction of magnetic field) and to $m_I = +1/2$ (parallel to the direction of magnetic field).



The energy levels are given by

$$E = \mu H_0$$

$$E_1 = -1/2 \left(\frac{\gamma h}{2\pi}\right) H_0$$

$$E_2 = 1/2 \left(\frac{\gamma h}{2\pi}\right) H_0$$

when the nucleus absorbs energy. it moves from lower energy state to higher state E_2. It means the absorption of energy

$$\Delta E = E_2 - E_1$$

If ν is the frequency of radiation absorbed

then $E = h\nu$ $\quad \nu = \frac{E}{h}$

$$\nu = \frac{E_2 - E_1}{h}$$

$$= \frac{\frac{1}{2}\left(\frac{\gamma h}{2\pi} H_0\right) + \frac{1}{2}\frac{\gamma h}{2\pi} H_0}{h}$$

$$= \frac{\frac{2}{2}\left(\frac{\gamma h}{2\pi} H_0\right)}{h}$$

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

This is the condition for resonance and is called ~~Larmor~~ Larmor frequency.

Bloch equations.

The spinning electron, when placed in the magnetic field experiences a torque L. The magnetic field causes the angular momentum to change and the rate of change of angular momentum to ~~change~~ with respect to time is equal to the torque experienced by magnetic moment ie,

$$\frac{\partial P}{\partial t} = L \quad \text{---} \ (1)$$

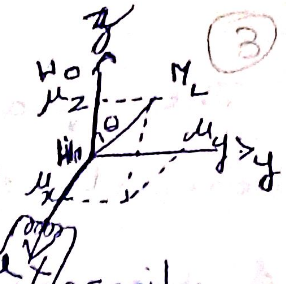
where P is the angular momentum.

L - torque.

From electromagnetic theory

$L = \mu \times H_0$ (H_0 - magnetic field) — (2)

③



$$\frac{\partial P}{\partial t} = \mu \times H_0 \quad \text{— ③}$$

multiplying with γ on either side

$$\gamma \frac{\partial P}{\partial t} = \gamma(\mu \times H_0)$$

$M = \gamma \cdot P$

$$\frac{\partial M}{\partial t} = \gamma\frac{\partial P}{\partial t} + P\frac{\partial \gamma}{\partial t}$$

0

$$\frac{\partial M}{\partial t} = \gamma(\mu \times H_0) \quad \text{— ④}$$

~~where M moment~~.

If M is the vector sum of individual moments μ's. then eqn ④ becomes,

$$\frac{dM}{dt} = \gamma(M \times H) \quad \text{— ⑤}$$

$$\therefore M \times H = \begin{vmatrix} i & j & k \\ M_x & M_y & M_z \\ H_x & H_y & H_z \end{vmatrix}$$

$$= i(M_y H_z - M_z H_y) - j[M_x H_z - M_z H_x) + k(M_x H_y - M_y H_x].$$

$$\therefore \frac{dM}{dt} = \gamma\left[i(M_y H_z - M_z H_y) - j[(M_x H_z - M_z H_x] + k(M_x H_y - M_y H_x)\right] \quad \text{— ⑥}$$

The quantity H in these equations consists of H_0 plus the magnetic vector of the applied radio frequency H_1 which is equivalent to rotating the magnetic field with a frequency 'ω'.

$$\left.\begin{aligned} H_x &= H_1 \cos\omega t \\ H_y &= -H_1 \sin\omega t \\ H_z &= H_0 \end{aligned}\right\} \quad -(7)$$

Sub (7) in (6) we get

$$\frac{dM_x}{dt} = \gamma\left[M_y H_z - H_z H_y\right]$$

$$= \gamma\left[M_y H_0 - M_z(-H_1 \sin\omega t)\right]$$

$$= \gamma\left(M_y H_0 + M_z H_1 \sin\omega t\right) \quad -(8)$$

$$\frac{dM_y}{dt} = -\gamma\left[M_x H_z - M_z H_x\right]$$

$$= -\gamma\left[M_x H_0 - M_z H_1 \cos\omega t\right] \quad -(9)$$

$$\frac{dM_z}{dt} = \gamma\left[M_x H_y - M_y H_x\right]$$

$$\gamma\left[M_x(-H_1 \sin\omega t) - M_y (H_1 \cos\omega t)\right]$$

$$\gamma\left[-M_x H_1 \sin\omega t - M_y H_1 \cos\omega t\right]$$

$$= \gamma\left[-M_x H_1\right.$$

(11)

$$\frac{dM_z}{dt} = -\gamma\left[M_x H_1 \sin \omega t + M_y H_1 \cos \omega t\right] \quad \text{--- (10)}$$

These equations are known as Bloch equations.

In addition to the perturbing influence of H_1 we have the natural processes which tend to restore the Boltzmann equilibrium i.e. they tend to restore M_x and M_y to zero and M_z to M_0. Therefore eq 8, 9, 10 becomes:

$$\frac{dM_x}{dt} = \gamma\left[M_y H_0 + M_z H_1 \sin \omega t\right] - \frac{M_x}{T_2} \quad \text{--- (11)}$$

$$\frac{dM_y}{dt} = -\gamma\left[M_x H_0 - M_z H_1 \cos \omega t\right] - \frac{M_y}{T_2} \quad \text{--- (12)}$$

$$\frac{dM_z}{dt} = -\gamma\left[M_x H_1 \sin \omega t + M_y H_1 \cos \omega t\right] - \frac{(M_z - M_0)}{T_1} \quad \text{--- (13)}$$

where T_1 - is the time constant for the decay of the component of magnetization along z axis ($H_1^{\pm} \to H_0$) and is called longitudinal relaxation time. T_2 represents the decay of magnetisation in the xy plane and is referred to as transverse relaxation time.

Molecular spectroscopy (Jack D. Graybeal)

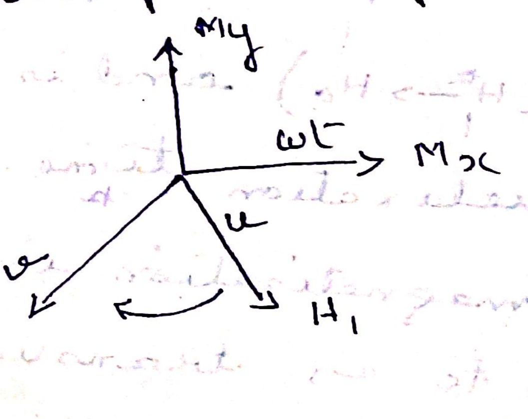
Annamalai notes

solution steady state

introduction

Solution of the above equation is straight forward but laborious. In the conventional NMR, H_0 is varied slowly, with constant H_0 which two resonance signals are predicted have the lorenzian shape, one is out of phase with H_1 called absorption (v mode) and the other is in phase (u mode) is called dispersive shape.

The Bloch equation given above takes simpler forms if they are referred to a system of axes rotating with the applied R.F. field. This means that we now have a set of axes rotating with angular velocity 'ω' about the z-axis and M_z, M_y are the components of M along and perpendicular to the direction of H_1. These are also known as the inphase out of phase components of M.



~~the bulk~~

Employing the classical mechanics of rotating bodies the relationship between the rates of change of magnetization relative to the laboratory (x, y, z) and the rotating (x', y', z') frames are illustrated in figure.

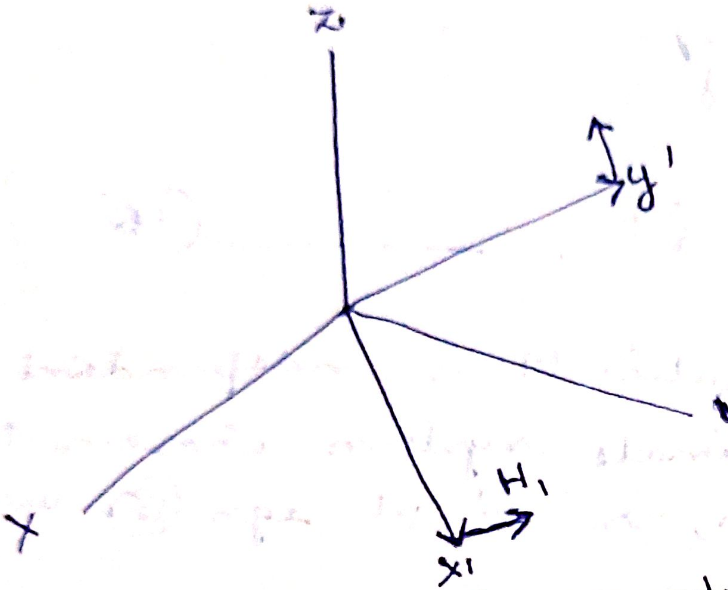


fig rotating coordinate system.

In the rotating co-ordinate systems the vectors M, H, and ω become

$$M' = M'_x \hat{i}' + M'_y \hat{j}' + M'_z \hat{k}'$$

$$H'_1 = \hat{i}' H_1$$

$$\omega' = -\omega \hat{k}' \qquad \text{——— (14)}$$

where M'_x and M'_y are the transverse components of the magnetization in the x'y' axis system in the rotating frame.

For an observer located in the rotating frame the unit vector $\hat{i}'$, $\hat{j}'$ and $\hat{k}'$ will appear to be stationary and the apparent variation of the total magnetization can be expressed as

$$\frac{dM'}{dt} = \frac{dM'_x}{dt}\hat{i}' + \frac{dM'_y}{dt}\hat{j}' + \frac{dM'_z}{dt}\hat{k}' \qquad \text{——— (15)}$$

For an observer located in the stationary axis system the unit vector in the rotating systems will change at a rate given by

$$\frac{d\hat{i}'}{dt} = \omega' \times \hat{i}'$$

$$\frac{d\hat{j}'}{dt} = \omega' \times \hat{j}'$$

$$\frac{d\hat{k}'}{dt} = \omega' \times \hat{k}' \quad \text{———} \quad (16)$$

The total magnetization M is independent of the choice of coordinate system chosen to describe its motion, so $M' = M$. eqn (15) becomes

$$\frac{dM}{dt} = \frac{dM_x'}{dt}\hat{i}' + \frac{dM_y'}{dt}\hat{j}' + \frac{dM_z'}{dt}\hat{k}' + M_x'\frac{d\hat{i}'}{dt} + M_y'\frac{d\hat{j}}{dt} + M_z'\frac{d\hat{k}'}{dt}.$$

$$\frac{dM}{dt} = \frac{dM'}{dt} + \omega' \times M' \quad \text{———} \quad (17)$$

eq(6) can be written as a vector eqn

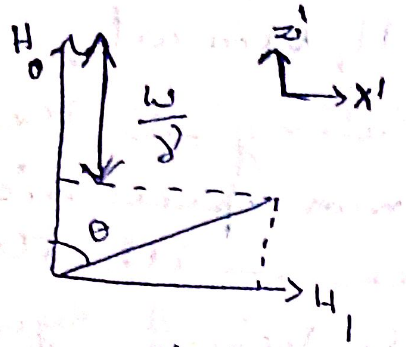
$$\frac{dM}{dt} = \gamma(M \times H_0 + M \times H_1) - \frac{(M_x\hat{i} + M_y\hat{j})}{T_2} - \frac{(M_z - M_0)\hat{k}}{T_1} \quad \text{———} \quad (18)$$

Sub (17) in (18) we get

$$\frac{dM'}{dt} = \gamma\left[M' \times \frac{\omega}{\gamma} + M' \times H_0 + M' \times H_1\right] - \frac{(M_x\hat{i} + M_y\hat{j})}{T_2} - \frac{(M_z - M_0)\hat{k}}{T_1} \quad \text{———} \quad (19)$$

(b)

The sum $H_0 + \omega/\gamma = H_e$ effective magnetic field. These relationship are illustrated in fig



effective mag. field

At some point in time the two axis system will be coincidental & equation (19) becomes

$$\frac{dM'}{dt} = \gamma(M' \times H_e') + \gamma(M' \times H_1') - \frac{M_x' \hat{i}' + M_y' \hat{j}'}{T_2} - \frac{(M_z - M_0)}{T_1} \hat{k}' \quad \text{(20)}$$

Thus the vector form of bloch eqn is

$$\frac{dM_x'}{dt} = (\gamma H_0 - \omega) M_y' - \frac{M_x'}{T_2} \quad \text{(21 a)}$$

$$\frac{dM_y'}{dt} = (\gamma H_0 - \omega) M_x' + \gamma M_z' H_1 - \frac{M_y'}{T_2} \quad \text{(21 b)}$$

$$\frac{dM_z'}{dt} = \frac{dM_z}{dt} = -\gamma M_y' H_1 - \frac{(M_z - M_0)}{T_1} \quad \text{(21 c)}$$

A unidirectional oscillating magnetic field $2H_1 \cos\omega t$ can be regarded as being composed of two counter rotating field components. $H_1 \cos\omega t \pm H_1 \sin\omega t$, but only the component rotating in the same direction as the Larmor precession of the nuclei can be in resonance with the nuclear spins. Hence the solution of eqn (21) can be obtained under <u>steady state condition</u> which exists after the oscillating magnetic field has been on for a long time and is characterized by $\frac{dM_x'}{dt} =$

$\omega_0 = \gamma H_0$

$$\frac{dM_y'}{dt} = \frac{dM_z'}{dt} = 0$$

∴ eqn 21 becomes

$$0 = (\omega_0 - \omega) M_y' - \frac{M_x'}{T_2} \longrightarrow (22a)$$

$$0 = (\omega_0 - \omega) M_x' + \gamma M_z' H_1 - \frac{M_y'}{T_2} \longrightarrow (22b)$$

$$0 = -\gamma M_y' H_1 - \frac{(M_z' - M_0)}{T_1} \longrightarrow (22c)$$

eq 22a

$$M_x' = (\omega_0 - \omega) M_y' T_2$$

eq 22c

$$\frac{M_z - M_0}{T_1}$$

sub eq (22a) in (22b) we get

$$(\omega_0-\omega)(\omega_0-\omega)M_y' T_2 + \gamma H_z' H_1 - \frac{M_y'}{T_2} = 0$$

$$(\omega_0-\omega)^2 M_y' T_2 + \gamma M_z' H_1 - \frac{M_y'}{T_2} = 0$$

$$(\omega_0-\omega)^2 M_y' T_2^2 + \gamma M_z' H_1 T_2 - M_y' = 0$$

$$M_y'\left[(\omega_0-\omega)^2 T_2^2 - 1\right] + T_2 \gamma H_1 H_z' = 0$$

$$M_y' = \frac{-T_2 \gamma H_1 M_z'}{\left[(\omega_0-\omega)^2 T_2^2 - 1\right]} \quad \text{—— (23)}$$

sub (23) in eqn (22c)

$$\frac{M_z'}{T_1} - \frac{M_0}{T_1} = -\gamma M_y' H_1$$

$$\frac{M_z'}{T_1} - \frac{M_0}{T_1} = +\gamma \frac{T_2 \gamma H_1 M_z' H_1}{\left[(\omega_0-\omega)^2 T_2^2 - 1\right]}$$

$$\frac{M_z'}{T_1} - \frac{M_0}{T_1} = \frac{\gamma^2 T_2 H_1^2 M_z'}{(\omega_0-\omega)^2 T_2^2 - 1}$$

$$\frac{M_z'}{T_1} - \frac{\gamma^2 T_2 H_1^2 M_z'}{(\omega_0-\omega)^2 T_2^2 - 1} = \frac{M_0}{T_1}$$

$$\frac{\left[(\omega_0-\omega)^2 T_2^2 - 1\right] M_z' - \gamma^2 T_2 T_1 H_1^2 M_z'}{T_1\left[(\omega_0-\omega)^2 T_2^2 - 1\right]} = \frac{M_0}{T_1}$$

$$M_z' \frac{\left[(\omega_0-\omega)^2 T_2^2 - 1 - \gamma^2 T_2 T_1 H_1^2\right]}{T_1\left[(\omega_0-\omega)^2 T_2^2 - 1\right]} = \frac{M_0}{T_1}$$

$$M_z' = \frac{T_1\left[(\omega_0-\omega)^2 T_2^2 - 1\right] M_0}{T_1\left[(\omega_0-\omega)^2 T_2^2 - 1 - \gamma^2 T_2 T_1 H_1^2\right]} \quad \text{—— (24)}$$

Sub (24) in (23)

$$M_y' = \frac{-T_2 \gamma H_1}{\left[(\omega_0-\omega)^2 T_2^2 - 1\right]} \frac{\left[(\omega_0-\omega)^2 T_2^2 - 1\right] M_0}{\left[(\omega_0-\omega)^2 T_2^2 - 1 - \gamma^2 T_2 T_1 H_1^2\right]}$$

$$= \frac{-M_0 T_2 \gamma H_1}{\left[(\omega_0-\omega)^2 T_2^2 - 1 - \gamma^2 T_2 T_1 H_1^2\right]} \quad \text{—— (25)}$$

Sub (25) in 22(a)

$$M_x' = \frac{(\omega_0-\omega) M_0 T_2 \gamma H_1 T_2}{\left[(\omega_0-\omega)^2 T_2^2 - 1 - \gamma^2 T_2 T_1 H_1^2\right]} \quad \text{—— (26)}$$

24, 25, 26 are the solutions of the Bloch's equations.