

# Magnetic Resonance

Magnetic resonance is the phenomenon in which at certain frequencies the magnetic system under study absorbs energy from an applied oscillating magnetic field.

Supposing that the system under study is a microscopic magnetic carrier with an angular momentum situated in a constant magnetic field, The carrier executes precessional motion. The oscillating magnetic field perpendicular to first field exerts a constant torque parallel to the first field. As a result, amplitude of the precessional motion increases, which means absorption of energy from the oscillating magnetic field. This energy absorption turns out to be maximum if the precessional frequency is equal to the frequency of the oscillating magnetic field.

Hence the phenomenon **magnetic resonance**.

# Nuclear Magnetic resonance

## Nature of the phenomenon

In general, atomic nuclei have angular momentum, and associated with it the magnetic moment. If  $I$  is the nuclear spin quantum number of a nucleus, then its angular momentum is given by

$$\hbar\sqrt{I(I+1)} \quad \text{With } I=0, 1/2, 1, 3/2, 2, \dots$$

The associated magnetic moment is

$$\mu = g \left( \frac{e}{2M_p c} \right) \hbar\sqrt{I(I+1)}$$

Where  $M_p$  is the proton mass and  $g$  is the inverse of gyromagnetic ratio

The possible component of angular momentum and magnetic moment along with the direction of an external magnetic field, say  $H_c$ , along  $z$  direction, are then given respectively by

$m_I \hbar$  with  $m_I = I, (I-1), \dots, -(I-1), -I$ , where  $m_I$  is magnetic quantum number

$$\mu_z = g \left( \frac{e}{2M_p c} \right) m_I \hbar$$

letting  $\frac{e}{2M_p c} = \mu_n$  The nuclear magneton, this is written as

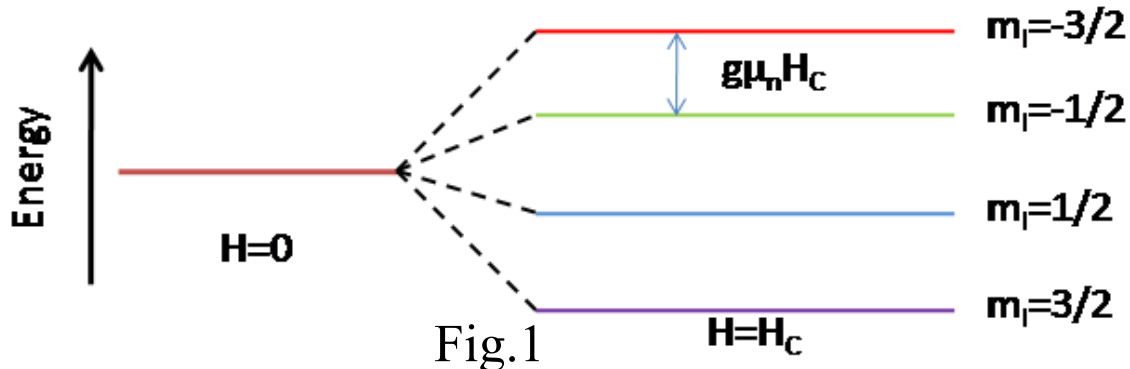
$$\mu_z = g \mu_n m_I \quad 1$$

Now, we consider that nucleus under consideration has  $I=3/2$ . For example  $\text{Na}^{23}$ . The possible components of the magnetic moment along  $H_c$  are then expressed as

$$-\frac{3}{2} g \mu_n \quad -\frac{1}{2} g \mu_n \quad \frac{1}{2} g \mu_n \quad \frac{3}{2} g \mu_n$$

Since the energy of a magnetic moment  $\mu$  in a magnetic field  $H$  is equal to  $-\mu \cdot H = -\mu_z \cdot H_c$ , we thus obtain for energy levels of the nucleus as

indicated in fig.1  $-\frac{3}{2} g \mu_n H_c \quad -\frac{1}{2} g \mu_n H_c \quad \frac{1}{2} g \mu_n H_c \quad \frac{3}{2} g \mu_n H_c$



The oscillating magnetic field, applied perpendicular to  $H_c$ , induces transitions between these levels, which means that the nucleus absorbs energy from the oscillating magnetic field. Since the transitions between these levels are governed by selection rule  $\Delta m_l = \pm 1$ , transitions are possible only between successive levels, separated in energy by  $g\mu H_c$ . So if an oscillating magnetic field is absorbed by the nucleus, its frequency  $\omega$  must be

$$\hbar\omega = g\mu_n H_c = g \left( \frac{e}{2M_p c} \right) \hbar H_c \quad 2$$

$$\omega = g \left( \frac{e}{2M_p c} \right) H_c \quad 3$$

$g \left( \frac{e}{2M_p c} \right) H_c$       Frequency of Classical precessional motion which the nucleus executes about  $H_c$

Equation (3) is the usual resonance condition, hence the phenomenon the nuclear magnetic resonance

NMR is caused by nuclear magnetic moments

## Analysis of the Phenomenon

Let us consider a system of magnetic nuclei under the influence of a constant magnetic field  $H_c$  in z direction plus an oscillating field  $2H_0 \cos \omega t$  along the x direction. We may consider the oscillating field as the sum of two circularly polarized components:

Right	Left	
$H_x = H_0 \cos \omega t$	$H_x = H_0 \cos \omega t$	4
$H_y = H_0 \sin \omega t$	$H_y = -H_0 \sin \omega t$	

Only left component will be in phase with the precession.

Now, let  $M$  be the magnetization of the whole system and  $J$  be the angular momentum in a magnetic field  $H$ . Then the torque acting on the system is

$$T = M \times H$$

$$T = \frac{dJ}{dt}$$

$$\frac{dJ}{dt} = M \times H$$

$$M \times H = \frac{1}{\gamma} \frac{dM}{dt}$$

However, since  $J$  and  $M$  are parallel to each other  
 $M = \gamma J$  with  $\gamma = g(e/2M_p c)$

$$\frac{dM}{dt} = \gamma M \times H \quad 5$$

Besides the influence of field ,two other sources also contribute to the rate of change of M. These are

- (i) Spin –lattice interaction
- (ii) Spin -spin interaction

## Spin –lattice interaction

If the system is in thermal equilibrium when only the constant field  $H_c$  applied, suppose that  $M_c$  represents the magnetization along the z direction. When this field is suddenly switched off ,the magnetization will gradually approach to zero. Similarly when the field is switched on ,a certain time interval is required to obtain equilibrium value  $M_c$ . Certain fraction of nuclear spin must flip from antiparallel to a parallel orientation relative to the field during this build-up and hence the rate of change of  $M_z$  .Assuming that the build-up time is characterized by  $\tau_1$ , the rate of change of  $M_z$  is

$$\left( \frac{\partial M_z}{\partial t} \right)_{sl} = - \frac{M_z - M_c}{\tau_1} \quad 6$$

$\tau_1$  is called spin –lattice relaxation time as it depends on how fast spins can loose energy to the lattice when the field is switched on.As  $M_z$  is longitudinal w.r.t . $H_c$  ,  $\tau_1$  is also called longitudinal relaxation time.

Combining equation (6) and z component of equation (5), we obtain for the total rate of change of  $M_z$

$$\frac{dM_z}{dt} = \gamma[-M_x H_0 \sin \omega t - M_y H_0 \cos \omega t] + (M_C - M_z) / \tau_1 \quad 7$$

### Spin –spin interaction

Now, Consider two neighboring identical spins i and j .Since both are precessing about  $H_C$  ,each will produce an oscillating field of the Larmor frequency at the position of other. As a result, transitions may be induced in which i and j simultaneously reverse their orientation, Thus affecting the rate of change of  $M_x$  and  $M_y$ . It is determined by  $\tau_2$  . We may assume

$$\left( \frac{\partial M_x}{\partial t} \right)_{ss} = -\frac{M_x}{\tau_2} \quad \left( \frac{\partial M_y}{\partial t} \right)_{ss} = -\frac{M_y}{\tau_2} \quad 8$$

$\tau_2$  is called the spin –spin relaxation time or the transverse relaxation time because  $M_x$  and  $M_y$  is transverse w.r.t.  $H_C$

**Note:**

$\tau_2$  is completely different from  $\tau_1$ .

$\tau_1$  is associated with the approach of the spin system to thermal equilibrium with the lattice,

$\tau_2$  is associated with an internal equilibrium of the spins among themselves.

Combining (8) with corresponding component equations of (5), we obtain for the total rate of change of  $M_x$  and  $M_y$

$$\frac{dM_x}{dt} = \gamma[M_y H_C + M_z H_0 \sin \omega t] - M_x / \tau_2 \quad 9$$

$$\frac{dM_y}{dt} = \gamma[M_z H_0 \cos \omega t - M_x H_C] - M_y / \tau_2 \quad 10$$

The equations (7), (9) and (10) are called the **Bloch equations**



## Some applications of the phenomenon

Nuclear magnetic resonance experiments have proved to be a powerful tool in studying the physical properties of solids

### Determination of nuclear magnetic moment

This is accomplished by determining the resonance frequency associated with a field  $H_C$  and hence  $g$  value of the nuclei under study as is obvious from equation (3). The  $g$  value thus calculated is used along with the value of nuclear spin  $I$  to calculate the max. Component of the magnetic moment from the relation  $(\mu_z)_{\max} = g\mu_n[I(I+1)]$ . This component is referred to as the nuclear magnetic moment in units of  $\mu_n$ .

### Structural studies

The nuclear resonance experiments also provide information about the structure of solids. The width and shape of a resonance absorption line are influenced by the magnetic interaction between the dipoles and this interaction is determined by the relative positions of the nuclei.

# Electron Spin Resonance

## Nature of the phenomenon

ESR is similar to NMR, The electron too has a magnetic moment and the quantized energy level in an external magnetic field and the transitions induced between these levels by an oscillating magnetic field with suitable frequency.

The possible components of spin magnetic moment in an external magnetic field, say  $H_C$  taken along z axis,  $\pm \frac{1}{2}g\mu_B H_C$

Accordingly, the energy levels are

$$+ \frac{1}{2}g\mu_B H_C, -\frac{1}{2}g\mu_B H_C$$

Where  $\mu_B$  is the Bohr magneton ( $e\hbar/2mc$ ), and  $g$  is about 2,

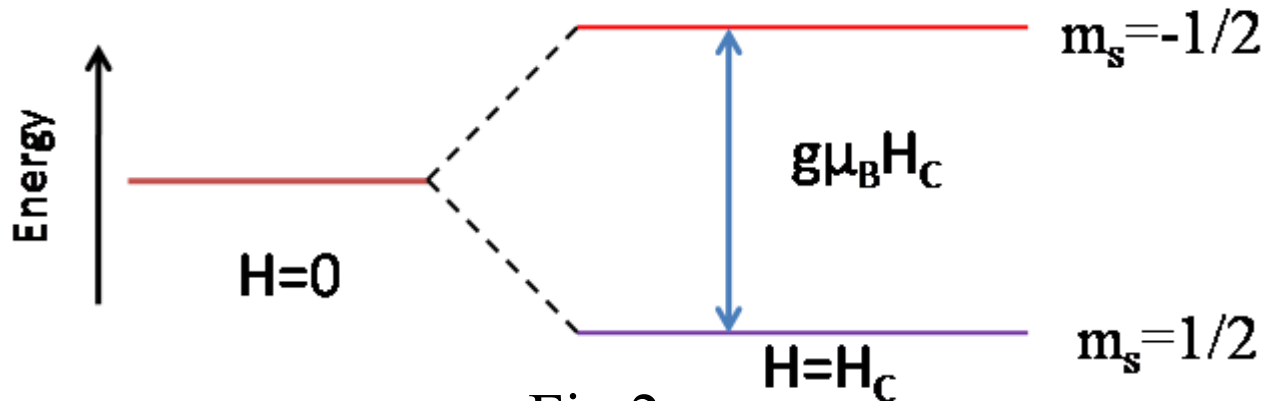


Fig.2

The oscillating magnetic field applied to induce transitions between these levels must then be of the frequency  $\omega$  such that

$$\hbar\omega = g\mu_B H_C \quad 11$$

$$\omega = (g\mu_B/\hbar)H_C = g(e/2mc)H_C \quad 12$$

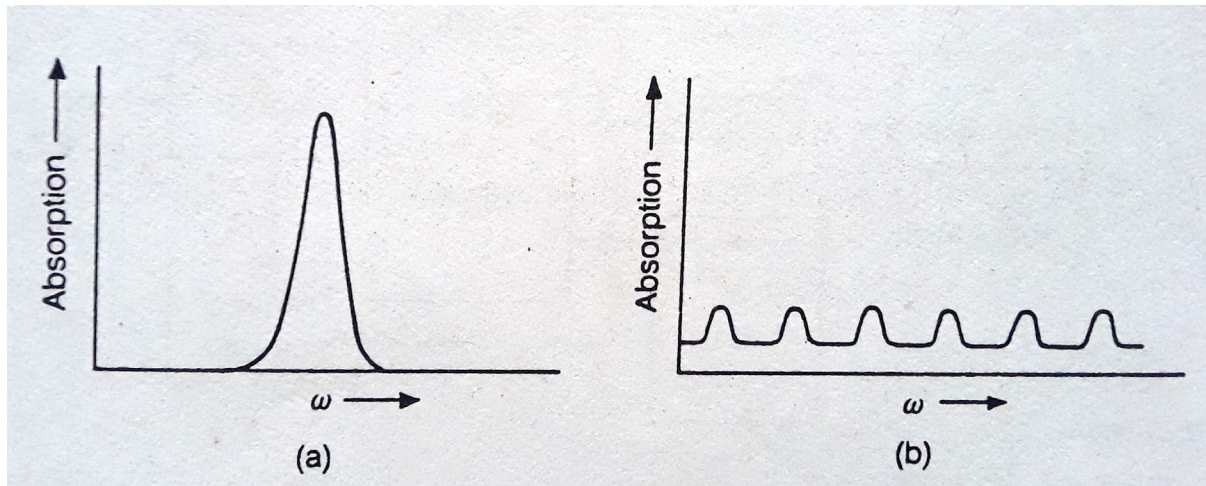
$g(e/2mc)H_C$  is the frequency of classical precessional motion which the electron executes about  $H_C$ .

Thus eqn. 12 is usual resonance condition, hence the phenomenon the **electron spin resonance (ESR)**

The electron spin resonance is therefore the technique of determining  $\omega$  and hence  $\mu_e$  for an electron in a given field.

However the condition of resonance given by eqn. is based on an ideal configuration for a single electron

The orientation of the magnetic moment of the nucleus in the field relative to that of the moment of electron influences the energy levels of the electrons. The nuclear magnetic moments may take  $2I+1$  quantized orientations in the magnetic field, and each of these orientation alters an electron energy level by a different amount.



Effect of hyperfine splitting on an ion with  $I=5/2$   
 (a) ideal case (b) hyperfine structure

Fig.3

Each original level is thus caused to split up into  $2I+1$  sublevels (for  $I < S$ ). Consequently each ideal spectral line split into  $2I+1$  lines by nuclear –electron interaction; this splitting is known as hyperfine splitting. A schematic of the hyperfine splitting is drawn fig.3 for a hypothetical ion with  $I=5/2$ .

Internal electric fields arising from inhomogeneities in the material etc also influence the position of spectral lines.

Requirement for the existence of ESR , is that ions and atoms involved should not have completely filled shells. This is because in the completely filled shells ,the electrons are paired by two by two and such shells therefore has no net spin. One large group of solids which can show resonance is thus group of paramagnetic materials.. It is for these reason that ESR in these materials is often called electron paramagnetic resonance(EPR).

# Applications of the Phenomenon

## Application to metals:

ESR in metals is due to the para magnetism of the valence electrons (Pauli paramagnetism) and is employed to find their paramagnetic susceptibility. We must note that the experimental determination of  $\chi_p$  by any conventional means is difficult, since we get total susceptibility  $\chi_T$ ,  $\chi_T = \chi_p + \chi_d$  where  $\chi_d$  is diamagnetic susceptibility. ESR however measures  $\chi_p$  alone. It may be remembered that a method which would measure either  $\chi_p$  or  $\chi_d$  separately would be of interest in exploring entire magnetic behavior of the non ferromagnetic metals, hence the importance of ESR.

## Study of imperfections and impurities in ionic crystal

Pure and perfect crystal do not show ESR, this is because all electron shells in them are completely filled. Imperfections and impurities often have uncompensated electron spins. For example, consider an F- centre in an alkali halide crystal; it is considered an electron is trapped at a negative ion vacancy, thus having a net spin. Consequently such crystal show ESR.