

Electron Spin Resonance.

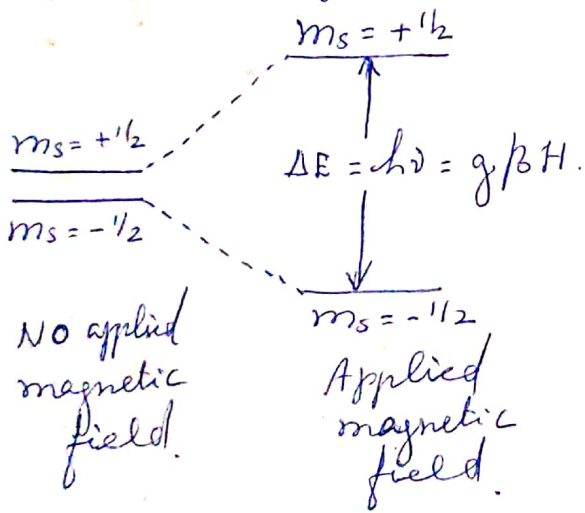
Majority of the stable molecules are held together by bonds in which electron spins are opposed; in this situation there is no net electron spin, no electronic magnetic moment, and hence no interaction between electron spin and the applied magnetic field. On the other hand some atoms and molecules contain one or more electrons with unpaired spins. These molecule, atom or ion absorbs electromagnetic radiation of microwave frequency (wavelength $10^1 - 10^3 \text{ cm}$) under the influence of magnetic field. This phenomenon is known as electron spin resonance (ESR) and it is exhibited by a paramagnetic species. It is also often referred to as electron paramagnetic resonance (EPR)

ESR is shown by stable paramagnetic substances like NO , O_2 and NO_2 and transition metal complexes. Unstable paramagnetic materials usually called free radicals or radical ions, may be formed either as intermediate in a chemical reaction or by irradiation of a normal molecule with UV or X-ray radiation.

Principle of ESR

Interaction between Electron spin and magnetic field

Let us begin with isolated electron. We know an electron has a spin quantum number $m_s = 1/2$. We also know it can have two orientations, one with spin angular momentum of magnitude $+(1/2)h/(2\pi)$ and the other with $-(1/2)h/(2\pi)$. The magnetic spin momentum quantum numbers corresponding to these orientations are $m_s = +1/2$ and $m_s = -1/2$. In the absence of magnetic field the two m_s states remains degenerate. On the application of a magnetic field, the two m_s states split. The $m_s = +1/2$ state is of an energy higher than the magnetic field than the $m_s = -1/2$ state



The energy of an electron in a magnetic field is given by $E = -\vec{\mu} \cdot \vec{H}$. where $\vec{\mu}$ is the magnetic moment in a specified direction i.e. $\vec{\mu}$ is the projection of μ in the direction of H . We have $\vec{\mu} = g\beta m_s \vec{H}$ (H is the strength of the magnetic field)

We have $\vec{\mu} = g\beta m_s$

$g =$ Lande' splitting factor
 $\beta =$ Bohr magneton $(9.273 \times 10^{-24} \text{ J T}^{-1})$
 $= (0.9273 \times 10^{-20} \text{ erg/gauss})$

unit of magnetic moment is Bohr magneton = 9842339372

For the electron, β has an inherent negative sign and includes the magnitude $h/2\pi$. Then for $m_s = +1/2$ state we have $E = -\mu H = -g(-\beta) 1/2 H = (1/2) g \beta H$.

For the $m_s = -1/2$ state, we have $E = -1/2 g \beta H$.

In an energy corresponding to a microwave frequency ν is fed to the electron and the applied field is such that $g \beta H = h\nu$, the energy will be absorbed by the $m_s = -1/2$ state and a transition between the two m_s states will take place.

[The proton has a nuclear spin quantum number $I = 1/2$, and it too has two orientations, one with the magnitude $+(1/2) h/2\pi$ and the other with $-(1/2) h/2\pi$. Since the proton has a positive charge associated with it, the $m_I = +1/2$ state will form the lower energy state in preference to the $m_I = -1/2$ state on the application of a magnetic field. Thus,

$$E = -\mu H = -1/2 g_p \beta_p H \text{ for } m_I = +1/2 \text{ state}$$

$$E = -\mu H = +1/2 g_p \beta_p H \text{ for } m_I = -1/2 \text{ state}$$

✓ Therefore $\Delta H = h\nu = g_p \beta_p H$.

The ESR instruments are of two types.

1. X-band ESR Spectrometer - frequency 9,400 megacycles/sec.
Magnetic field strength (H) - 3000 gauss. Magnetic field strength varies in the range 1-10,000 gauss.
2. Q-band ESR - frequency 35,000, megacycle/sec. H is around 12,500 gauss.

Most ESR work has been carried in X-band region. A higher sensitivity can be achieved by working at a high magnetic field.

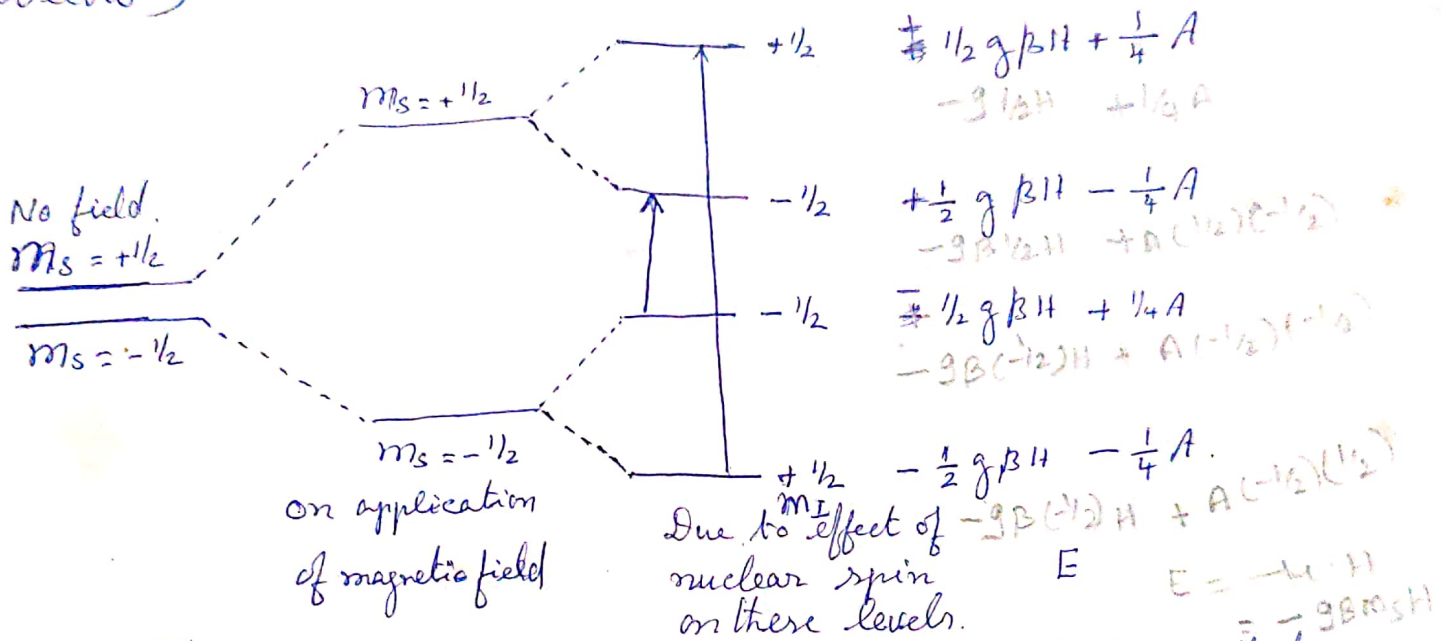
[Resonance condition is $h\nu = g\beta H$, an absorption signal will be obtained at 3000 gauss when an ESR spectrometer is operated at 8398 megacycles/sec. and $g = 2.0$] Earlier, ESR spectrum was recorded between absorption intensity and magnetic field.

Interaction between nuclear spin and electron spin - Hyperfine splitting

How does the nuclear spin affect an ESR signal?

Let us investigate the ESR spectrum of the simple system, i.e. the ^1H atom. This atom has just one proton with a nuclear spin quantum number $I = 1/2$ and a single electron. While the electron spin can have two orientations. One corresponding to the quantum number $m_s = -1/2$ and the other to $m_s = +1/2$.

The nuclear spin quantum numbers for each of these two m_s states may be $m_I = +1/2$ and $m_I = -1/2$. Thus a total of four energy level is possible. (shown below)



The energy of a particular m_s state will be affected by the nuclear spin-electron spin interaction energy. This energy varies as the product of m_s and m_I and is given by $A m_s m_I$, where A is the hyperfine splitting constant. The constant 'A' characterizes the degree of interaction of the unpaired electron with the nucleus. The energies are (different level) given by.

$$E = g \beta m_s H + A m_s m_I$$

The magnitude of 'A' is determined by the size of the nuclear magnetic moment and the density of the unpaired electron at the nucleus.

From the fig. we may note that if the electron spin and the nuclear spin are parallel prior to an ESR transition, there will be antiparallel after the transition and vice versa. A splitting of an ESR line due to an interaction between the nuclear spin and electron spin of the same atom is known as hyperfine splitting. The number of hyperfine splitting lines is given by the total number of orientation of the nuclear spin I by $(2I + 1)$. These lines are equally separated with a spacing A . If there are n equivalent nuclei of nuclear spin I , then the number of lines obtained is $(2nI + 1)$.

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The intensities of the transitions corresponding to $m_s = +1/2$ and $m_s = -1/2$ are the same but nearly three times as great as those corresponding to the $m_s = +3/2$ and $m_s = -3/2$ states. (Ref: Fig) This is so because $M_s = \pm 1/2$ had as many as three ways. When $m_s = \pm 3/2$ admit of only one arrangement.

g value and factors affecting it

The g factor is a dimensionless constant and its actual value for a free electron is 2.0023 due to a relativistic correction. A free radical also has this g value. This is because in a free radical the unpaired electron is not confined to a localized orbital but can move about freely over the orbitals. From the g value of a transition metal complex, we can obtain very important information about the structure of the complex. For such complex in gas or solution phase, g is averaged over all orientations because of the free motion of the molecules. In crystal the movement of the molecule is restricted. In a cubic crystal field the metal-ligand bond lengths are the same along the three cartesian axes, and hence g remains the same i.e. $g_x = g_y = g_z$. Such a g is said to be isotropic.

C_6H_6
While deriving the magnetic moment of an ion assuming large multiplet width, we had relation $g = 1 + [J(J+1) + S(S+1) - L(L+1)] / 2J(J+1)$. For free e^- , $S=1/2, L=0, J=1/2$. This gives $g = 2.00$.

The z direction is defined coincident with the highest fold rotation which axis can be determined by the x-ray method.

If a crystal field is tetragonal, the metal-ligand distances along x and y axis are same but different z axis. The g value of such complex is anisotropic. The anisotropic g may be expressed as $g_x = g_y \neq g_z$. If the symmetry of a complex is rhombic, it gives three different g values, i.e. $g_x \neq g_y \neq g_z$. If a well formed single crystal is used, the ESR measurements can provide the g value based on the orientation of the crystal. The orientation is z axis which is determined by the x-ray method. The g_z value is equivalent to $g_{||}$, the g value obtained when the z axis is parallel to the external magnetic field. The g_{\perp} value is the g value obtained in any direction in the plane \perp to this direction.

Determination of g values.

We know that $h\nu = g\beta H$ or $g = h\nu / (\beta H)$. Thus, g can be conveniently determined if the microwave frequency (ν) at which the ESR spectrometer is operating and the resonance magnetic field (H) of the sample are known. The calculation of g from the experimental data ($H = 3250$ gauss, $\nu = 9.114 \times 10^9$ cycle/sec) can be done as

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6.

$$g = \frac{h\nu}{\beta H} = \frac{6.62517 \times 10^{-27} \text{ erg sec} \times 9.114 \times 10^9 \text{ cycle/sec}}{0.92731 \times 10^{-20} \text{ erg/gauss} \times 3250 \text{ gauss}} = 2.00$$

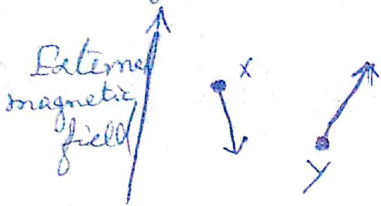
If the microwave frequency is not accurately known, the spectrum may be calibrated with the free radical diphenyl picrylhydrazyl (DPPH) for which $g = 2.0036$. The g value for a sample can then be calculated according to the relation.

$$g = 2.0036 (1 - \delta H / H)$$

where δH is the difference between the resonance magnetic field (H) of the sample to the DPPH. δH is negative if the sample has its centre at a resonance magnetic field lower than that of DPPH and it is positive if the sample has its centre at a resonance magnetic field higher than that of DPPH. [Negative δH gives $g > 2$, whereas a positive δH gives $g < 2$.]

energy. [The relaxation process is a mechanism by which a paramagnetic ion shares its excess energy either with the other nuclei or with the lattice.

The term lattice here indicate the immediate environment of the excited state species: The time taken for a fraction of this excess energy to dissipate is known as the relaxation time.]



Relaxation.

Spin-Lattice Relaxation: Spin-Lattice Relaxation

is a mechanism by which the excess energy of a paramagnetic ion is transferred to the vibrational degrees of freedom of the lattice.

The time constant for the rate of energy transfer from the magnetic spin to the crystal lattice is known as spin-lattice relaxation time.

Time (T_1) . T_1 strongly depends on temperature. The interaction

Spin-Spin Relaxation. (Dipolar interaction)

{ Spin-Spin relaxation is a mechanism by which a paramagnetic ion shares its excess energy with the neighbouring electron spins and the spin-spin relaxation time is denoted by T_2 .

Also known that the local magnetic field is produced

11.1 INTRODUCTION

Electron spin resonance (ESR), also called Electron paramagnetic resonance (EPR), is a spectroscopic technique confined to the study of those species having one or more unpaired electrons. The method takes advantage of angular momentum of the electron and its magnetic moment to reveal a wealth of information. The angular momentum may arise from both spin and orbital motions. Associated with the angular momentum there will be a magnetic moment. In most of the cases of interest, the magnetic moment arises from spin angular momentum only. Among the large number of paramagnetic systems, the most important ones are transition metal ions, free radicals, ions and molecules having an odd number of electrons etc.

The spin and charge of the electron confer on it a spin magnetic moment μ_s , given by Eq. (3.13)

$$\mu_s = -g\mu_B \frac{S}{\hbar} \quad (11.1)$$

where g is the gyromagnetic ratio and μ_B is the Bohr magneton. If angular momentum is expressed in \hbar , Eq. (11.1) reduces to

$$\mu_s = -g\mu_B S. \quad (11.2)$$

The orbital magnetic moment μ_L is given by

$$\mu_L = -\mu_B L \quad (11.3)$$

where L is the orbital angular momentum of the electron in units of \hbar . The total magnetic moment

$$\mu = \mu_s + \mu_L = -g\mu_B S - \mu_B L \quad (11.4)$$

If the system has only spin magnetic moment,

$$\mu = -g\mu_B S \quad (11.5)$$

The negative sign indicates that μ and S are in the opposite directions.

11.2 PRINCIPLE OF ESR

When an electron spin having magnetic moment μ is placed in a magnetic field B , the interaction energy

$$E = -\mu \cdot B = -\mu B \cos \theta \quad (11.6)$$

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The component of μ along the direction of an applied magnetic field $\mu_z = -g\mu_B m_s$

where θ is the angle between μ and B . As $\cos \theta = m_s/s$, substituting the value of μ from Eq. (11.5)

$$E = g\mu_B B m_s \quad (11.7)$$

It may be noted here that we considered only the spin magnetic moment. Since spin s is equal to $\frac{1}{2}$ for an electron, $m_s = \pm\frac{1}{2}$ and we get two levels with energies (Figure 11.1)

$$E_{-1/2} = -\frac{1}{2}g\mu_B B, \quad E_{1/2} = \frac{1}{2}g\mu_B B$$

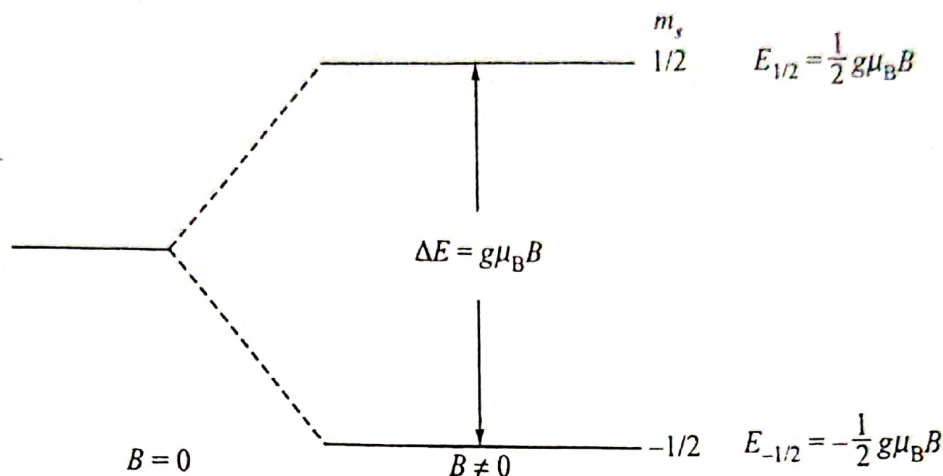


Figure 11.1 Zeeman splitting of an unpaired electron in a magnetic field B .

If electromagnetic radiation of frequency ν satisfying the condition

$$h\nu = E_{1/2} - E_{-1/2} = g\mu_B B \quad (11.8)$$

is present, transition between these Zeeman levels occur which is studied by ESR. Equation (11.8) gives the **resonance condition** for ESR observation. For free electron, $g = 2.0023$. In a field of 0.34 T, from Eq. (11.8)

$$\nu = \frac{2.0023(9.274 \times 10^{-24} \text{ JT}^{-1})0.34 \text{ T}}{6.626 \times 10^{-34} \text{ J}\cdot\text{s}} = 9528 \text{ MHz}$$

This frequency falls in the microwave region. Hence, microwave source and techniques have to be applied for the observation of ESR.

Successful observation of the ESR spectrum requires suitable values for the frequency ν and the magnetic field B to satisfy Eq. (11.8). For magnetic field of 0.34 T; ν comes out to be about 9.5 GHz. Spectrometers operating around this frequency are often referred to as X-band spectrometers. Spectrometers operating at higher magnetic fields ($B = 1.3 \text{ T}$) with corresponding higher microwave frequency ($\sim 35 \text{ GHz}$) are also available. They are called Q-band spectrometers.

11.3 ESR SPECTROMETER

Basic requirements: The basic relation for the observation of ESR transition is the one given by Eq. (11.8). For continuous absorption one can either vary the frequency ν across resonance keeping the field B constant or the magnetic field is varied keeping the frequency

constant. The latter method is usually preferred since it is easier to vary the magnetic field keeping the stability at very high levels. In electromagnetic radiations, the electric field, the magnetic field and the direction of propagation are mutually perpendicular. In ESR experiment, it is the magnetic component of the electromagnetic radiation that interacts with the magnetic dipole associated with the unpaired electron. If the oscillating magnetic field vector of the radiation is parallel to the applied magnetic field, only an oscillation of the energy levels occurs and not a reorientation of the electron magnetic moment. Transition between levels will take place only when there is a reorientation of the electron magnetic moment. Therefore, for successful observation of ESR absorption, the oscillating magnetic field must be applied perpendicular to the applied magnetic field.

Population in the lower level will be considerably high even for larger external magnetic fields. Though higher population in the lower level leads to larger absorption cross-section and higher sensitivity, one prefers to work with reasonable fields only as this corresponds to a sample cavity of fairly large dimensions ($2 \times 1 \times 4$ cm). Also, it is more difficult to get highly homogeneous magnetic fields of very high value over a larger region.

Some of the basic requirements of a X-band ESR spectrometer are:

- (i) An electromagnet capable of supplying a homogeneous magnetic field which can be varied linearly on either side of the magnetic field
- (ii) Source of microwave radiation in the region of 9.5 GHz
- (iii) Suitable sample cavity
- (iv) Arrangements for transmitting the radiation energy into the sample cavity
- (v) Detection system to measure the variation in microwave power
- (vi) Suitable oscilloscope or recorder.

Description of the set-up: A simple block diagram of a balanced bridge ESR spectrometer is given in Figure 11.2. The usual source of radiation is a klystron oscillator which produces monochromatic radiation of the required frequency. The radiation from the source is transmitted to the sample cavity through a microwave impedance bridge. The rectangular

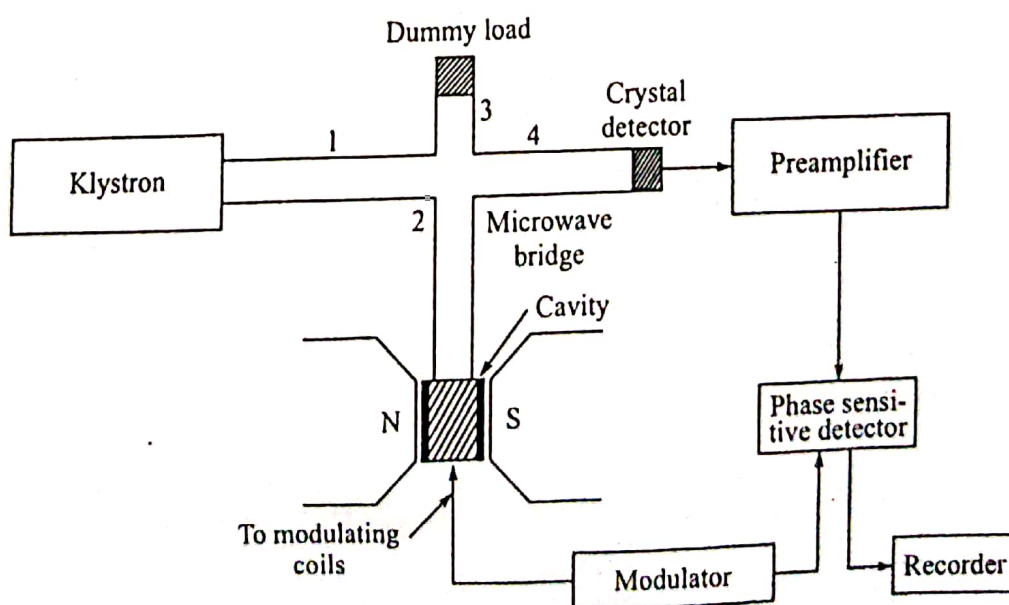


Figure 11.2 Block diagram of a simple balanced bridge ESR spectrometer.

microwave cavity which contains the sample is kept in between the pole pieces of the electromagnet. A dummy load is kept in the third arm and a semiconducting crystal in the fourth arm of the microwave bridge. The radiations that arrive in the 4th arm are detected by the crystal. It is then amplified and fed to a suitable recorder. Phase sensitive detectors are usually used to detect ESR signals and represented as absorption or first derivative curves (Figure 11.3). The magnetic field is swept over a small range across the resonance condition by varying the current in a pair of sweep coils mounted on the cavity walls.

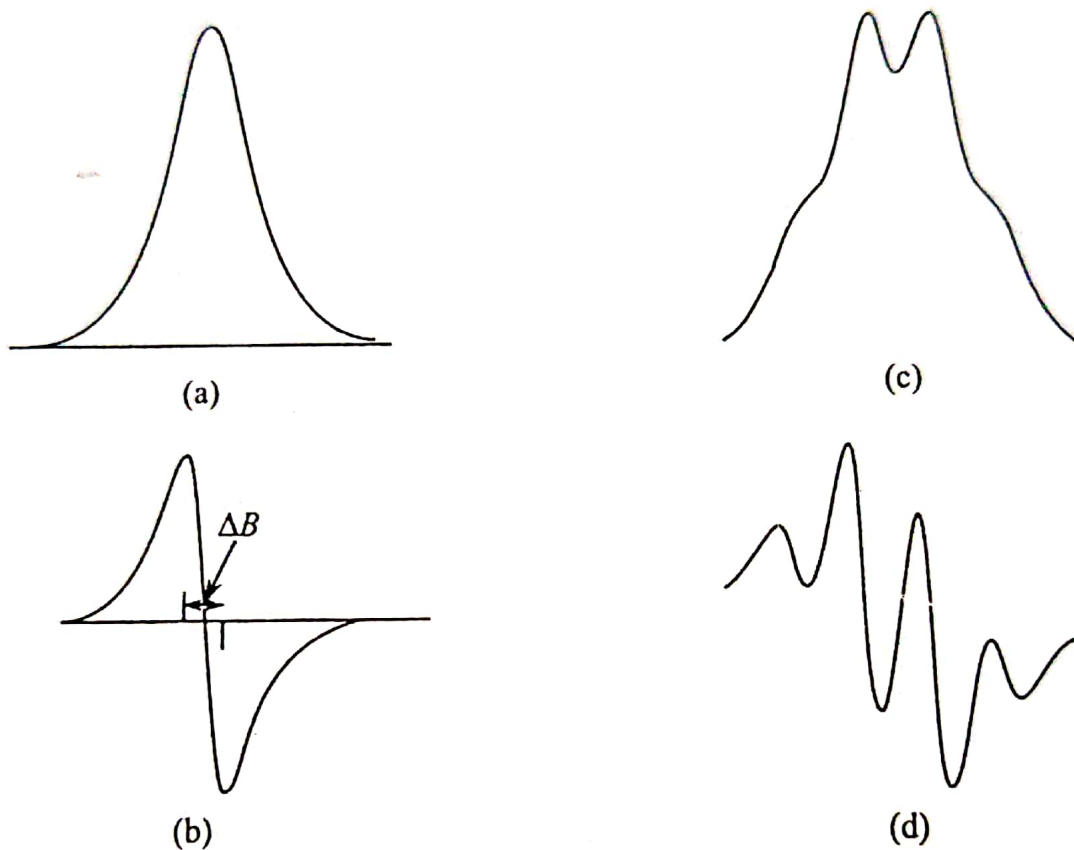


Figure 11.3 ESR signal: (a) a single absorption line, (b) its first derivative, (c) four equally-spaced overlapping absorption lines, (d) first derivative of the spectrum in (c).

Working: When the bridge is in a balanced position, microwave power flows only in the two arms—the one to cavity and the other to the dummy load. There will not be any power in the fourth arm. Power in the fourth arm will be there only when the bridge is not balanced. Thus, if balance exists, initially no signal appears at the detector and when the sample absorbs, the balancing of the bridge is lost and power appears in the fourth arm. The width of ESR lines are fairly large and hence the spectrum is usually recorded in the first derivative mode which enables one to fix up the frequency position and estimation of intensity more precisely. Another advantage of derivative mode is that it gives a well-defined linewidth ΔB (Figure 11.3). Even if there are overlapping signals, it is still possible to do a good estimate of ΔB .



SIGNATURE OF HALL INVIGILATOR

Free radical and

Biological Systems . ESR studies can be

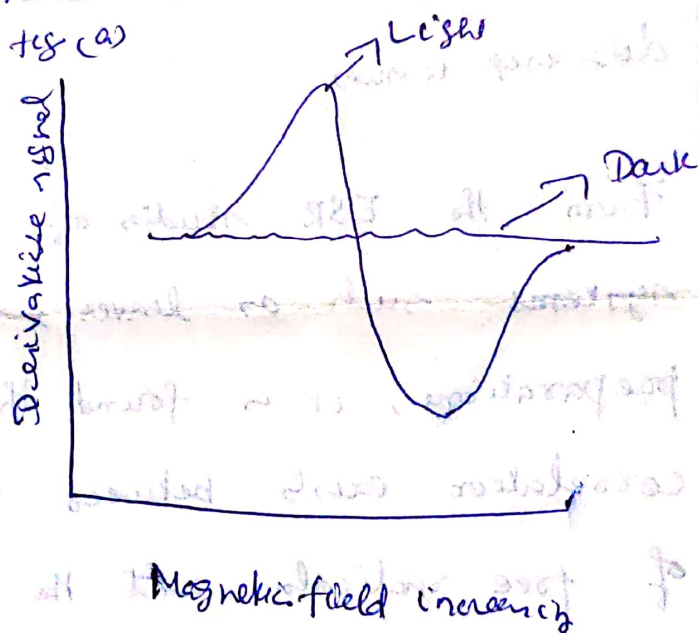
successfully applied to biological systems.

1) The presence of free radicals has been studied by ESR in healthy and diseased tissues.
diseased tissues

2) From the ESR studies of various biological systems such as leaves, seeds and tissue preparations, it is found that a definite correlation exists between the concentration of free radicals and the metabolic activity of the material.

3) Most of the oxidative enzymes function via one-electron redox reactions involving the production of either enzyme-bound free radicals or by a change in the valance state of a transition metal ion. This has been confirmed by ESR studies.

4) Much of the ESR work on photosynthesis has been carried out with photosynthetic bacteria. When these bacteria are cross-irradiated with near-infrared light (700 - 900 nm), a single line ESR signal with $g = 2.0025$ and $\Delta H \approx 10$ G is observed. However a weak ESR signal is obtained for the photosynthetic bacteria ^{in dark}. This is shown in fig (a)



The g -factor (2.0025) is characteristic of an organic free radical which might arise from a large conjugated system. The oxidation of bacteria chlorophyll *in vitro* produces an ESR signal which closely resembles the ESR spectrum shown in fig (a)

- 5) ESR studies has been used in the analysis of haemoglobin. Its liquid
6. More recently e.s.r signals have been observed in samples of nucleic acids including DNA & RNA and has been attributed to the presence of transition metal ions

Application of ESR spectroscopy

- i) It decides about the rate of unpaired electrons
- (i) The number of line components decide about the number and type of nuclei present in the neighbour group of the odd electron
- (ii) The relative intensities of the spectrum lines in an ESR spectrum confirm the type of nuclei which are responsible for the splitting pattern. Summation of the intensities can be utilized to evaluate the total number of free electrons in the sample.
- (iii) From the ESR spectrum the g value can be measured by comparing the position of the line with that of the standard substance of known g value. $g \text{ DPPH } = 2.0036$