
UNIT 11 ELECTRON SPIN RESONANCE SPECTROSCOPY

Structure

- 11.1 Introduction
 - Objectives
- 11.2 Principle
- 11.3 The Fundamental Equation
- 11.4 ESR Spectrometer
- 11.5 Presentation of the ESR Spectrum
- 11.6 The ESR Spectra of Some Simple Systems
 - ESR spectrum of Hydrogen Atom
 - ESR spectra—Some More Examples
- 11.7 The g -value
- 11.8 Some Applications of ESR Spectral Studies
- 11.9 Summary
- 11.10 Terminal Questions
- 11.11 Answers

1.1 INTRODUCTION

In the last unit, you have studied about the Nuclear Magnetic Resonance (N.M.R.) Spectroscopy. We hope that you have clearly understood the principle of N.M.R. spectroscopy and other concepts explained there. We assume that you can apply the knowledge gained about N.M.R. spectroscopy in structure elucidation of simple molecules.

Similar to the nuclei of some atoms, the free or unpaired electrons have spin and show magnetic properties. Thus, systems containing unpaired electrons can be studied by a technique, called Electron Spin Resonance (E.S.R.) spectroscopy in a manner similar to N.M.R. spectroscopy. Therefore, we will reuse here some of the concepts of Unit 10.

In this unit, we will first introduce you to the principle behind E.S.R. spectroscopy. Then we will familiarise you with the instrumentation. After that you will know how an ESR spectrum looks like? We will then discuss nuclear hyperfine interaction using simple examples. Finally we will focus our attention on the applications of ESR spectral studies.

Objectives

After studying this unit, you should be able to:

- discuss the principle behind ESR spectroscopy,
- give the condition for absorption of radiation in ESR spectral studies,
- describe salient features of instrumentation used in ESR spectrum recording,
- explain nuclear hyperfine splitting in simple radicals,
- give the significance of g values, and
- illustrate the use of ESR spectral studies in the structure elucidation of some simple molecules.

You may recall that an electron has both orbital angular momentum and spin angular momentum. However, in case of molecules, only the contributions from spin angular momentum are important. Within a molecule, there are strong internal electric fields directed along the chemical bonds. In a diatomic molecule such a field is directed along the internuclear axis. This internal field holds the orbital angular momentum of the electrons in fixed orientations. They cannot line up with an external magnetic field and their contribution is not significant. Thus, orbital angular momentum is said to be quenched. Thus, the major contribution comes from spin angular momentum.

11.2 PRINCIPLE

Similar to the case of a nucleus having spin and magnetic moment, the electron has spin and magnetic moment. When the electron is kept in a magnetic field, the magnetic dipole precesses about the axis of the applied field with the frequency called *Larmor precession* similar to the case of a nucleus. Parallel to the treatment of NMR, here also there are two spin states differing in energy. When an electromagnetic radiation of suitable frequency is applied, the transition from one spin state to another takes place.

Similar to NMR spectroscopy, for an assembly of unpaired electrons, the ratio of electron population in two levels is given by Boltzmann distribution and is expressed

$$\text{as } \frac{N_\alpha}{N_\beta} = e^{-\Delta E/RT}$$

The ratio of populations in two energy levels are calculated by substituting the ΔE values in the above equation and here also the lower energy level is slightly more populated. It is this excess population which is responsible for the net upward transitions resulting in the phenomenon of electron spin magnetic resonance. Thus, the following species may show an ESR spectrum:

- (i) Free radicals having odd number of electrons
- (ii) Odd electron molecules, e.g. NO, NO₂, ClO₂ etc.
- (iii) O₂ in triplet state
- (iv) Some transition metal complexes, organometallic compounds and catalysts containing metal ions having incomplete 3d, 4d or 5d orbitals
- (v) Rare earths and actinides having incomplete 4f, 6d, etc. orbitals
- (vi) Some impurities

SAQ 1

Which of the following would show an ESR spectrum?

- (i) $\cdot\text{CH}_3$ (ii) N₂ (iii) CO₂ (iv) $\cdot\text{C}_6\text{H}_6^-$
-
-

11.3 THE FUNDAMENTAL EQUATION

You are aware from Unit 1, Block 1 that an electron has spin which can be designated by the spin quantum number, s . The spin quantum number has a value of $\frac{1}{2}$. You may also recall that the magnitude of the spin angular momentum $|\vec{s}|$ of the electron can be represented as

$$|\vec{s}| = \sqrt{s(s+1)} \hbar$$

If we substitute $s = \frac{1}{2}$ in the above equation, we get

$$s = \sqrt{\frac{1}{2}\left(\frac{1}{2} + 1\right)} \hbar = \sqrt{\frac{1}{2} \times \frac{3}{2}} \hbar = \frac{\sqrt{3}}{2} \hbar$$

You are also aware that this spin angular momentum (s) of the electron can have its

components (s_z) in the direction of the magnetic field (in the z direction) which are half integral multiples of \hbar , i.e.

$$s_z = m_s \hbar$$

where m_s can take values $+\frac{1}{2}$ and $-\frac{1}{2}$.

You are also aware from Sec. 10.2, (Unit 10) that a spinning charge generates a magnetic moment. The magnetic moment of the electron μ_e is related to its spin angular momentum (s) by the following equation.

$$|\vec{\mu}_e| = -\frac{g_e e}{2m} |\vec{s}|$$

Substituting the value of s from above equation, we get

$$|\mu_e| = -\frac{g_e e}{2m} \sqrt{s(s+1)} \hbar$$

$$|\mu_e| = -\frac{g_e e \hbar}{2m} \sqrt{s(s+1)} = -g_e \beta_e \sqrt{s(s+1)} \quad \dots(11.1)$$

where

β_e is the Bohr magneton and is equal to $\frac{e\hbar}{2m}$. Here, e and m are the charge and mass of the electron, respectively.

g_e is a dimensionless constant and is called the electron g factor. It has a value 2.00232 for a free electron.

You may remember that in Unit 10, a similar equation, Eq. 10.1, was used for the case of a nucleus. From Eq. 11.1, the component of the magnetic moment in the direction of the field (μ_z) will be related to the component of the angular momentum in the z direction (m_s) by the following equation.

$$\mu_z = -g_e \beta_e m_s \quad \dots(11.2)$$

The interaction of the magnetic moment (μ_z) with the applied field of strength B_z applied along z axis is given by their product.

$$\begin{aligned} \text{Interaction} &= E = -\mu_z B_z \quad \dots\dots(11.3) \\ &= g_e \beta_e m_s B_z \quad (\text{using Eq. 11.2}) \end{aligned}$$

Remember that m_s can take values from $+s, \dots, -s$. For a single electron, $s = \frac{1}{2}$ and $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$. Corresponding to the two values of m_s , as $+\frac{1}{2}$ and $-\frac{1}{2}$, the two values of energy can be obtained using Eq. 11.3 as follows.

$$E = +\frac{1}{2} g_e \beta_e B_z \quad (\text{for } m_s = +\frac{1}{2}) \quad \dots(11.4)$$

and
$$E = -\frac{1}{2} g_e \beta_e B_z \quad (\text{for } m_s = -\frac{1}{2})$$

Thus, the electron spin has two energy states in a magnetic field. These energy states are shown in Fig. 11.1.

The magnetic moment of the electron $|\mu_e|$ can also be expressed as follows

$$|\vec{\mu}_e| = \gamma \vec{S}$$

Note that the negative sign indicates that the magnetic moment vector is in the opposite direction to that of the angular momentum vector.

$$\mu_z = \gamma m_s \hbar$$

$$E = -\gamma m_s \hbar B_z$$

The value of Bohr magneton can be calculated by substituting the values for the various constants.

$$\begin{aligned} \beta_e &= \frac{e \hbar}{2m} \\ &= \frac{(1.602 \times 10^{-19} \text{ C})(6.626 \times 10^{-34} \text{ J s})}{2.2\pi \cdot (9.109 \times 10^{-31} \text{ kg})} \\ &= \frac{(1.602 \times 10^{-19} \text{ C})(6.626 \times 10^{-34} \text{ J s})}{4 \times 3.14 (9.109 \times 10^{-31} \text{ kg})} \\ &= 9.274 \times 10^{-24} \text{ C J s kg}^{-1} \\ &= 9.274 \times 10^{-24} \text{ A s J s kg}^{-1} \\ &= 9.274 \times 10^{-24} \text{ A s}^2 \text{ J kg}^{-1} \\ &= 9.274 \times 10^{-24} \text{ J T}^{-1} \\ 1 \text{ T} &= 1 \text{ kg s}^{-2} \text{ A}^{-1} \end{aligned}$$

T represents tesla, the S.I. unit of magnetic flux density.

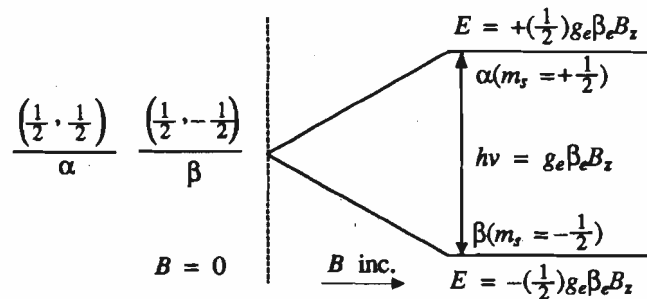


Fig. 11.1: Two energy levels of an electron in the presence of magnetic field.

You can see in Fig. 11.1 that the lower energy state corresponds to $m_s = -\frac{1}{2}$ which is in contrast with the case of nuclei about which you studied in Unit 10. This lower energy state is represented by β and can be designated by its quantum numbers (s, m_s) as $(\frac{1}{2}, -\frac{1}{2})$. In this state, the magnetic moment is *parallel* to the applied field. Similarly, the higher energy state can be denoted by α and can be designated by quantum numbers $(\frac{1}{2}, \frac{1}{2})$. In this state, the magnetic moment is *antiparallel* to the applied field.

In the absence of the magnetic field, the two states (α and β) have the same energy and are said to be *degenerate*.

Note that the basic equations for ESR follow the same pattern of NMR.

It is also evident from Fig. 11.1 and Eq. 11.4 that the energy difference between the two states is as given below:

$$\Delta E = g_e \beta_e B_z \quad \dots\dots(11.5)$$

From Eq. 11.6, we can say that

$$\begin{aligned} h\nu &= g_e \beta_e B_z \\ &= \frac{g_e e \hbar}{2m} B_z \\ &= \gamma \hbar B_z \end{aligned}$$

Application of an electromagnetic radiation (oscillating field) perpendicular to the applied field B_z , induces transitions from the lower to the higher energy state provided the following resonance condition is satisfied:

$$h\nu = \Delta E = g_e \beta_e B_z \quad \dots\dots(11.6)$$

and

$$\begin{aligned} \nu &= \frac{\gamma \hbar B_z}{h} \\ &= \frac{\gamma \hbar B_z}{h \cdot 2\pi} \\ &= \frac{\gamma B_z}{2\pi} \end{aligned}$$

where ν is the frequency of the applied radiation.

Eq. 11.6 shows that the energy separation between the two levels and hence frequency of the radiation absorbed (ν), is proportional to the applied field, (B_z). Therefore, you may say that e.s.r. spectra can be studied by using the radiation of any frequency provided we use the appropriate applied field. Most commonly, fields of 0.34 T and 1.25 T are used. The corresponding frequencies for the free electron being 9.5×10^9 Hz and 35×10^9 Hz.

Spectrometer frequency (ν /Hz)

X-band	9.5×10^9
K-band	23×10^9
Q-band	35×10^9

$$1 \text{ GHz} = 10^9 \text{ Hz}$$

So the frequencies mentioned on R.H.S can also be written as 9.5 GHz, 23 GHz and 35 GHz

The frequency 9.5 GHz lies in the X-band of the microwave region and the frequency 35 GHz lies in the Q band of the microwave region. The details of instrumentation of an ESR spectrometer are given in the next section.

To test your understanding of the above discussion, try the following SAQ.

SAQ 2

A specimen of ZnO shows a strong esr line at the frequency 9.45 GHz. Calculate the g-value of the line.

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11.4 ESR SPECTROMETER

The layout of ESR spectrometer is shown in Fig 11.2, you can see that the ESR spectrometer is similar to the NMR spectrometer in principle. You can see in Fig. 11.2 that the source of microwave radiation is klystron. The radiation obtained from source is channeled through a waveguide to the sample which is kept in the magnetic field. When the transitions between spin levels take place, the energy from the microwave radiation is absorbed. The absorbed radiation is then detected by a phase-sensitive detector and the spectrum is recorded as a derivative spectrum. Let us study next section to know what do we mean by a derivative spectrum.

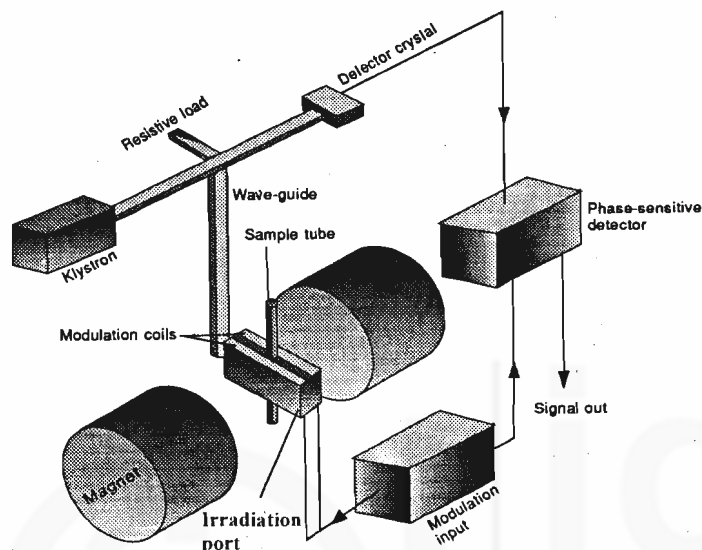


Fig. 11.2: The ESR spectrometer.

11.5 PRESENTATION OF THE ESR SPECTRUM

The ESR spectrometer operates at a fixed microwave frequency and the magnetic field is swept. The ESR spectra are not presented as absorption curve which was the case for NMR spectrum but as derivative curves as said earlier. The first derivative (i.e. slope) of the absorption curve is plotted against the strength of the magnetic field. Such a comparison of spectral presentation is shown in Fig. 1.3. Fig. 1.3 (a) shows an absorption curve whereas Fig. 1.3 (b) shows the derivative curve.

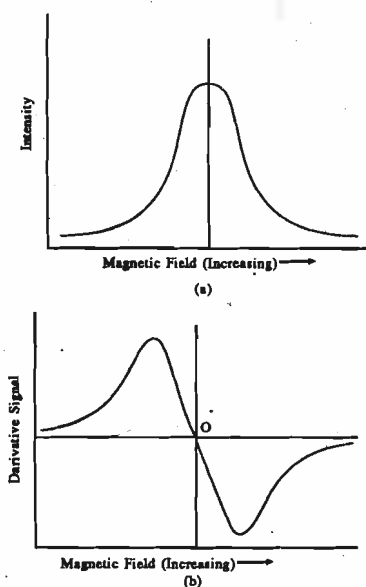


Fig. 1.3: (a) An absorption curve.
(b) A derivative curve.

The ESR spectrometer is similar to an NMR spectrometer. But since the Bohr magneton (β_e) of an electron is about 10^3 fold larger than that for the nuclei, the frequency required for the ESR experiment falls in the microwave region of the electromagnetic radiation instead of radiofrequency region as was the case for an NMR experiment. Also the ESR spectra are not represented as absorption curves (as is the case with NMR spectra) but as derivative curves.

ESR Spectrum can be recorded for gases, solutions, powders, single crystals and frozen solutions.

In case of an ESR spectrum, the absorption signal is broad and it is difficult to know the point of maximum absorption. The recording of spectra as a derivative is useful because it helps to identify the point of maximum absorption which is obtained as a point of intersection of two lines. This point is shown as point O in Fig. 1.3 (b). We will now discuss the ESR spectrum of some simple systems.

11.6 THE ESR SPECTRA OF SOME SIMPLE SYSTEMS

If the applied magnetic field (B_z) is the only magnetic field acting on the unpaired electron, the ESR spectrum would show a single line with a frequency specified in terms of the g value (as given by Eq. 11.6, $h\nu = g_e \beta_e B_z$)

Such is the case of the ESR spectrum of SO_3^- anion where *no magnetic nuclei* are present and the observed spectrum is a single line.

You have studied in Unit 10 that coupling between the nuclear spins (spin-spin coupling) causes a splitting of the nuclear magnetic energy levels resulting in the splitting of signals in NMR spectra. Similarly when the magnetic nuclei are present in the system, the spin of the electron interacts with the magnetic moments of the nuclear spin. This leads to the splitting of the spectral line into a number of lines and is known as the *nuclear hyperfine interaction*.

Let us study the case of hydrogen atom to understand hyperfine interaction.

11.6.1 ESR spectrum of Hydrogen Atom

The ESR spectrum of hydrogen atom shows two equally intense lines which are 506.8 G apart. This is shown below in Fig. 11.4(a).

Note that the positive values ($+\frac{1}{2}$) of spin quantum number (m_s for electron and m_I for nucleus) are designated as α and negative values ($-\frac{1}{2}$) are represented by β . Thus, we can represent the energy levels obtained after hyperfine splitting by specifying their (m_s, m_I) values or using α, β notation. The subscripts e and p in α_e, β_e and α_p, β_p denote electron and proton, respectively. A third way of representing the spin of an electron or a proton and thus specifying various energy levels is, by using arrows as \uparrow or \downarrow . This notation was used in Unit 10, Fig. 10.10.

$1T = 10^4 G$

Note that the hydrogen atom represents the case of an interaction between an electron and a single proton in the magnetic field.

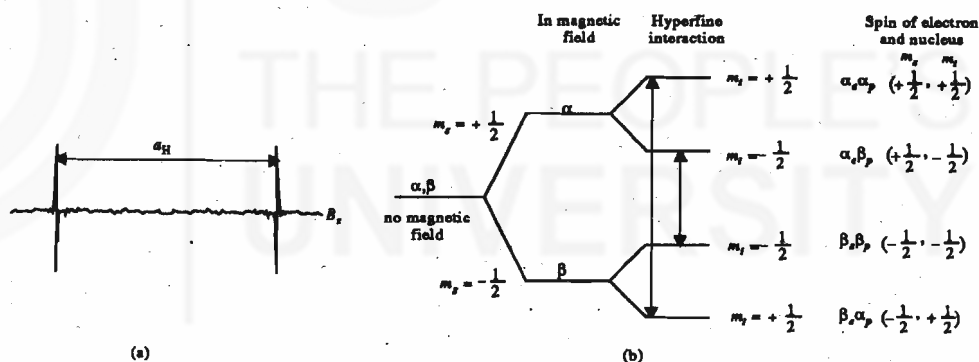


Fig. 11.4: (a) ESR spectrum of hydrogen atom. (b) The energy levels obtained as a result of nuclear hyperfine interaction.

The origin of these two lines as a result of splitting due to nuclear hyperfine interaction can be explained as follows. In the presence of magnetic field, an unpaired electron has two energy levels corresponding to two spin states denoted by

$$m_s = +\frac{1}{2} \text{ and } m_s = -\frac{1}{2}.$$

If we consider the interaction of these levels with a single nuclei (as in the case of hydrogen) having $m_I = +\frac{1}{2}$ and $-\frac{1}{2}$, we get four energy levels as shown in Fig. 11.4 (b).

The selection rules for the transitions are

$$\Delta m_s = \pm 1 \text{ and } \Delta m_I = 0.$$

The transitions which are allowed by these selection rules are also shown in

Fig. 11.4(b). The energies of the two allowed transitions are given by the following expression.

$$\begin{aligned} \Delta E &= h\nu = g_e \beta_e B_z \pm m_I a \\ &= g_e \beta_e B_z \pm \frac{1}{2} a \end{aligned} \quad \dots(11.7)$$

where a is hyperfine splitting constant and has the value 1420.4 MHz for hydrogen atom.

Let us now study a little more complex systems.

11.6.2 ESR Spectra – Some More Examples

Let us now study the case of deuterium. The nuclear spin quantum number $I = 1$ in this case. Hence, there are three values of the component of angular momentum vector m_I as given below.

$$\begin{aligned} m_I &= I, (I - 1), \dots, 0, \dots, -(I - 1), -I \\ &= +1, 0, -1 \end{aligned} \quad \dots(11.8)$$

Similar to the case of hydrogen atom, the interaction of nuclear spin with both the values of m_s of electron ($\pm 1/2$) yields six energy levels as shown in Fig. 11.5 (a).

By applying the selection rules, the three allowed transitions are as shown in Fig. 11.5 (a). This leads to the splitting of the signal into 3 components as shown in Fig. 11.5 (b). In general, we can say that if an electron interacts with a nucleus of spin I the ESR signal splits into $(2I + 1)$ components.

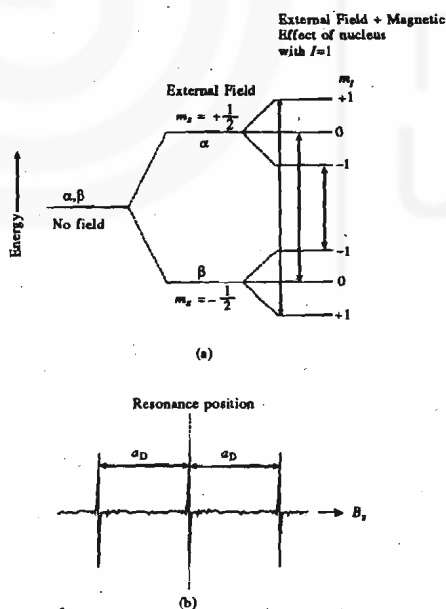


Fig. 11.5: (a) Energy levels of deuterium arising due to nuclear-electron interaction, (b) ESR spectrum of deuterium.

We will now discuss the ESR spectra of some species which contain more than one magnetic nuclei.

Let us first consider a single electron in presence of two protons. The two protons interact equally with the electron and give rise to six energy levels. By using the selection rules $\Delta m_s = \pm 1$ and $\Delta m_I = 0$, three transitions are possible as shown in Fig. 11.6. These three transitions will show three signals in the ESR spectrum.

Since an electron can approach the proton much more closely than can another proton, the coupling is much stronger and the splitting of ESR spectral lines is much greater than those of NMR spectral lines. Hence in proton NMR spectra, the coupling constant is of the order of 10 Hz whereas in ESR spectra, the hyperfine splitting constant is of the order of 10 MHz.

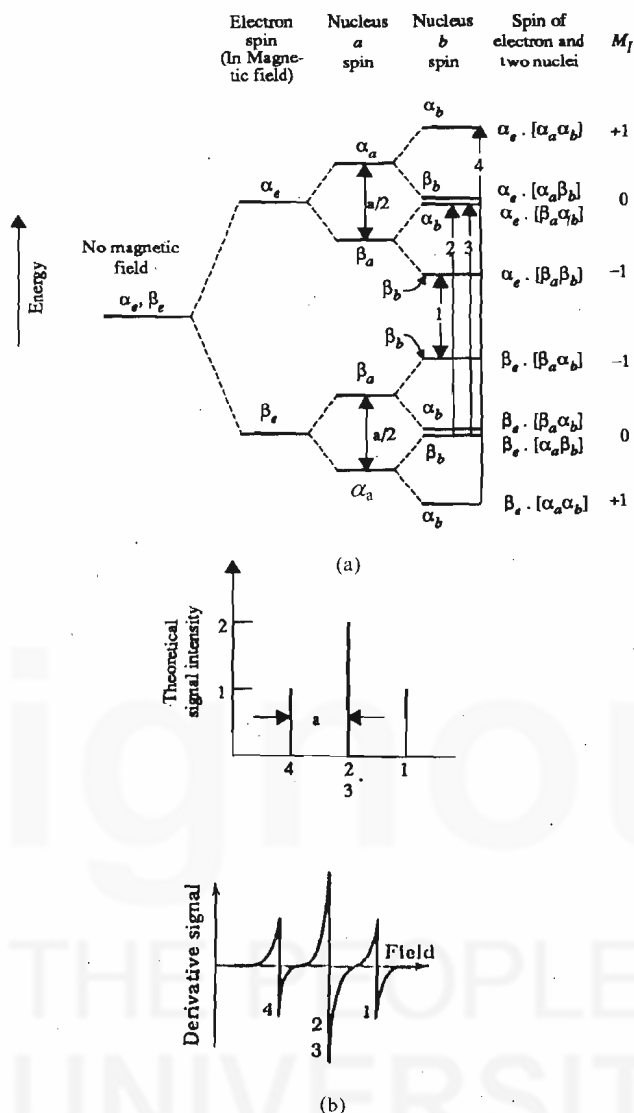
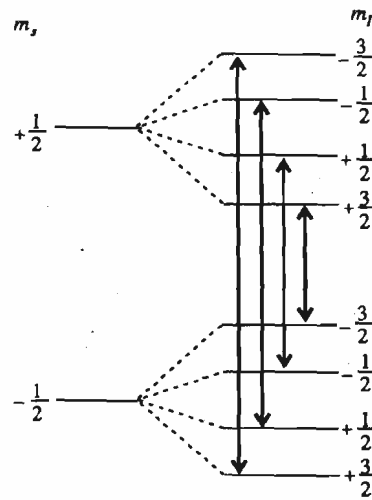


Fig. 11.6 (a) ESR energy level diagram for the interaction of one electron with two protons. (b) ESR spectrum.

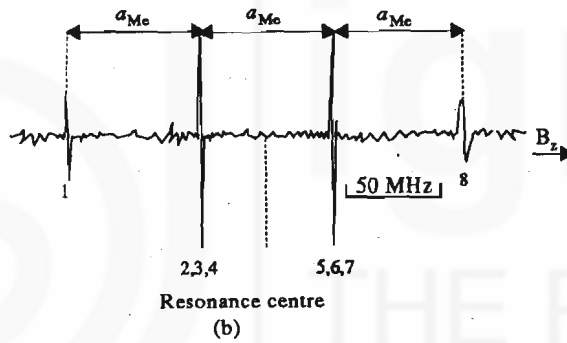
The simplest example of such a species is methyl radical, $\cdot\text{CH}_3$. It contains three equivalent hydrogen atoms. Thus, net $I = 1/2 + 1/2 + 1/2 = 3/2$ in this case. Hence $m_I = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ in the direction of the applied magnetic field. Interaction of each of these m_I values with $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$ will yield eight energy levels as shown in Fig. 11.7 (a).

The application of selection rules tells us that 4 transitions are allowed. These transitions are shown in Fig. 11.7 (a). The ESR spectrum of methyl radical obtained as a result of these transitions is shown in Fig. 11.7 (b). You can see that the signals are not of equal intensity and their ratio of intensity is 1: 3: 3: 1. This pattern of splitting and intensity can be understood easily if we add the splitting caused by each equivalent nucleus in turn. This is shown in detail in Fig. 11.7 (c) for one, two and three protons. Note that in this case since the hyperfine splittings are same (i.e. hyperfine splitting constant is having the same value), there was equal spacing between the splitted lines. For such cases where equivalent protons are involved, Pascal triangle can be used for determining the number of lines obtained after splitting and

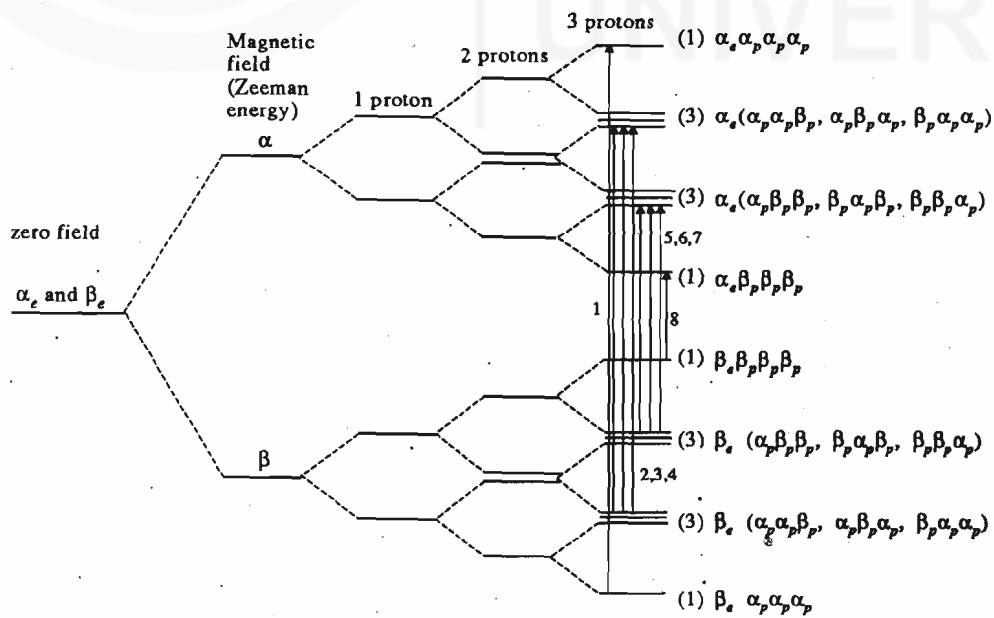
Since both the electron and the proton have spin quantum number $\frac{1}{2}$, the splitting pattern due to hyperfine splitting in ESR spectra resembles to that of spin-spin splitting in case of NMR spectra.



(a)



(b)



(c)

Fig. 11.7: (a) The energy levels and allowed transitions in methyl radical.
 (b) ESR spectrum of methyl radical. The numbers indicate the transition shown in part (c).
 (c) Identical splitting caused by three equivalent protons.

their relative intensity. This is shown below.

Pascal triangle

Number of Equivalent protons	Intensity ratio	Number of lines observed
0	1	1
1	1 1	2
2	1 2 1	3
3	1 3 3 1	4
4	1 4 6 4 1	5
5	1 5 10 10 5 1	6
6	1 6 15 20 15 6 1	7
7	1 7 21 35 35 21 7 1	8
8	1 8 28 56 70 56 28 8 1	9

Thus for n equivalent nuclei having spin quantum number I , the interaction with an ESR spectral line will lead to its splitting into $2nI + 1$ components.

For a proton

$$I = \frac{1}{2}, \text{ So } 2nI + 1 = 2 \times n \times \frac{1}{2} + 1$$

$$= n + 1.$$

Thus, n equivalent protons will split an ESR signal into $n + 1$ components.

Let us come to a little different case of *non-equivalent* protons. Consider a simple system where there are two *non-equivalent* protons interacting with an electron. Firstly, the original line will be split by the first proton to a doublet. Let us denote the splitting constant due to the interaction with first proton by a_1 . This is depicted in Fig. 11.8 (a). Then, the second proton again splits each line of the doublet into two lines and this time we represent the splitting constant as a_2 . Since a_1 and a_2 are different, we get 4 lines. You can compare this splitting pattern with that obtained with two *equivalent* protons as predicted by Pascal triangle. This is shown in Fig. 11.8 (b).

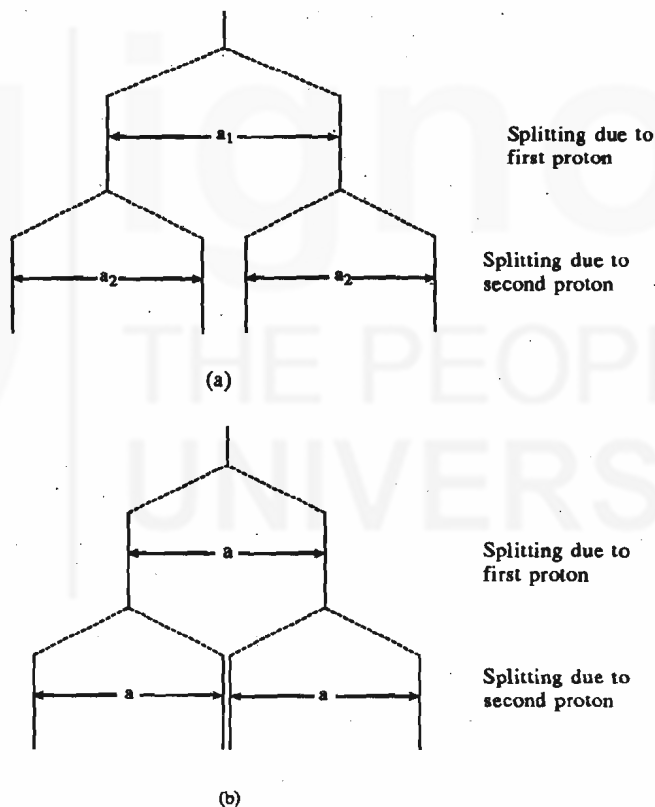
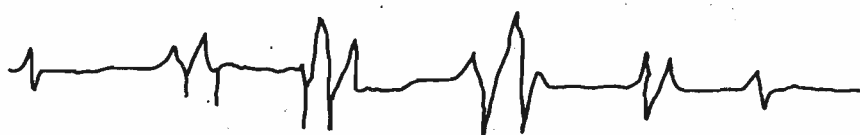


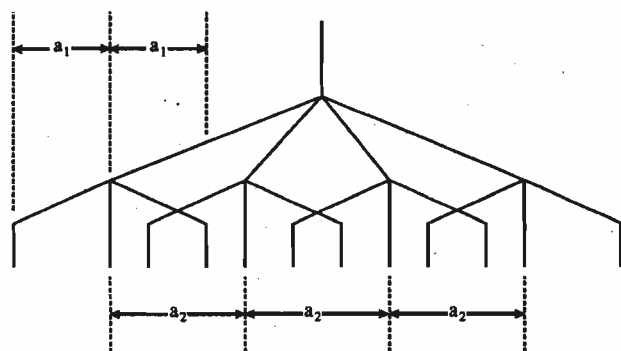
Fig. 11.8: (a) Splitting by two non-equivalent protons.
(b) Splitting by two equivalent protons.

We will now take the example of ethyl radical, $\cdot\text{C}_2\text{H}_5$ which has two sets of protons having different splitting constants. We can write ethyl radical as $\cdot\text{CH}_2\text{CH}_3$. The ESR spectrum of ethyl radical is shown in Fig. 11.9 (a).

The pattern of lines observed in the spectrum can be explained if we first consider the splitting of the signal due to two CH_2 protons. This will lead to a triplet having the intensity in the ratio of 1:2:1. Let the splitting constant for this be denoted as a_1 as shown in Fig. 11.9 (b). Each component is further split by methyl (CH_3) protons into four components having intensity in the ratio 1: 2: 2: 1. The splitting constant is denoted as a_2 .



(a)



(b)

Fig. 11.9: (a) The ESR spectrum of ethyl radical.
(b) Splitting pattern of the ESR spectrum.

Similarly, in case of $\cdot\text{CH}_2\text{OH}$ radical the signal in the ESR spectrum is first split due to the two protons of CH_2 group into a triplet in the ratio 1: 2: 1. Then, each component of this triplet is further split into a doublet by coupling with the H of the OH group. The observed spectrum thus looks as shown below in Fig. 11.10.

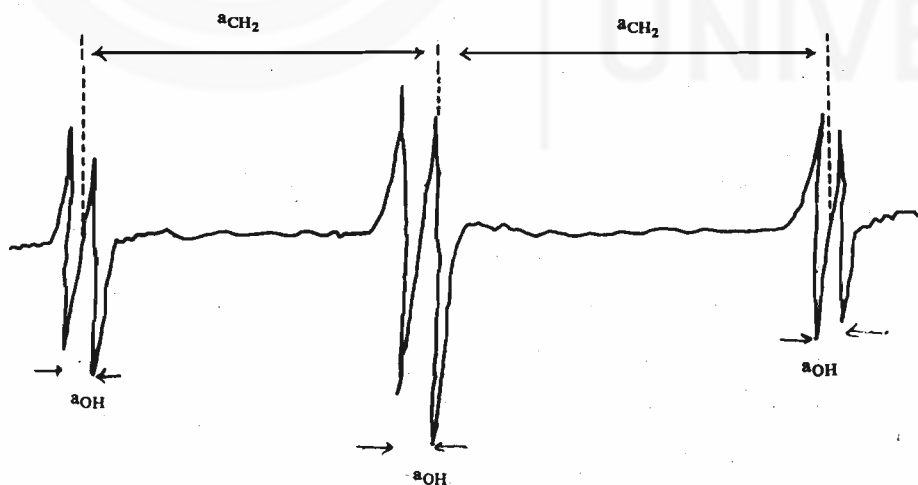


Fig. 11.10: ESR spectrum $\cdot\text{CH}_2\text{OH}$.

We can thus generalise that when the splitting is caused by both a set of n equivalent nuclei of spin I_i and a set of m equivalent nuclei of spin I_j , then the number of lines is given by $(2n I_i + 1) (2m I_j + 1)$.

After understanding the above discussion, answer the following SAQ.

SAQ 3

Predict the number of components and their intensities in the ESR spectrum of $\cdot\text{C}_6\text{H}_6$.

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11.7 THE g VALUE

You are aware of the g value of free electron from Eq.11.1 where we represented it by g_e . You have also seen that g_e is related to the energy difference, ΔE according to Eq. 11.5. Thus, we can describe the variation in ΔE in terms of changing g_e values. This is in contrast to NMR spectroscopy where we kept g_N fixed and introduced shielding constant (σ) to describe the different resonance energies. Since for NMR, we had $B_{\text{eff}} = B_z (1 - \sigma)$ and $\Delta E_{\text{NMR}} = g_N \beta_N B_{\text{eff}} \Delta m_I = g_N \beta_N (1 - \sigma) B_z \Delta m_I$.

$$\text{Similarly, } \Delta E_{\text{ESR}} = g_e \beta_e B_{\text{eff}} \Delta m_s = g_e \beta_e (1 - \sigma) B_z \Delta m_s \quad \dots(11.9)$$

If we combine g_e and $(1 - \sigma)$ in Eq. 11.9 and write it as g ;

[i.e. $g = g_e (1 - \sigma)$], then we can write Eq. 11.9 as follows.

$$\Delta E_{\text{ESR}} = g \beta_e B_z \Delta m_s \quad \dots(11.10)$$

You are already aware that for a free electron g is represented as g_e and is equal to 2.00232. But, when we talk about the g factor of a radical or a complex in the context of the resonance condition given by Eq. 11.5, we mean g which is inclusive of shielding constant as

$$g = g_e (1 - \sigma)$$

The g value of a substance gives information about its electronic structure and hence can be used in its identification just like chemical shifts in the NMR spectra.

It may also be mentioned here that the g value we were referring above (Eq. 11.5) was for isotropic systems, i.e. systems which were *without* directional properties. But the systems which are *anisotropic*, i.e. systems which *have* directional properties (e.g. a crystal), show different g values depending upon its direction of measurement. For such a system, when g values are measured by applying the field along the three coordinate axes, they are termed as g_{xx} , g_{yy} and g_{zz} . Again, we can refer the g value as g_{\parallel} (g parallel) or g_{\perp} (g perpendicular) depending upon whether we are measuring g values parallel to the axis of symmetry or perpendicular to it. You can understand this with the help of the following diagram, (Fig. 11.11).

Fig. 11.11 shows a as the axis of symmetry. When we measure g along this axis, we represent it as g_{\parallel} and designate it as g_{zz} . The other two g values along the other two principle axes perpendicular to g are called g_{\perp} and are designated as g_{xx} and g_{yy} .

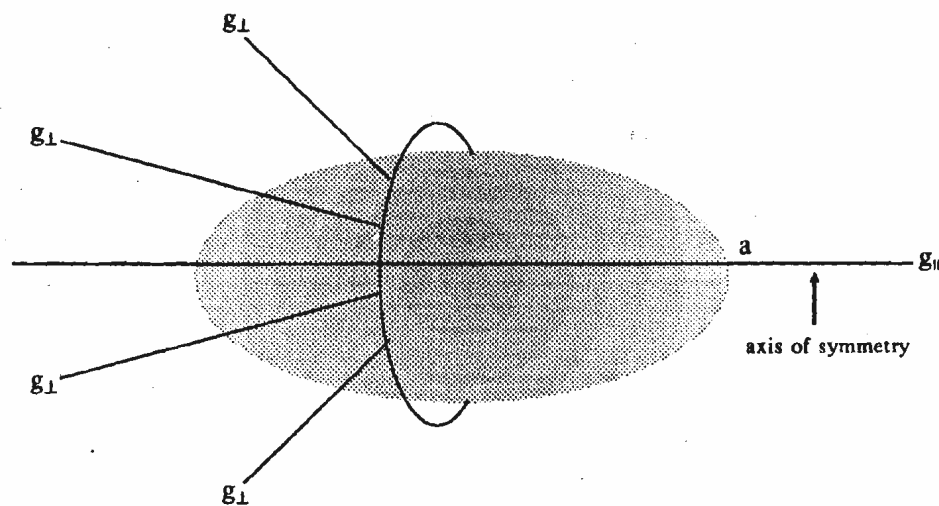


Fig. 11.11: $g_{||}$ and g_{\perp} .

The g values for organic radicals are almost isotropic and differ very little from g_e for the free electron. This is illustrated below in Table 11.1.

Table 11.1: The g value of some organic radicals

radical	g value
$\cdot\text{CH}_3$	2.00255
$\cdot\text{CH}_2\text{CH}_3$	2.0026
$\cdot\text{CH}_2\text{OH}$	2.0033
$\cdot\text{CH}_2\text{CHO}$	2.0045
$\cdot\text{CH}_2\text{COCH}_3$	2.0042

The g values of some species such as $\text{ROO}\cdot$, $\text{R}_2\text{NO}\cdot$ and inorganic radicals differ from g_e . This is because the unpaired electron is localised in a particular orbital giving rise to spin orbital coupling. Some examples of inorganic radicals being $3d^3$ ions (V^{2+} , Cr^{3+} and Mn^{4+} having g values in the range 1.98-1.99) and $3d^5$ ions (Fe^{3+} , Mn^{2+} and Cr^+ have g values close to 2.00).

11.8 SOME APPLICATIONS OF ESR SPECTRAL STUDIES

The study of ESR spectrum has wide applications as given by the following examples:

(i) Study of Free Radicals:

Free radicals can be studied by ESR spectroscopy even in small concentrations. The hyperfine structure of the ESR spectrum is a kind of fingerprint that helps to identify the radical present in a sample. Besides using nuclear hyperfine splitting to explain the number of magnetic nuclei present nearby the unpaired electron as discussed in Sec. 11.5, it can also help in mapping the unpaired spin density. This can be done by using McConnell Equation as given below:

$$a = Q\rho \quad \dots(11.11)$$

Here a is the observed hyperfine splitting constant, Q is the hyperfine splitting constant (or coupling constant) for unit density and ρ is the electron density.

For example, in case of hydrogen atom $a = 50$ mT and ρ for 1s orbital is 1; hence $Q = 50$ mT.

For $\cdot\text{CH}_3$ radical, $a = 2.3$ mT. Using $Q = 50$ mT, ρ can be calculated as

$$\rho = \frac{2.3}{50} = 0.046.$$

This means electron spends 5% of its time in 1s orbital of each hydrogen atom and remaining 85% of its time near carbon.

(ii) In the Study of Organometallic Compounds:

The ESR spectra of the single electron reduction product of $\text{SFeCo}_2(\text{CO})_9$ and $\text{PhCCo}_3(\text{CO})_9$ show 15 line spectrum ($a = 5$ G) and 22 line spectrum ($a = 10$ G), respectively. This thus indicated the delocalisation of the added electron on the cobalt atoms present.

Thus, 2 Co in $\text{SFeCo}_2(\text{CO})_9$ will give $2 \times 2 \times 7/2 + 1 = 15$ lines and 3 Co in $\text{PhCCo}_3(\text{CO})_9$ will give $2 \times 3 \times 7/2 + 1 = 22$ lines.

(iii) Transition Metal Complexes

Here, observed g values help to determine whether unpaired electron is localised on transition metal atom or on adjacent ligand.

11.9 SUMMARY

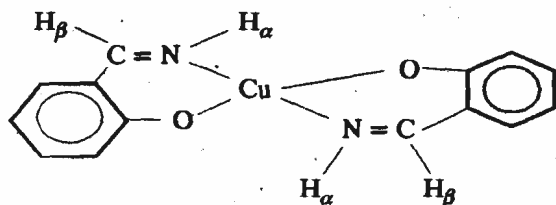
In this unit, you studied that

- ESR transitions occur in the microwave region of the electromagnetic spectrum and are accompanied by a change in the spin of the unpaired electron.
- ESR spectra are recorded as derivative curves.
- The coupling of the electron and nuclear spins results in nuclear hyperfine interaction. This results in the splitting of ESR line. The splitting is denoted by the hyperfine splitting constant, a . The splitting pattern helps in the determination of structure of the free radical.
- The g -factor for the electron is a universal constant and has the value $g = 2.00232$. The deviation from this g value indicates the departure from free radical behaviour (delocalisation).

11.10 TERMINAL QUESTIONS

1. The benzene anion has $g = 2.0025$. At what magnetic induction B_z would its ESR spectral line be centred at frequency 9.350 GHz?
2. How many ESR spectral lines are observed if an unpaired electron, delocalised on two non-equivalent protons, is placed in magnetic field?
3. An ESR spectrum shows only three lines. Explain how it could arise from:
 - (a) Hyperfine coupling to two nuclei with spin = 1/2
 - (b) Hyperfine coupling to a nucleus with spin = 1.
4. The ESR spectrum of a radical with a single magnetic nucleus is split into four lines of equal intensity. What is the spin of the nucleus?
5. How many lines would you expect in the ESR spectra of bis (acetylacetonato) copper (II) if I for copper is $\frac{3}{2}$?

6. Predict the ESR spectrum pattern for $\text{NO}(\text{SO}_3)_2^{2-}$ radical if $I = 1$ for nitrogen which is here the only nucleus having spin.
7. In the ESR spectrum of $\text{K}_3\text{Mo}(\text{CN})_6$, 25% isotopes of Mo show spin $I = \frac{5}{2}$. Predict the pattern of lines around a central line from 75% non-magnetic isotope.
8. The ESR spectrum of bis (salicylaldiminato) copper (II)



showed four main groups of lines, each of which contains 15 lines.

$$I \text{ for Cu} = \frac{3}{2}$$

$$I \text{ for N} = 1$$

$$\text{and } I \text{ for H} = \frac{1}{2}$$

Assume H_α are not participating in hyperfine splitting and explain the origin of lines.

11.11 ANSWERS

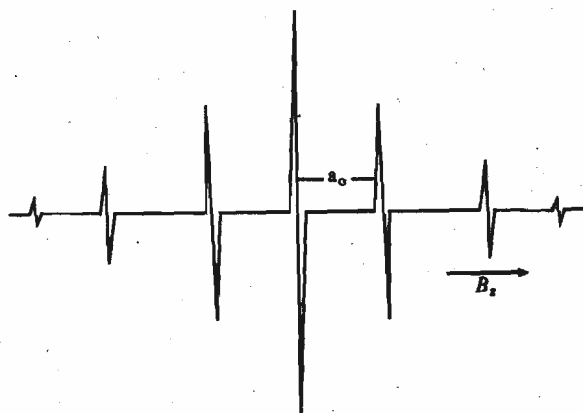
Self Assessment Questions

1. (i) $\cdot\text{CH}_3$ and (iv) $\cdot\text{C}_6\text{H}_6^-$.

2. $g = \frac{h\nu}{\beta B_z}$ (from Eq.11.6)

$$= \frac{(6.626 \times 10^{-34} \text{ J s}) (9.55 \times 10^9 \text{ Hz})}{(9.274 \times 10^{-24} \text{ J T}^{-1}) (0.1569 \text{ T})} = 4.3$$

3. According to the Pascal triangle when the number of protons is six, there will be 7 lines in the ESR spectrum having the intensity in the ratio 1: 6: 15: 20: 15: 6: 1.



Terminal Questions

$$\begin{aligned}
 1. \quad B_z &= \frac{h\nu}{\beta g} \\
 &= \frac{(6.626 \times 10^{-34} \text{ J s}) (9.35 \times 10^9 \text{ Hz})}{(9.27408 \times 10^{-24} \text{ A m}^2) (2.0025)} \\
 &= 3.334 \times 10^{-1} = 0.3334 \text{ T} \\
 &= 3334 \text{ G} \quad (1 \text{ T} = 10^4 \text{ G})
 \end{aligned}$$

2. In the presence of a magnetic field the unpaired electron will have two energy levels giving rise to a single ESR line. This line will split further into a doublet due to the first proton ($I = \frac{1}{2}$). This doublet will further split into two doublets due to second proton, because each proton has different hyperfine splitting constant. The splitting due to two non-equivalent protons is shown in Fig. 1.8(a). With selection rules $\Delta m_l = 0$, four lines will be observed in the ESR spectrum.

3. (a) For two equivalent nuclei ($I = 1/2$) gives the total $I = 1$; so $(2nI + 1)$ rule gives $2 \times 1 \times 1 + 1 = 3$ lines, with an intensity distribution of 1: 2:1.

(b) In case we have a nucleus with spin $I = 1$; then by using $2nI + 1$, we get $2 \times 1 \times 1 + 1 = 3$ lines in the spectrum. These lines will be of equal intensity.

4. Since we have obtained 4 lines of equal intensity in ESR spectrum suggesting interaction of a single nucleus. By using the equation $2nI + 1$ where $n = 1$, we have $2 \times 1 \times I + 1 = 4$

$$2I + 1 = 4$$

$$2I = 3$$

$$I = \frac{3}{2}$$

So, the spin of the nucleus interacting would be $\frac{3}{2}$.

5. 4 lines using $2nI + 1$.

6. $I = 1$; hence $2nI + 1 = 2 \times 1 \times 1 + 1$

$$= 3 \text{ lines with equal intensity}$$

7. Around a central line, six smaller signals (three on each side) should appear from 25% Mo having $I = \frac{5}{2}$ because

$$2nI + 1 = 2 \times 1 \times \frac{5}{2} + 1$$

$$= 6$$

8. Four main group of lines originate from Cu ($I = \frac{3}{2}$) hyperfine coupling.

No. of lines in each of these four major peaks = $(2nI_i + 1)(2mI_j + 1)$

$$= (2 \times 2 \times 1 + 1)(2 \times 2 \times \frac{1}{2} + 1)$$

$$= 5 \times 3 = 15$$