

Lecture 23 Title: Electron Spin resonance spectroscopy

Page-0

In this lecture, we will learn about the applications of the magnetic field effect on atoms which we have learnt in previous lectures.

Here, the electron Spin resonance spectroscopy (EPR) or sometimes known as electron spin resonance (ESR) will be discussed.

Since the magnetic field interacts with the spin, the spin of the system has to be nonzero. Because of this reason, the system having free electrons or unpaired electrons is required for this spectroscopic study.

We will start with the basic understanding of this spectroscopy and then we will discuss a few applications of it.

Electron Paramagnetic Resonance (EPR), sometimes referred to as Electron Spin Resonance (ESR), is a widely accepted spectroscopic technique in various research fields.

The resonance occurs between the spin of the unpaired electron and the electromagnetic field under a static magnetic field.

This technique is used to study paramagnetic centers on various oxide surfaces, which are frequently encountered in heterogeneous catalysis.

The observed paramagnetic centers include surface defects, inorganic or organic radicals, metal cations or supported metal complexes and clusters.

Each of these paramagnetic species will produce a characteristic EPR signature.

Diamagnetic oxide materials can also be studied using suitable paramagnetic probes, including nitroxides and transition metal ions.

Let us start with ground state $^2S_{1/2}$ of hydrogen atom having single electron. Here, $L=0$,

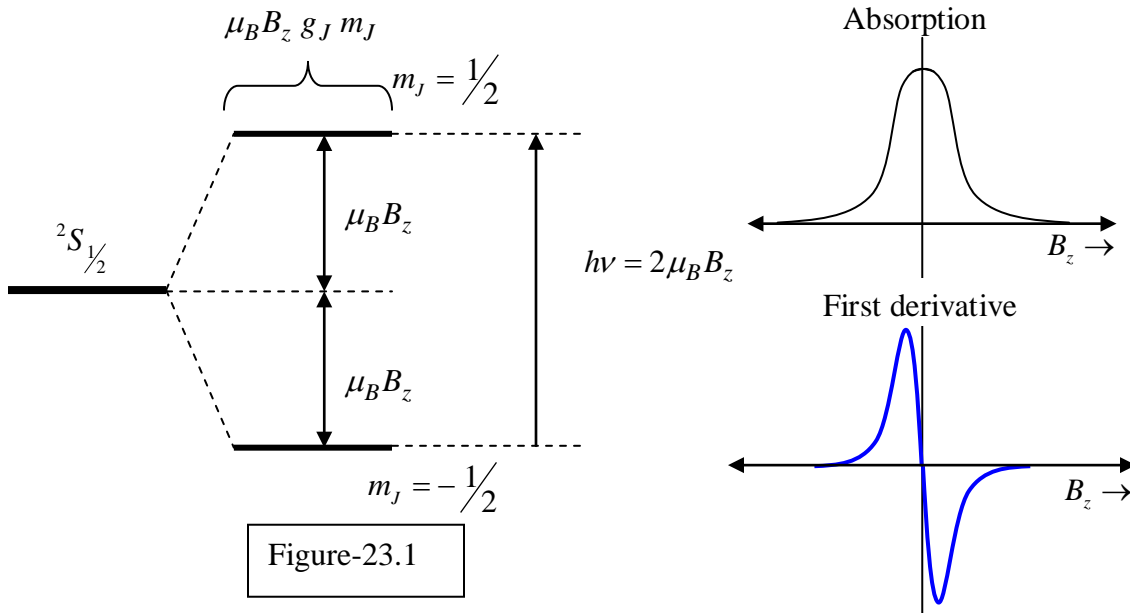
$S=1/2$, and $J=1/2$. Under the magnetic field this level splits into two energy levels, essentially due to the spin projection $m_s = 1/2$ and $m_s = -1/2$ because $m_L = 0$.

The splitting energy due to the magnetic field is $E_{mag} = g_J \mu_B B_z$ as shown in figure 23.1.

The value of $g_J = 2$.

The transition between this level is governed by the magnetic dipole selection rule

$\Delta l = 0, \Delta S = \pm 1$. This transition changes the spin projection by ± 1 .



Since,

$$h\nu = g_J \mu_B B_z = 2\mu_B B_z \dots\dots\dots(23.1)$$

Here, $g_J = g_s$ because $L = 0$

$$h\nu = g_s \mu_B B_z = 2\mu_B B_z$$

$$\frac{\nu}{B_z} = \frac{2\mu_B}{h} = \frac{2 \times 9.27 \times 10^{-21} \text{ erg / gauss}}{6.626 \times 10^{-27} \text{ erg - sec}} = 2.8 \text{ MHz / gauss}$$

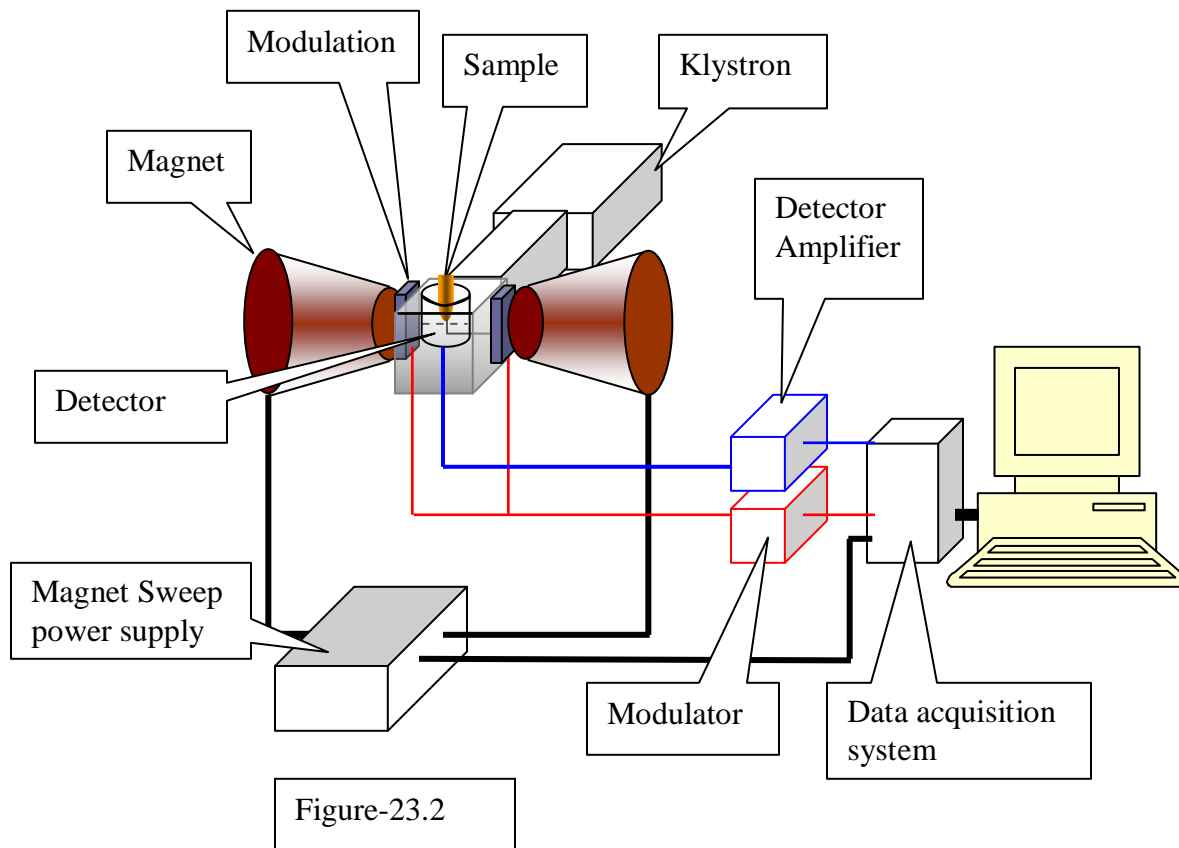
It can be seen that the frequency required for the transition to occur is about 2.8 MHz per Gauss of applied field.

This means that for the magnetic field usually employed in the laboratory, the radiation required belongs to the microwave region.

When the magnetic field used is about 3400 Gauss, the corresponding applied frequency required is in the microwave region of the electromagnetic spectrum, (~9 to 10 GHz).

This corresponds to a wavelength of about 3.4 cm and is known as the X - band frequency.

The following figure-23.2 represents the block diagram of the experimental set up for E.S.R



The experimental set up consists of

1. Microwave radiation source is Klystrons or gun oscillator
2. A sample cell is a cavity where the microwave is transmitted through waveguide
3. A d.c magnetic field and a sweeping circuit for changing the magnetic field.
4. A detection system basically a rectifier crystal for measuring the absorption
5. A data acquisition and a phase sensitive signal processing unit
6. A computer to control the magnet as well as storing the data

Page-4

The ratio of the electron population in the $m_J = +\frac{1}{2}$ state $n_{+\frac{1}{2}}$ to the $m_J = -\frac{1}{2}$ state $n_{-\frac{1}{2}}$

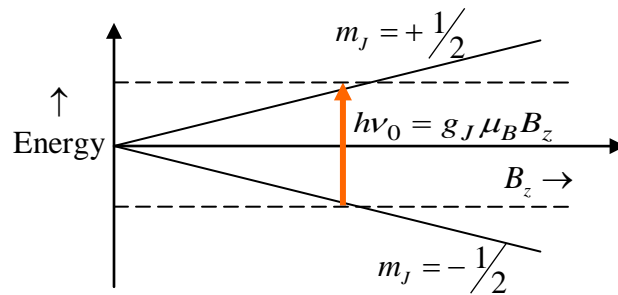
at a given temperature is given by $\frac{n_{+\frac{1}{2}}}{n_{-\frac{1}{2}}} = e^{-\Delta E/kT} = e^{-g_J \mu_B B_z / kT}$

To improve the sensitivity of the measurement, either B_z increases or temperature decreases

For common EPR experiments one of the frequency is selected for microwave radiation

Band	ν_0 (MHz)	λ (cm)	B_z (Gauss)
X	9,500	3	3,400
K	36,000	0.8	13,000

For resonance condition, (figure-23.3) instead of varying ν_0 , the magnetic field is varied.



At resonance condition, the absorption takes place. So the graph obtained is the absorption versus the magnetic field.

To measure the value of the magnetic field correctly, the first derivative of the absorption curve is recorded, as shown in the figure.

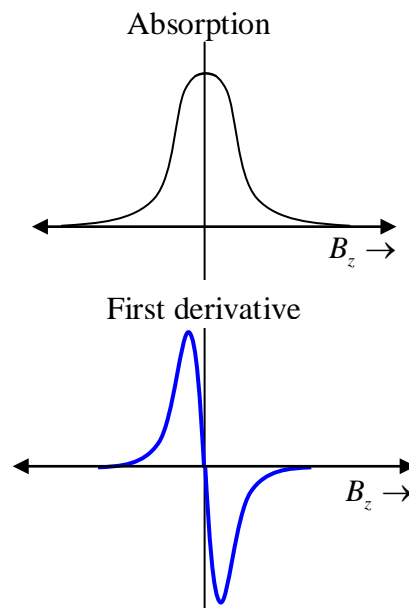


Figure-23.3

Now we will consider the interaction of electron magnetic moment and the nuclear spin. As discussed in the previous lecture, the interaction energy (Back-Goudsmit Effect) is

$$(m_J g_J - m_I g_I) \mu_B B_z + A' m_I m_J \dots\dots\dots(23.2)$$

when the magnetic field strength is higher than the hyperfine interaction.

Using this relation, we see that the electron Zeeman levels split further into four levels due to the nuclear spin.

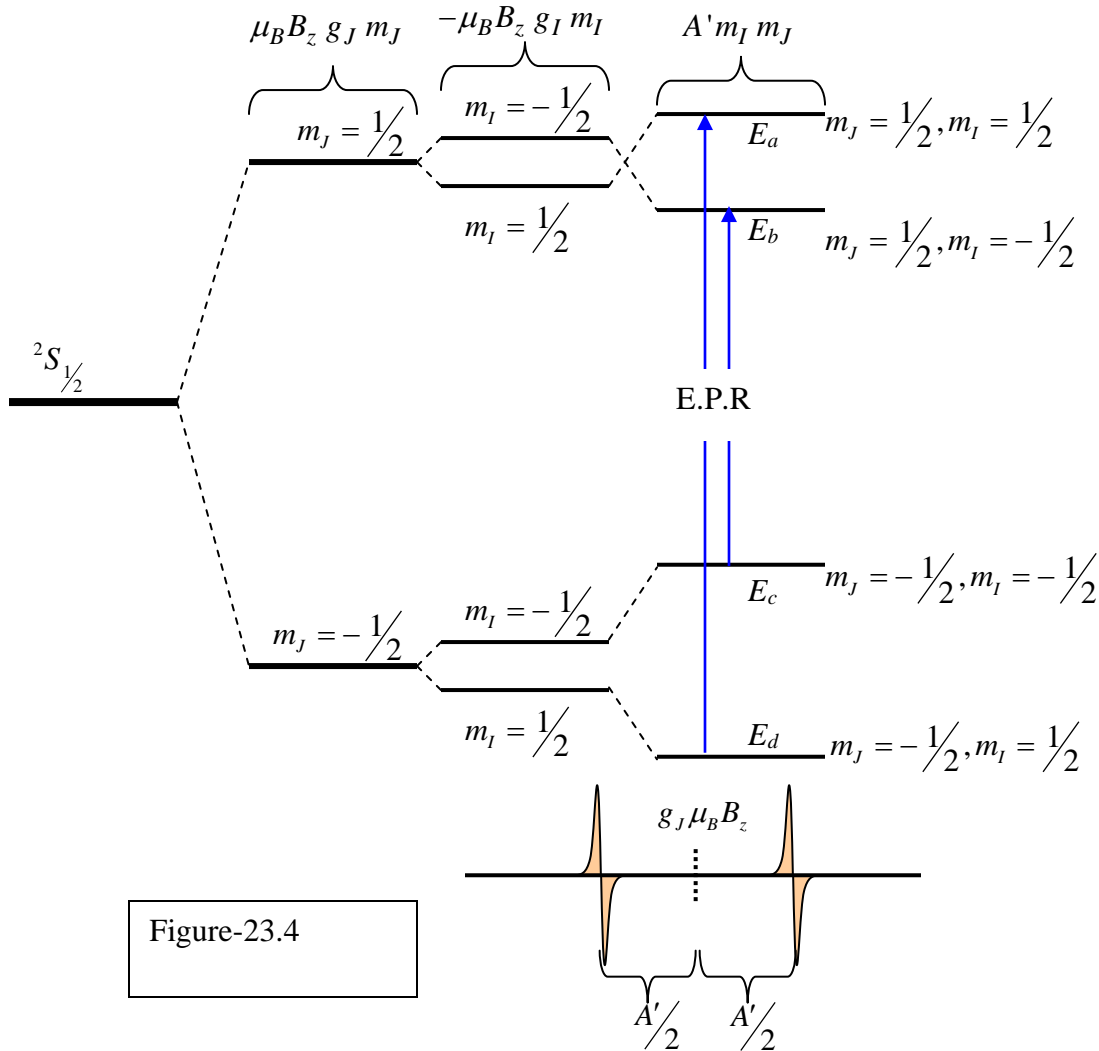


Figure-23.4

The E.P.R Selection rule : $\Delta m_J = \pm 1$, $\Delta m_I = 0$.

The reason for this is that these transitions are magnetic dipole transitions of electron where the m_J changes by 1. But this cannot change the nuclear spin simultaneously. So the m_I will be unchanged during the transition.

Applying this E.S.R. selection rule two transitions are observed.

Page-6

We calculate now the energies of these levels and see the energies of these two transitions. Substituting the value of $m_J = \pm \frac{1}{2}$ and $m_I = \pm \frac{1}{2}$ in equation 23.2, we get

$$E_a = \frac{1}{2} g_J \mu_B B_z - g_I \mu_B B_z + \frac{A'}{4} \quad m_J = \frac{1}{2}, m_I = \frac{1}{2}$$

$$E_b = \frac{1}{2} g_J \mu_B B_z + g_I \mu_B B_z - \frac{A'}{4} \quad m_J = \frac{1}{2}, m_I = -\frac{1}{2}$$

$$E_c = -\frac{1}{2} g_J \mu_B B_z + g_I \mu_B B_z + \frac{A'}{4} \quad m_J = -\frac{1}{2}, m_I = -\frac{1}{2}$$

$$E_d = -\frac{1}{2} g_J \mu_B B_z - g_I \mu_B B_z - \frac{A'}{4} \quad m_J = -\frac{1}{2}, m_I = \frac{1}{2}$$

And the two transition energies are

$$\nu_1 = E_a \leftarrow E_d = g_J \mu_B B_z + \frac{A'}{2}$$

$$\nu_2 = E_b \leftarrow E_c = g_J \mu_B B_z - \frac{A'}{2}$$

So these two transitions are separated by the hyperfine constant A' between them. This is a direct measure of the Fermi contact term (A_F) for the hydrogen atom discussed in previous lectures.

The intensity of both the transitions will be equal as shown in figure 23.4.

Note:

Since in the transition energy expression $g_I \mu_B B_z$ does not appear, from now on we will drop this term for the discussion as well as we will not include it in the diagram.

Let us consider that the electron is interacting with two similar protons with $I = \frac{1}{2}$ and $\frac{1}{2}$. According to coupling of angular momenta, we have the value of coupled $I = 1, 0$ and the value of $m_I = 1, 0, -1$

As shown in figure 23.5, each electron Zeeman level splits into three levels. Using E.S.R selection rule $\Delta m_J = \pm 1$, $\Delta m_I^1 = 0$, $\Delta m_I^2 = 0$, there will be three transitions. The separation between the two transitions is A' . The intensity ratio is 1:2:1, because the middle line is consisting of two transitions as shown in figure 23.5

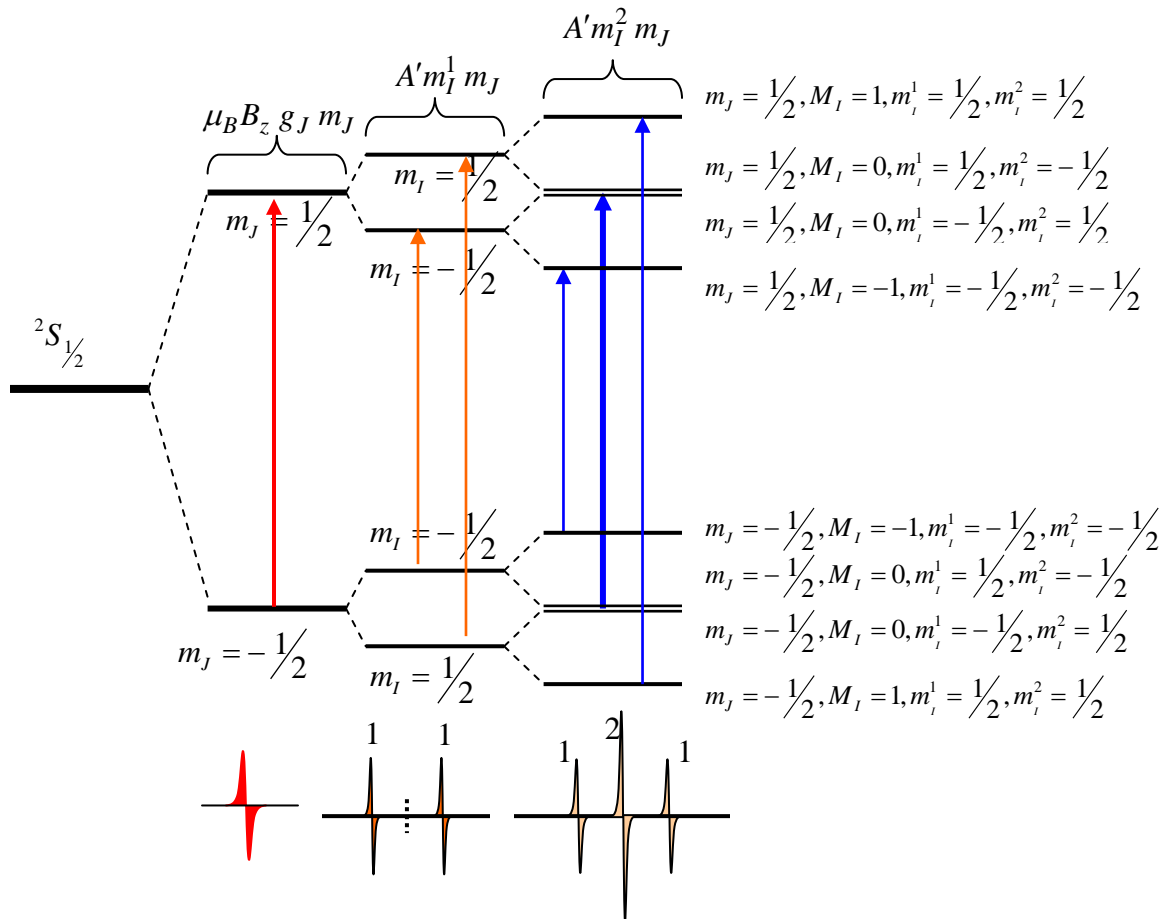


Figure-23.5

Let us take an example of Benzene radical.

Electron delocalized to all six $\text{>}\cdot\text{C}-\text{H}$ bonds

Here all protons will be interacting with the electron same way, so the hyperfine interaction will be same.

So let us predict the E.S.R. spectrum of benzene radical. There will be $(6+1) = 7$ lines.

The intensities of the lines of the spectrum follow the binomial expansion $(1+x)^n$.

For six equivalent protons, the intensity ratios 1:6:15:20:15:6:1

This can be determined by Pascal's triangle given below in figure-23.6.

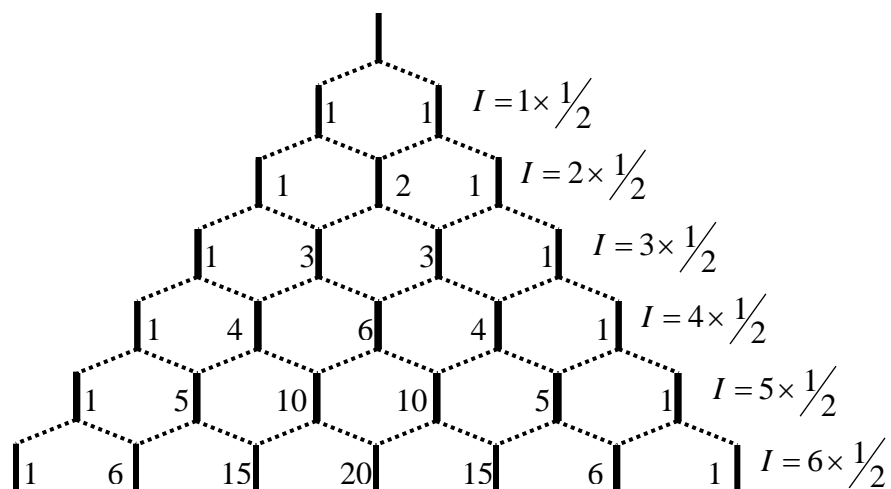
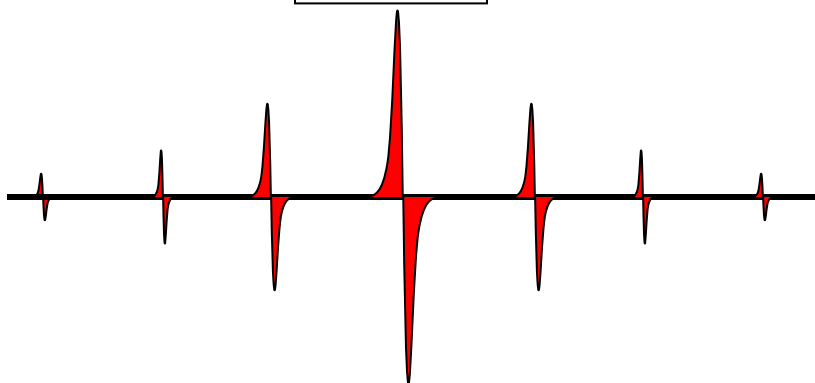


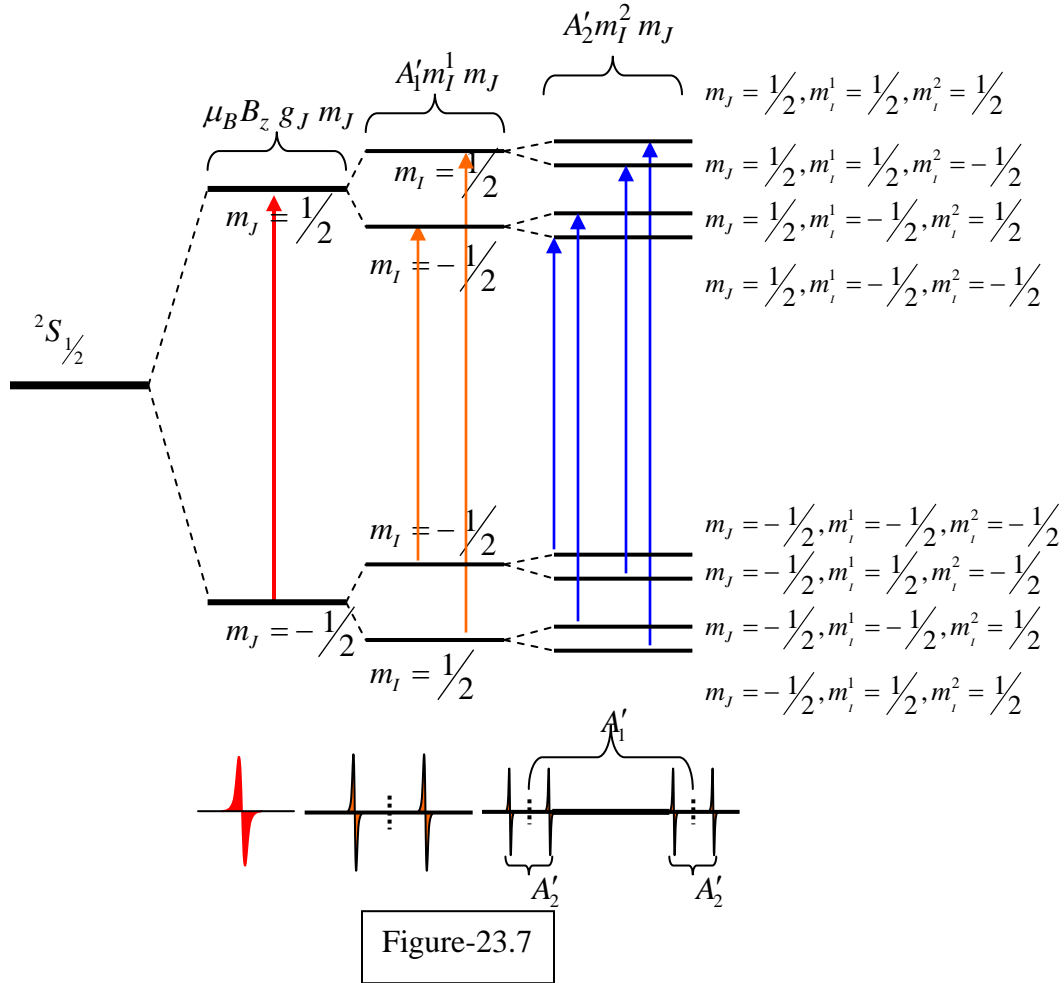
Figure-23.6



For nonequivalent protons, we write the interaction energy as

$$E_{mag} = m_J g_J \mu_B B_z + A'_1 m_I^1 m_J + A'_2 m_I^2 m_J$$

The energy level diagram is shown in figure-23.7

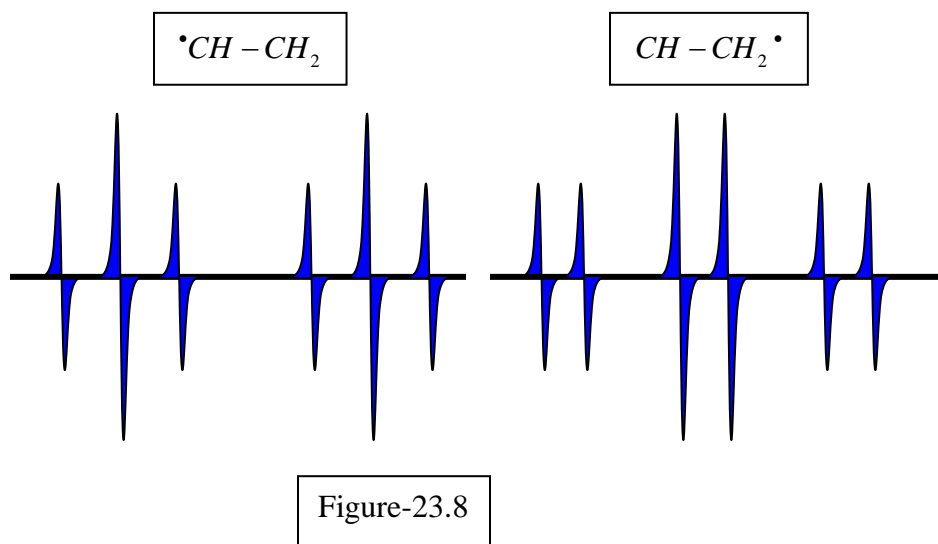


Here we consider that the interaction with proton-1 is greater than proton-2, i.e. $A'_1 > A'_2$. So the first, the transition splits into two because of the first proton-1, the separation is A'_1 . And then each of these transitions further splits into two, a total of four transitions. The separation between the transitions is A'_2 .

Let us predict the E.S.R spectrum of the radical fragment $\cdot CH - CH_2$

It should contain six lines - a large doublet arising from the interaction with the CH fragment (producing two lines) and a smaller triplet due to the electron interacting more weakly with the two remote protons of the CH_2 fragment (producing three lines). The resulting diagram is shown in Figure.

In the case where the radical is $CH - CH_2 \cdot$, the resulting pattern is also predicted to contain six lines, now triplet will have large compare to doublets as shown in Figure 23.8.



Here we will focus some applications of E.S.R

(a) Structural determination of radicals.

Methyl radical $\cdot\text{CH}_3$ has three equivalent $\text{>}\cdot\text{C}-\text{H}$ bonds. This provides four lines. The splitting between the lines is 25 Gauss.

The structure can be planar or tetrahedral.

For most planar aromatic radicals, the value of A' is 25 Gauss.

The theoretical value of the splitting in planar form is ~ 41 Gauss

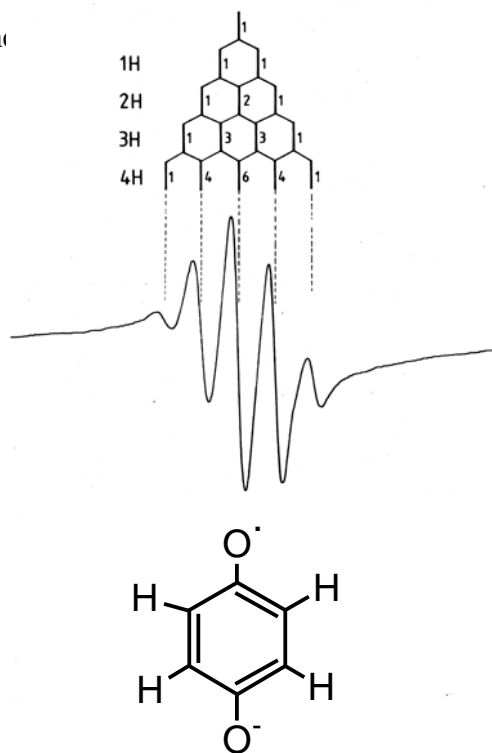
The theoretical value of the splitting in tetrahedral form is ~ 300 Gauss.

Therefore, the structure of the methyl radical is planar.

(b) Benzoquinone anion radical:

Four identical $\text{>}\cdot\text{C}-\text{H}$ bonds provide five lines

- 1 proton – splits into 2 lines 1:1
- 2 protons split into 3 lines 1:2:1
- 3 protons split into 4 lines 1:3:3:1
- 4 protons split into 5 lines 1:4:6:4:1



(c) E.S.R for solid sample

In crystal, the crystal field can interact strongly with \vec{L} and splits into $2L+1$ sublevels. Each of these sublevels further split into $2S+1$ sublevels when the external magnetic field is applied.

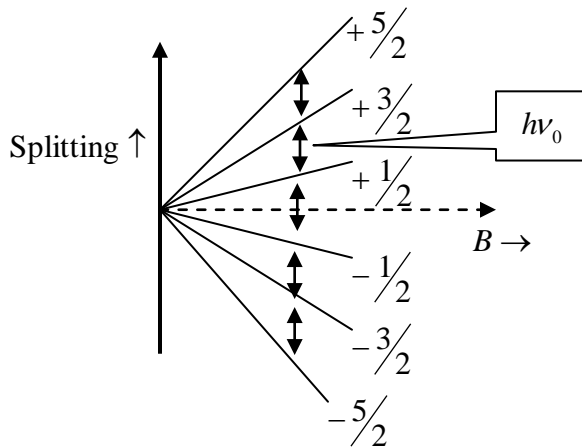
The magnetic dipole selection rule

$$\Delta m_j = \pm 1$$

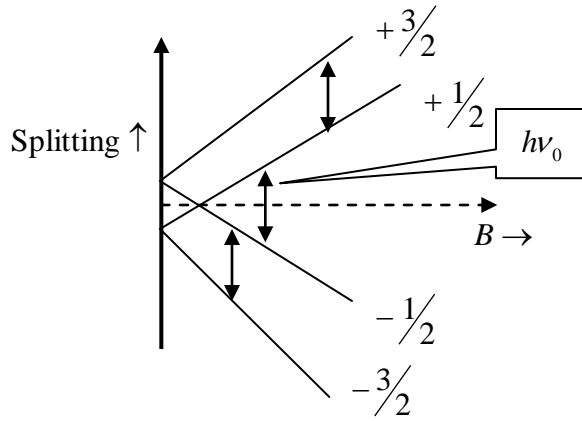
In another case, the spin degeneracy is removed in the crystal when weak spin orbit coupling is present. In this case the spin degeneracy is removed without external magnetic field.

This is illustrated in two different cases

For Mn^{++} , spin orbit coupling is zero. On applying magnetic field the ground state ($^6S_{5/2}$) splits into $(2 \times \frac{5}{2} + 1 = 6)$ levels. Since the separation between the sublevels is same, all the resonance occur at the same frequency.



In case of Cr^{+++} , spin degeneracy is removed by crystal field, and the sublevels are not equally placed. So the resonances occur at different frequencies.



Further, if the paramagnetic ion has nuclear spin, each sublevel will further split and the separation between the splitted sublevels provides information of the hyperfine constant.

This study provide information about

- (i) Type of ion.
- (ii) Symmetry of the crystal.

Recap

In this lecture we have learnt, the Electron Paramagnetic Resonance (EPR), sometimes referred to as Electron Spin Resonance (ESR) spectroscopic technique which is a widely accepted tool to determine the structure, conjugations and spin in various research fields.

This technique is used to study paramagnetic centers on various oxide surfaces, which are frequently encountered in heterogeneous catalysis such as surface defects, inorganic or organic radicals, metal cations, metal complexes and clusters.

Diamagnetic oxide materials can also be studied using suitable paramagnetic probes, including nitroxides and transition metal ions.

In biology, spin labeling and conformational studies are carried out in biomolecules with suitable probe such as nitroxide radicals etc.