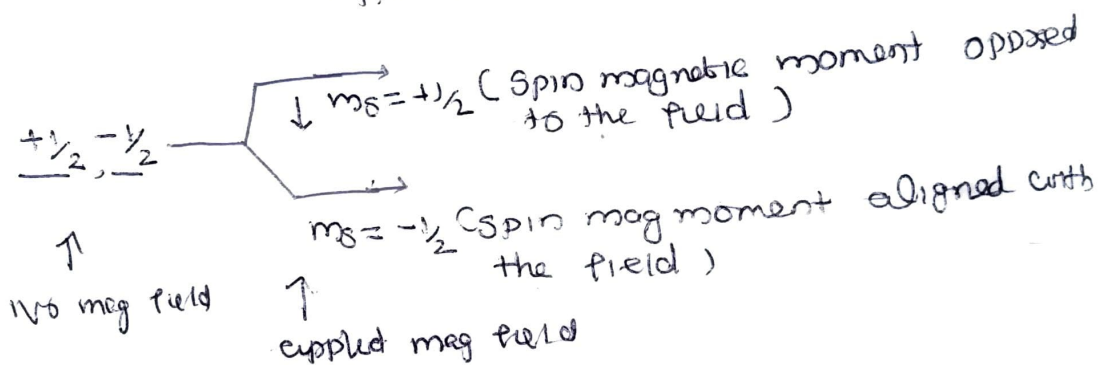


# Electron Spin Resonance Spectroscopy

EPR, or ESR or Electron magnetic resonance is a branch of absorption spectroscopy, in which radiation of low frequency is absorbed by molecules possessing electrons with unpaired spin

when an  $\bar{e}$   $S=1/2$  spin mag quantum numbers have  $m_s = +1/2, -1/2$

$m_s = +1/2, -1/2$  (~~are~~ doubly degenerate in the absence of applied mag field)



$$\text{Energy of transition } E = h\nu = g \beta H_0$$

$h$  = Planck's constant

$\nu$  = frequency of the radiation

$\beta$  = Bohr magneton ( $9.273 \times 10^{-24} \text{ J T}^{-1}$ )

$H_0$  = applied mag field

$g$  = spectroscopic splitting factors. (not a constant)

For free  $\bar{e}$   $g = 2.0023$

The magnitude of  $g$  depends upon the orientation of the molecule containing the unpaired  $\bar{e}$  with respect to the mag field. In solution or in the gas phase,  $g$  is averaged over all orientations bec<sup>2</sup> of the free motion of the molecule. If the paramagnetic radical or ion is located in a perfectly cubic crystal site, the  $g$  line is independent of the orientation of the crystal

and is said to be isotropic. In a crystal site of lower symmetry the g value depends upon the orientation of the crystal and is said to be anisotropic.

$$g = \frac{h\nu}{\beta H_0}$$

Factors affecting the magnitude of g values

The value of g for an unpaired  $e^-$  in a gaseous atom or ion for which Russell-Saunders coupling is applicable is given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad \text{--- (1)}$$

For free  $e^-$  :  $J = L + S$

$$= 1 + \frac{\frac{1}{2}(\frac{1}{2}+1) + \frac{1}{2}(\frac{1}{2}+1) - 0(0+1)}{2 \times \frac{1}{2}(\frac{1}{2}+1)}$$

L = 0  
S = 1/2  
J = 1/2

= 2.0

The actual value for a free  $e^-$  is 2.0023, where the contribution 0.0023 is due to a relativistic correction. For the halogen atoms ( $^2P_{3/2}$ , L=1, S=1/2, J=3/2) in the gas phase g values predicted by eqn (1) have been found to agree exactly with experimental values. No such agreement is found, when the unpaired  $e^-$  is placed in a chemical environment, either in a free radical or in a transition metal ion complex crystal lattice. In such chemical environments the orbital motion of the electron is strongly perturbed and the orbital degeneracy is removed (quenched), however complete removal of the orbital degeneracy is prevented by spin-orbit coupling (sustaining effect). Because of this quenching and sustaining competition, the orbital degeneracy is partly, but not completely removed and the net mag moment result to the g value different from 2.0023, value expected if the orbital degeneracy were completely removed.



In most free radical, the  $g$  values are nearly equal to the free  $e$  value ( $g = 2.0023$ ). The small deviation ( $\pm 0.05$  or smaller) are observed bec<sup>2</sup> of mixing low lying excited state with ground state

In transition metal <sup>complexes</sup> three cases arises

① The effect of spin-orbit coupling is much larger than that of the crystal field effect. eg: rare earth ions. Here LS coupling is not disturbed by the crystal field effect, bec<sup>2</sup> of shielding of  $f$  electrons. So  $J$  is a good quantum no, and they behaves very much like free ions. Thus the  $g$  value calculated from the eqn ① will be in good agreement with experimental values.

② The effect of crystal field is strong enough to break coupling b/w  $L$  and  $S$  and hence  $J$  is no longer a good ~~quantum~~ quantum number. Thus orbital degeneracy of  $J$  is removed partly, but not completely bec<sup>2</sup> of spin-orbit coupling and gives rise to a value diff from 2.0023. eg: First row transition metal ions

③ effect of crystal field is very large that LS coupling is broken down completely. eg:  $4d$  and  $5d$  transition metals

### Hyperfine splitting

Hyperfine structure occurs as a result of the magnetic interaction b/w electronic spin  $S$  and nuclear spin  $I$ . As a result of this interaction ESR signals or peaks are split into several line (HFS). Absorption signal will be splitted into  $2I+1$  components. ( $I =$  nuclear spin)

Selection rule for hyperfine transitions  
 $\Delta m_s = \pm 1$     $\Delta m_l = 0$

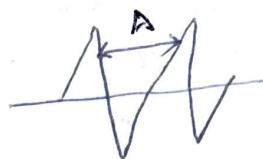
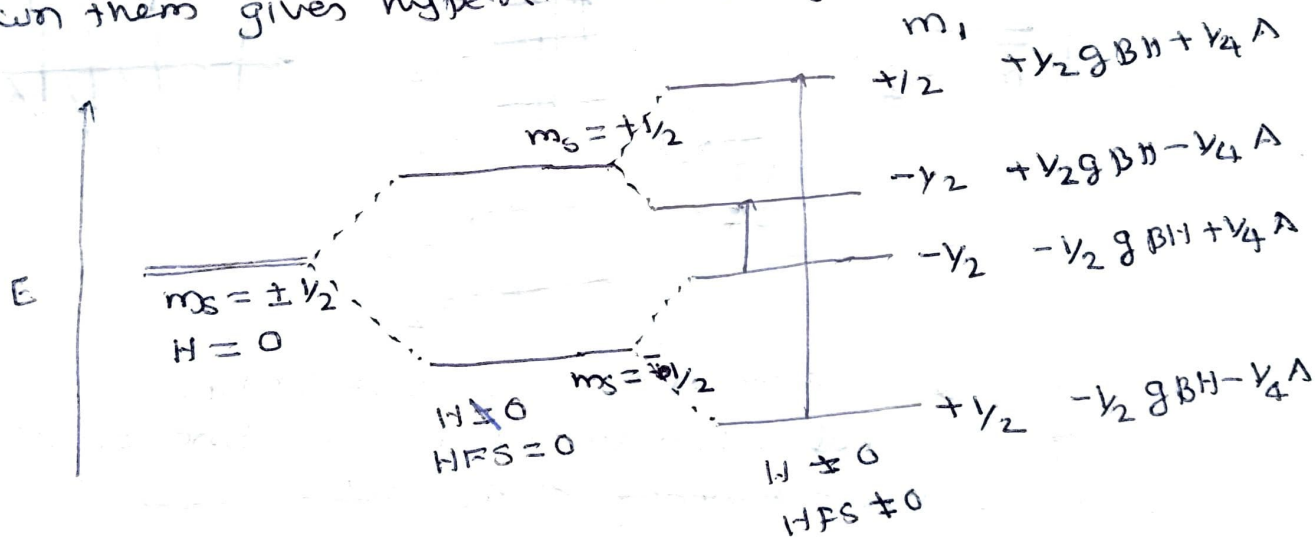
The energies of levels are given by -

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

A = hyperfine coupling constants (in eV or milli eV)

### Hydrogen atom

it contains an unpaired  $e^-$  with  $s = 1/2$  and a proton with nuclear spin  $I = 1/2$ . In the absence of magnetic field (H), the electron spin energy levels are degenerate i.e.  $m_s = +1/2 = -1/2$ . Application of external mag field removes the degeneracy b/w them. i.e.  $m_s = -1/2$  sublevel going down and the  $m_s = +1/2$  sublevel going up. Each of these electron sublevels will be splitted by two by interaction with nuclear spin. Thus gives a equal intense doublet, the spacing b/w them gives hyperfine coupling constant A



The magnitude of A value depends on

- ① the ratio of nuclear mag moment to the nuclear spin.
- ② The electron spin-density in the immediate vicinity of the nucleus.
- ③ Anisotropic effect

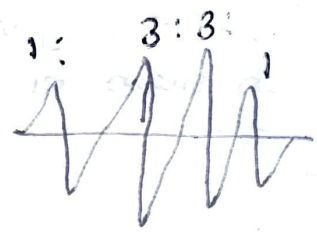
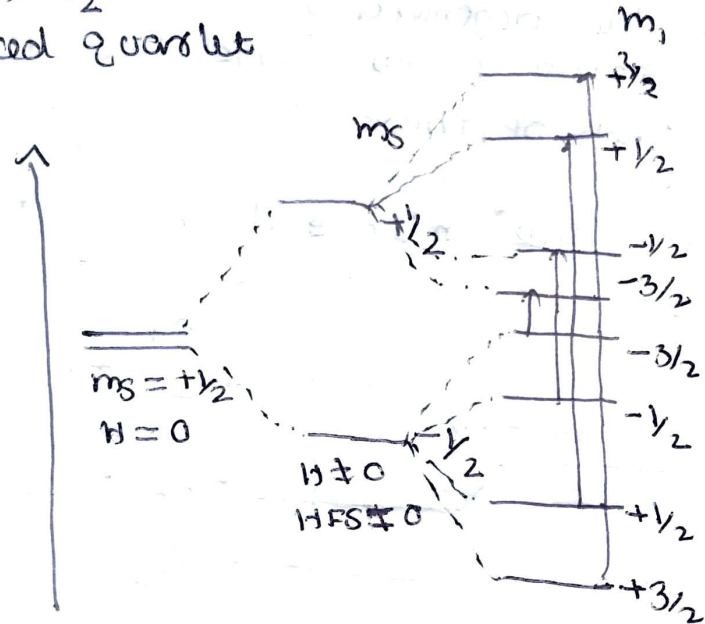


# Methyl radical - $\text{CH}_3$

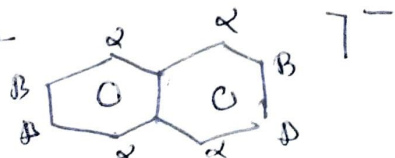
When the absorption spectrum is split by  $n$  equivalent nuclei of equal spin  $l$ , the number of lines is given by  $2nl+1$ .

Methyl radical contains unpaired  $e^-$  with spin  $S=1/2$  and three equivalent protons. For a proton  $l=1/2$  for three equivalent protons  $m_l$  can have values:

$+\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ . Also  $m_s = \pm \frac{1}{2}$ . Thus it will give equally spaced quartet



- If a radical contains  $n$  non-equivalent protons on to which  $e^-$  is delocalized, a spectrum consisting of  $2^n$  lines will arise corresponding to the  ~~$\text{CH}_3 = 2^3 = 8$  lines~~
- If the odd  $e^-$  is delocalized over a number  $n$  of equivalent protons  $2n+1$  lines will appear in the spectrum (i.e.  $n+1$  lines) eg:  $\text{Cl}_3^-$   $2 \times 3 \times \frac{1}{2} + 1 = 4$  lines
- If the odd  $e^-$  is delocalized over two sets of non-equivalent protons, the number of lines expected is  $(2n+1)(2m+1)$  eg: The naphthalene negative ion which can be prepared by adding sodium to naphthalene contains two different sets of four equivalent protons.

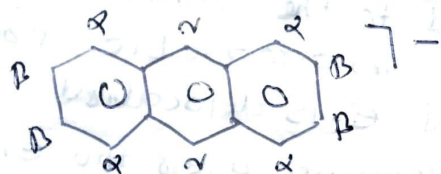


So it will give total 25 lines

$$(2n_{\alpha} + 1)(2n_{\beta} + 1)$$

$$(2 \times 4 \times \frac{1}{2} + 1)(2 \times 4 \times \frac{1}{2} + 1)$$

$$5 \times 5 = 25 \text{ lines.}$$

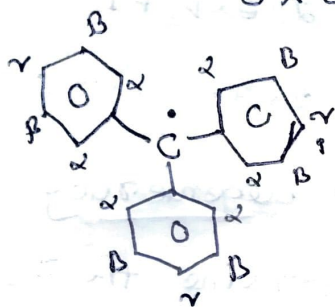


Anthracene negative ion

$$(2n_{\alpha} + 1)(2n_{\beta} + 1)(2n_{\gamma} + 1)$$

$$(2 \times 4 \times \frac{1}{2} + 1)(2 \times 4 \times \frac{1}{2} + 1)(2 \times 2 \times \frac{1}{2} + 1)$$

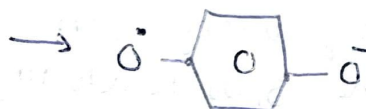
$$5 \times 5 \times 3 = 75 \text{ lines.}$$



Triphenyl methyl radical

$$(2 \times 6 \times \frac{1}{2} + 1)(2 \times 6 \times \frac{1}{2} + 1)(2 \times 3 \times \frac{1}{2} + 1)$$

$$7 \times 7 \times 4 = 196 \text{ lines}$$



1,4-Benzosemiquinone radical anion

$S = \frac{1}{2}$  for unpaired  $e^-$  interact with 4 equivalent

protons ( $I = \frac{1}{2}$ ) then  $m_1 = +2, +1, 0, -1, -2$  ESR

Spectrum will be quintet with 1:4:6:4:1 ratio.

several

→ If the  $e^-$  is delocalized on nuclei with spins greater than  $\frac{1}{2}$ , the number of peaks is predicted

$$2nI + 1$$

eg:  $(SO_3)_2NO^-$  anion - in this unpaired  $e^-$  interacts

with the nitrogen nucleus with  $I = 1$ , here  $m_s = \pm \frac{1}{2}$

and  $m_1 = +1, 0, -1$ . Thus ESR spectrum gives

triplet. ~~with intensity 1:2:1~~

equivalent

→ an  $e^-$  delocalized on two nitrogen atom gives

$$2 \times 2 \times 1 + 1 = 5 \text{ peaks with intensities in the ratio } 1:2:3:2:1$$

$$\frac{49 \times 4}{196}$$



For  $^{63}\text{Cu}$  ( $I = 3/2$ ) interacting with an odd  $e^-$  gives a hyperfine pattern of four lines (quartet) of equal intensity.  
 $2 \times 3/2 + 1 = 4$  lines

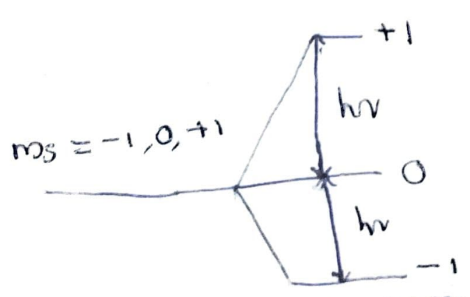
→ The hyperfine coupling constant  $A$  in H atom is  $50.68 \text{ mT}$ . This is related to the probability density of the  $e^-$  at the nucleus. In aromatic free radicals, where the unpaired  $e^-$  is delocalised over the molecular orbitals extending over the entire molecule, the probability of finding the electron on a given nucleus is small, hence hyperfine coupling constant is also small.

- $\text{C}_6\text{H}_5^-$  - septet  $A = 0.375 \text{ mT}$   $2 \times 6 \times 1/2 + 1 = 7$
- $\text{Cl}_3$  - quartet  $A = 2.3 \text{ mT}$   $2 \times 3 \times 1/2 + 1 = 4$

Zero field splitting and Kramers degeneracy

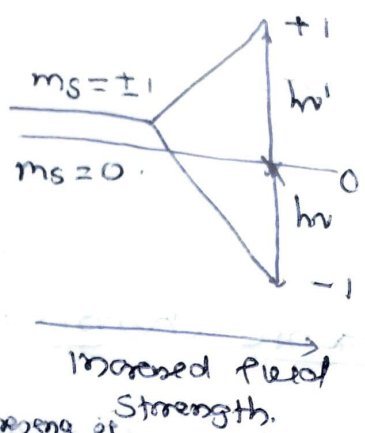
When a metal ion is placed in a crystalline field, the degeneracy of the d orbitals will be resolved by the electrostatic interactions. The spin degeneracy will remain until a magnetic field is applied. When the species contains more than one unpaired  $e^-$ , the spin degeneracy can also be resolved by the crystal. Thus the spin levels may be split even in the absence of mag field. This phenomenon is called zero-field splitting. However when the species contains an odd number of unpaired  $e^-$ s, the spin degeneracy of every level remains doubly degenerate. This is known as Kramers degeneracy.

$S = 1$



Two transitions  $0 \rightarrow 1$   
 $0 \rightarrow -1$  are degenerate only one signal is observed

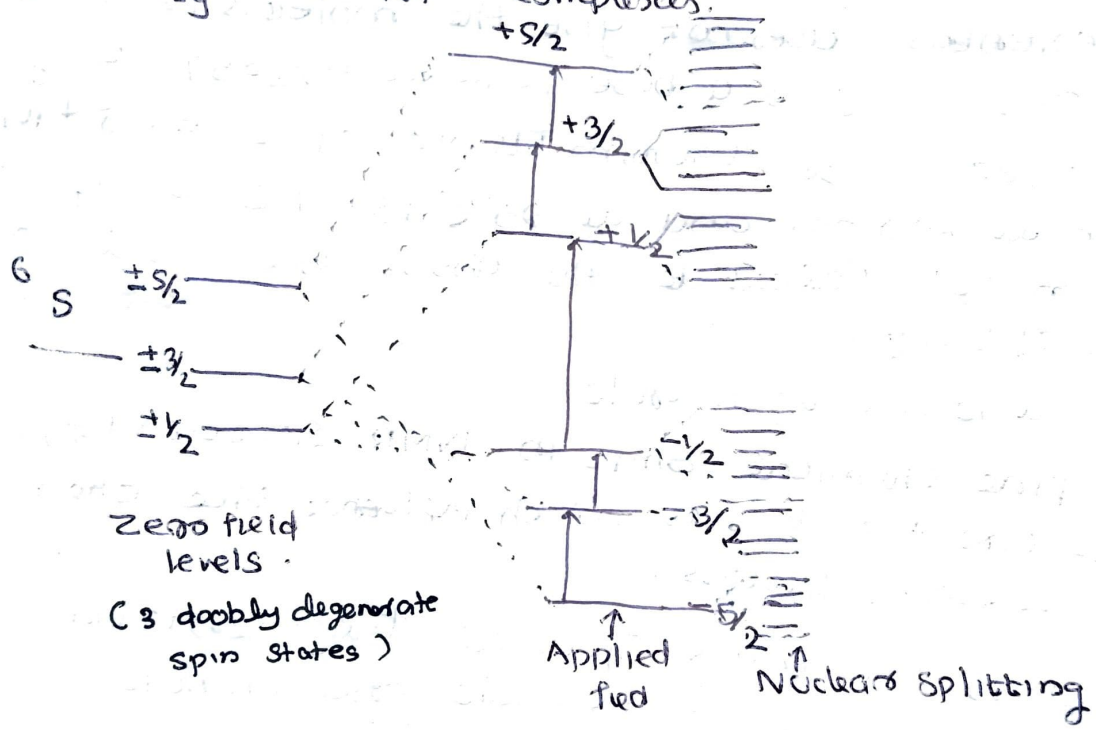
increased field strength.  
 NO zero-field splitting



Zero field splitting removes the degeneracy of  $m_s$  and subsequent splitting by the applied field occurs, then two resulting transitions are not degenerate. Spectra will give two signals

(in the presence of Zero field splitting)

eg:  $\lambda_{2g}$  state  $Ni^{II}$  -complexes.



Splitting of the levels in the octahedral  $Mn^{II}$  complex

consider the case of  $Mn^{2+}(d^5)$  system, which contains an odd number of  $e$ 's and Kramers degeneracy will exist here. The term symbol for the free ion ground state is  $6s$ . The zero-field splitting produces three doubly degenerate spin states ( $m_s = \pm 5/2, \pm 3/2, \pm 1/2$ ). Each of these is split into two singlets by the applied field, producing six levels. As a result of this splitting, five transitions are expected

~~$5/2 \rightarrow 3/2$~~   $-5/2 \rightarrow -3/2$ ,  $-3/2 \rightarrow -1/2$ ,  $-1/2 \rightarrow 1/2$ ,  $1/2 \rightarrow 3/2$   
 $+3/2 \rightarrow +5/2$  (  $\Delta m_s = \pm 1$  )



# Techniques in ESR Spectroscopy

Refer from Bancroft - Page No-255.

See page NO-127-129

## University Questions

check 2 Theoretical chemistry of organic chemistry  
2007

- ① Name the calibrant used in ESR spectroscopy. what are its advantages?
- ② neopentane does not give the molecular ion peak, but gives a base peak at  $m/z = 57$ . why?
- ③ The percentage transmittance of a  $5 \times 10^{-4} M$  soln at 250 nm and at 23°C is 19.2 using a 10 mm cell. Calculate the absorbance and molar absorptivity?
- ④ what is nitrogen rule?
- ⑤ Define chemical shift in NMR spectroscopy. what are the factors which influence the chemical shift values? Discuss.
- ⑥ Explain the mass spectral fragmentation patterns observed in alcohols and phenols?
- ⑦ With a block diagram, explain the principles and instrumentation of a mass spectrometer.
- ⑧ Calculate the magnetic field required for resonance in ESR  $g_e = 2.0025$  frequency is 930 MHz  
Bohr magneton =  $9.27 \times 10^{-24} J T^{-1}$
- ⑨ Calculate O-D stretching frequency. The O-H stretching frequency is  $3300 \text{ cm}^{-1}$ .

- (10) Schematically plot and explain the proton NMR spectra of 1-chloropropane and 2-chloropropane.
- (11) What are fluxional molecules. With a specific example, explain how NMR spectroscopy is useful in their study.
- (12) How is recoil-less emission and resonant re-absorption of  $\alpha$ -rays achieved in Mossbauer Spectroscopy.
- (13) How is Mossbauer spectrum useful in identifying oxidation states. Give examples?

\* McConnell equation

The magnitude of splitting depends on the distribution of the unpaired electron near the magnetic nuclei present. The ESR spectrum can be used to map the molecular orbital occupied by the unpaired electron. This mapping is done by McConnell equation.

$$a = Q P \quad \text{where } Q = 2.25 \text{ mT}$$

$Q = \text{empirical constant}$

$P = \text{unpaired } e^- \text{ density on a C atom}$

$a = \text{hyperfine splitting constant observed for the H atom to which it is attached.}$