“ELECTRON SPIN RESONANCE SECTROSCOPY”

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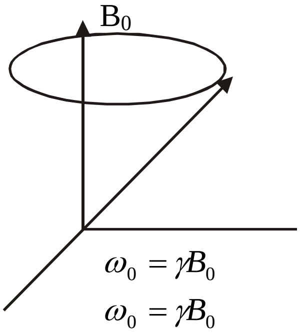
Introduction



$$\omega_0 = \gamma B_0$$
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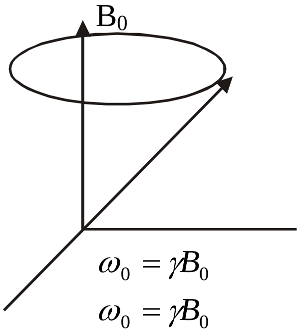

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Electron paramagnetic Resonance (EPR), often called Electron Spin Resonance (ESR) was discovered by Soviet physicist **‘Zavoisky’** in 1945.

ESR is a branch of absorption spectroscopy in which electromagnetic radiation having frequency in the microwave region is absorbed by paramagnetic substances to induce transitions between magnetic energy levels of electrons with unpaired spin i.e. electronic spin **$S < 0$**. The magnetic energy splitting is done by applying a strong static magnetic field, which is exposed to an orthogonal low amplitude high frequency field. The free electron behave as a spinning, negatively charged particle with a resulting magnetic moment. By virtue of its charge and spin an electron acts as a bar magnet and can thus interact with an external magnetic field.

Types of Substances with Unpaired Electrons :

a) Stable Paramagnetic Substances :

These include stable substances which can be studied very easily eg. NO, O_2 and No_2 and transition metal ions and rare earth elements.

b) Unstable Paramagnetic Substances :

These can be produced either as the intermediate in chemical reaction or by irradiation of stable molecules with a beam of nuclear particles or with U.V. or X-ray radiation i.e. the free radicals or radicals ions.

THEORY OF ESR

i) ELECTRON BEHAVIOUR :

In ESR, the energy levels are produced by the interaction of the magnetic moment of an unpaired electron in a molecule ion with an applied magnetic field. The ESR spectrum results in due to the transitions between three energy levels by absorbing radiation microwave frequency.

The magnetism of an electron can be expressed by saying that an electron with a magnetic moment μ which is proportional to **e/m**, where e and m having their usual meanings has a spin, S=$\frac{1}{2}$. This particle like proton has 2 magnetic energy levels. The lower level corresponds to m=$-\frac{1}{2}$ and higher to m=$+\frac{1}{2}$

The magnetic moment thus given by:

μ = $-g\beta_s$ …. (1)

g = spectroscopic splitting factor
or g – factor or gyromagnetic ratio.

g = ~2 or 2.0023193

β = Bohr magneton

i.e. = $\frac{eh}{4\pi m_e} = 9.2740 x 10^{-24} J/T$

e & m_e being electronic charge and mass,

h = planck's constant

When electrons placed in magnetic field they will have their energies changed by certain number of ergs.

$$E = \mu H = -g\beta_s H = \pm\frac{1}{2}\ (g\beta H) \qquad …. (2)$$

Where H = field strength of external magnetic field.

S.I. units = Tesla (T)

But in EPR gauss (1G = 0.0001T)

Thus the difference in energy ΔE between the two levels is given by

$$\Delta E = g\beta H = h\upsilon \qquad \text{…. (3)}$$

The overall magnetic momentum, **μeff** can be expressed via overall angular momentum. J & g values :

$$\mu\text{eff} = g\beta\,[J(J+1)]^{1/2} \qquad \text{…. (4)}$$

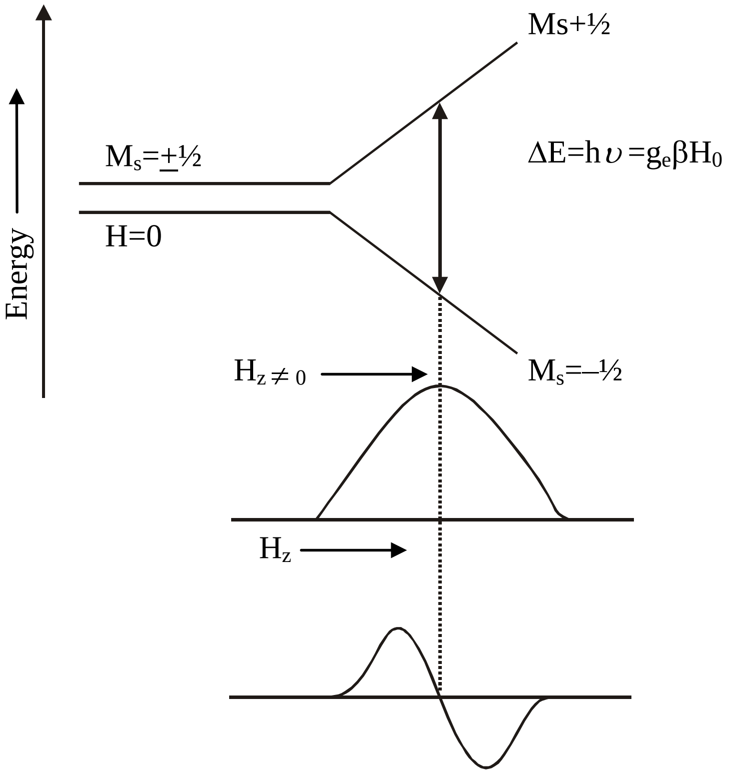
In ESR spectroscopy unlike others, there is splitting of the energy levels and hence the frequency capable of causing transitions between these levels is a function of magnetic field strength H.

For the unpaired electrons there are thus 2 energy levels.

The population difference between the two energy levels of a sample having unpaired electrons in the thermodynamic equation in magnetic field is given by Boltzman law :

$$\frac{n_1}{n_2} = \exp = \frac{\Delta E}{kT} = \exp\frac{-g\beta H}{kT} \qquad \text{…. (5)}$$

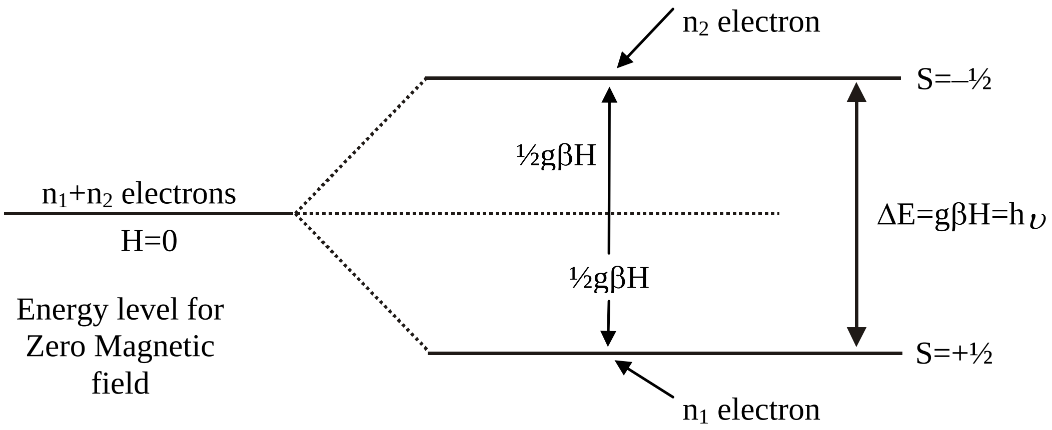
n_1 and *n_2* = population in upper and lower level respectively.



a) Absorption Spectrum

b) Derivative spectrum

ENERGY LEVEL DIAGRAM SHOWING ESR SPECTRUM



ENERGY LEVELS FOR MAGNETIC FIELD H

Energy levels in ESR spectroscopy

When radiation is supplied to the sample of frequency 2 in such a manner that energy between the electron states (i.e. $h\upsilon=\Delta E=g\beta H$), then resonance occur.

ii) THE G-FACTOR:

The g-actor is one of the important quantities determined from the ESR spectra of odd-electron systems.

The value for g for an unpaired electron in gaseous atom or ion, for which Russel-Saunders coupling is applicable is given by the expression.

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

For a free electron (S=½, L=0, J=½) value of g=2.0 is easily calculated from the above equation. Thus the actual value is 0.0023 due to relativistic correction. From the relation

$\upsilon = g\beta Ho/h$, we see that

$G = h\upsilon/\beta Ho$.

Thus, the g-factor is essentially a measure of the ratio between frequency and magnetic field, for the free electron g has a value 2.0023. The organic radicals such as methyl radical, have the g-value very close to the free electron g-value molecule containing the unpaired electron with respect to the magnetic field.

In a solution or in the gas phase, g is averaged over all orientations because of the free motion of the molecules, but in a crystal movement is restricted. If the paramagnetic radicals or ion is located in a perfectly cubic crystal site (eg. Octahedral or tetrahedral site), the g-value 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 is said to be **anisotropic**.

The g_z value is equivalent to $g_{||}$, the g value obtained when z axis is parallel with the external magnetic field. The g value along x and y axes are g_x and g_y, which in a tetragonal site are equal and referred to as $g\perp$, the g-value thus obtained with the external magnetic field perpendicular to the z-axis. If θ is angle between magnetic field and z axis, the experimental g value is given by the following equation for a system with axial symmetry.

$$g^2 = g_{||}^2 \mathrm{Cos}^2\theta + g\perp^2 \sin^2\theta$$

iii) HYPERFINE SPLITTING :

The detection of electron spin resonance signal proves the presence of unpaired electrons in the sample. The intensity of the absorption line is proportional to the number of unpaired electrons. The ESR spectroscopy has been widely used in studying various photochemical, electro-chemical reaction proceeding via free radical mechanism because of the presence of hyperfine structure which is the result of the interaction between the unpaired electrons and magnetic nuclei in the paramagnetic species. It further gives two important informations:

1) It tells about the environment of the molecule and distribution of the electron density within the molecule.

2) It allows identification of paramagnetic substance in number of cases.

The resonance frequency of an electron actually depends upon the magnetic field at the electron and electron infact is affected by the applied field, Ho and any local field due to magnetic fields of nuclei, H_{local}.

Thus the equations :

$\Delta E = g\beta H = h\upsilon$ becomes

$h\upsilon = g.\ \beta(H_O+H_{local})$

The effect of magnetic moments of nuclei on ESR spectrum is known as **hyperfine interaction** and is responsible for splitting of ESR line, giving rise to **hyperfine structure**.

When an unpaired electron comes in the vicinity of a nuclear with a spin I, an interaction takes place which causes the absorption signal to be split into **2I+1** components, where I is the spin quantum number of the nucleus. The cause of splitting in an isotropic system is the nuclear spin electron spin coupling arising mainly from the **Fermi contact term**.

This effect is simply illustrated by considering as an example of hydrogen atom (I=½ for the proton). The proton thus has a magnetic moment and the electron will be affected by the magnetic field of the nucleus (a proton) as well as that of the applied magnetic field. The energy of the electron will be modified by the orientation of the magnetic moment of the proton which can also be parallel or antiparallel to the magnetic field.

The relative orientation of the nuclear magnetic moment and the electron magnetic moment causes a splitting of original 2 level to 4 level.

THE SELECTION RULE FOR THE HYPERFINE TRANSITION IS:

$$\Delta m_S = \pm 1, \; \Delta m_I = 0$$

This selection rule may be interpreted by saying that the nuclear motion is much slower than the electronic motion so that during the time electron changes its spin orientation, the nucleus, being heavier has no time to reorient its spin so that $\Delta m_I=0$

The EPR spectrum of a **Hydrogen atom** in a solid matrix consists of 2 peaks of equal intensity centered at g=2.0023. The two-energy levels of a free electron in a magnetic field are shown in the Figure with $m_S=-½$ aligned with the field and $m_S=+½$ aligned opposed to the field. (The spectrum of a free electron would consist of a single peak corresponding to a transition between these levels).

For each value of electron spin angular momentum quantum number m_s, the nuclear spin angular momentum quantum number m_I, can have values of ±½, giving rise to four different energy levels.

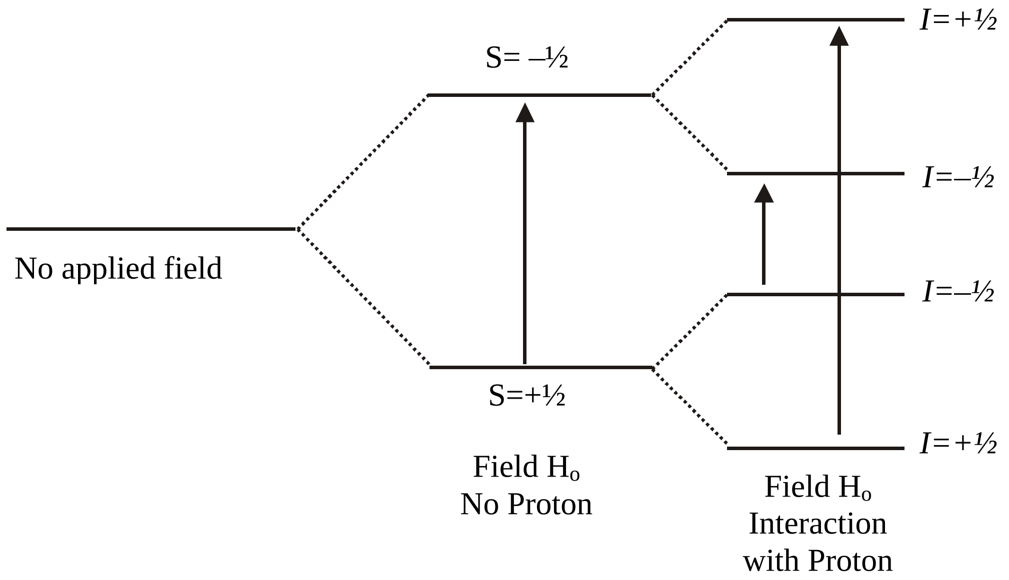
INTERACTION OF UNPAIRED ELECTRON WITH ONE PROTON

Possible orientations of electrons and nuclear magnetic moments

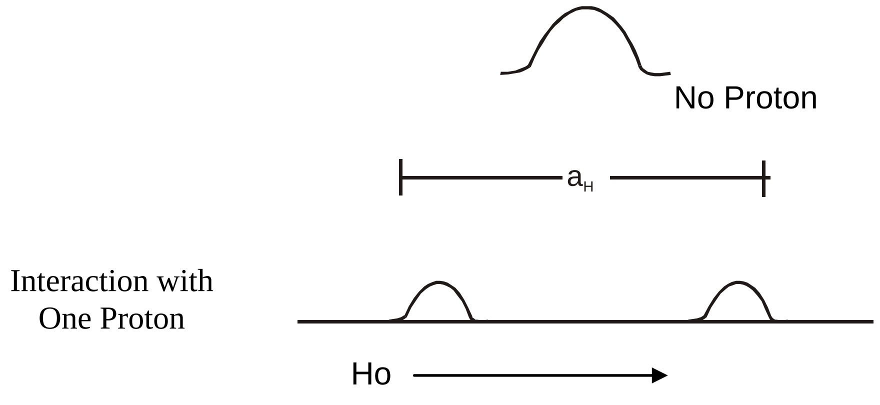
a)

Splitting of energy levels

b)



c) Splitting of Spectral Line



When the interaction between the 2 energy states and the nuclear spin due to proton is considered, each energy state is further split up into energy levels corresponding to $m_I=+½$ & $m_I=–½$ when m_I is nuclear spin angular momentum quantum number. Thus two hyperfine lines are observed (splitting of original line into a doublet results) and the energy difference between the two values of the field at which the lines occur is called the **hyperfine splitting constant**.

The energies of 4 energy levels are :

$E_{½ , ½} = ½gβH + ¼A$

$E_{½ , –½} = ½gβH – ¼A$

$E_{–½ , –½} = –½gβH + ¼A$

$E_{–½ , ½} = –½gβH – ¼A$

The general expression for all the four energy level is

$E = gβHm_s + A m_s m_I$

A = hyperfine coupling constant. Usually measured in gauss such as MHz or $cm^{–1}$.

The magnitude of the splitting, expressed in terms of coupling constant A depends on following factors :

1) The ratio of the nuclear magnetic moment to the nuclear spin.
2) The electron spin density in the immediate vicinity of nucleus (Fermi contact interaction).
3) An anisotropric effect.

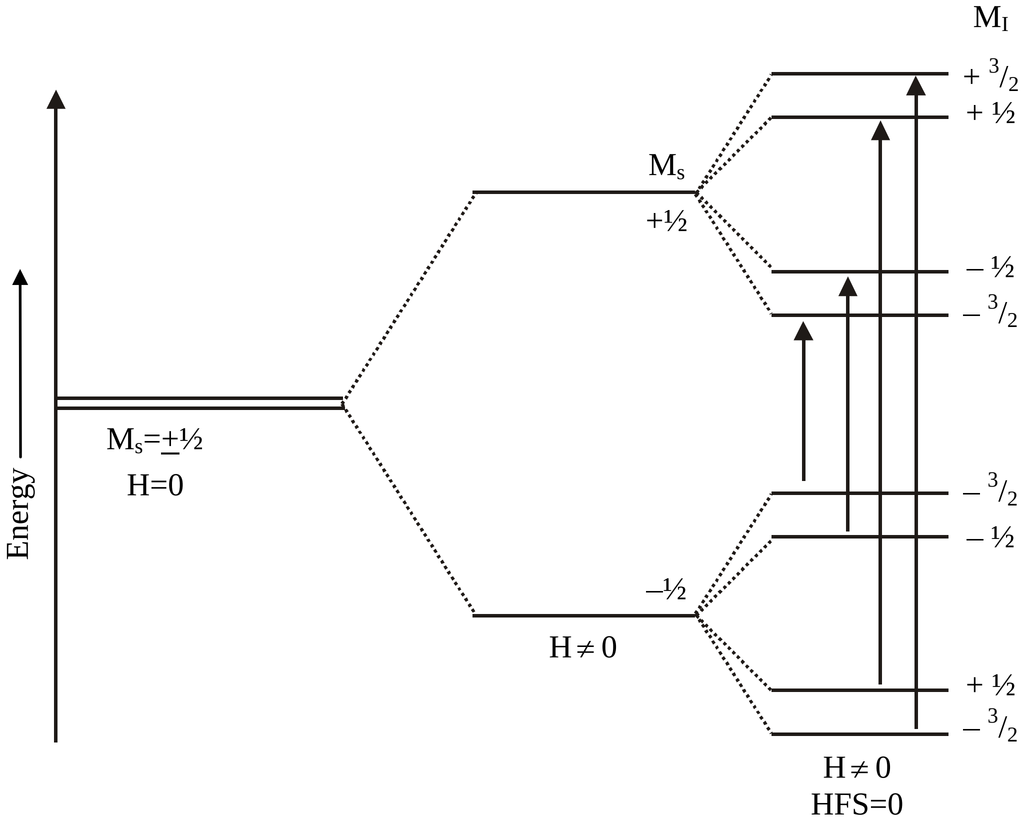
HYPERFINE SPLITTING IN CASE OF METHYL RADICAL (CH_3)

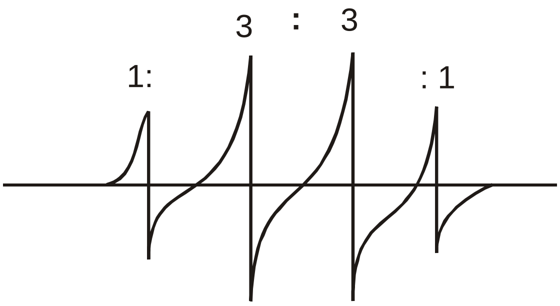
Possible Nuclear spin arrangements of protons in a Methyl Radical.

Addition of the nuclear spin angular momentum quantum nos. of individual protons results in four different values for total nuclear spin moment.

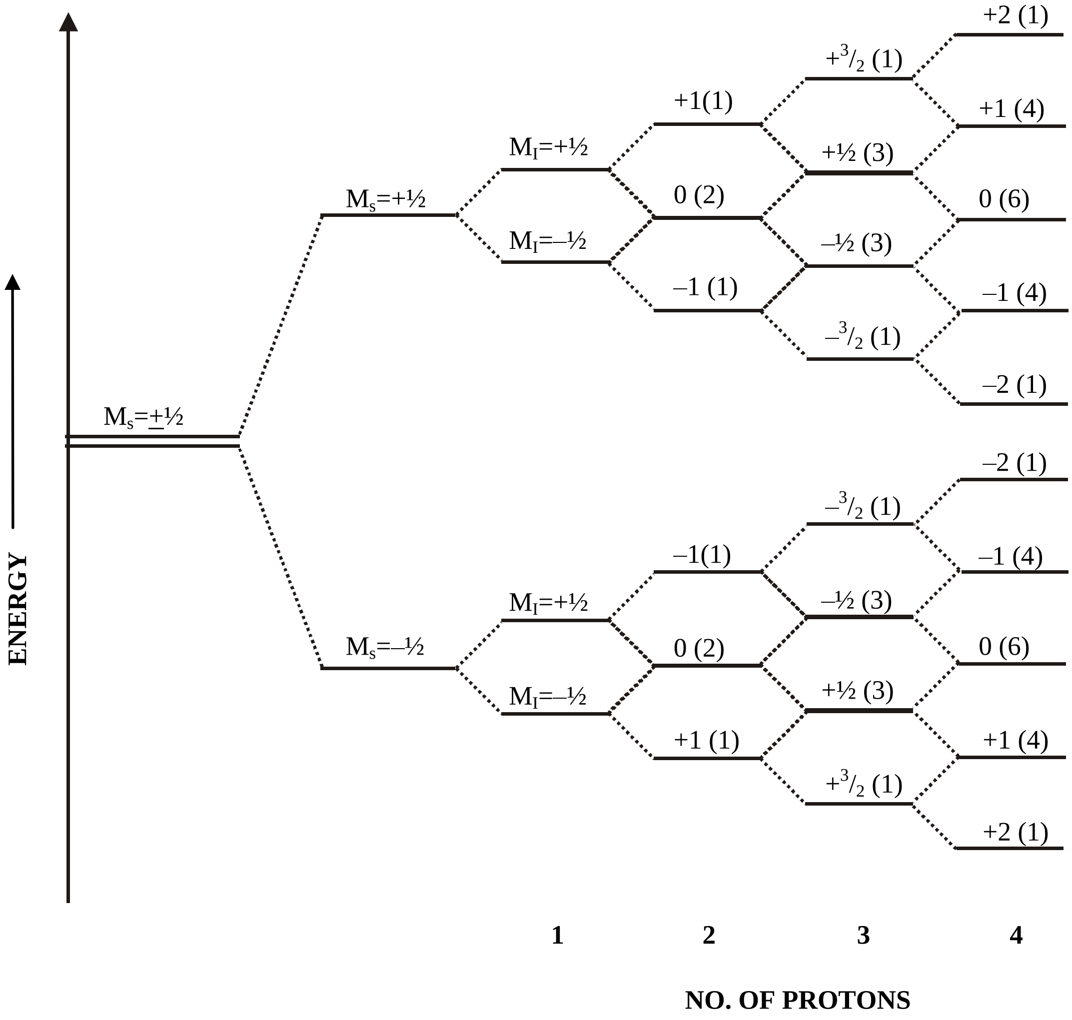
Here S = ½ & 3 equivalent protons. since for a proton I = ½, it is evident that for three equivalent protons $m_I = +{}^3/_2, +½, –½, –{}^3/_2$. Also $m_s = \underline{+}½$. This ESR spectrum contains four equally spaced lines i.e. a quartet **1:3 : 3 :1**

The hyperfine structure in the ESR spectrum of methyl radical CH_3





Thus the spectra expected for differing number of equivalent protons can be easily predicted by considering the splitting due to each proton in turn as illustrated in the given figure.



Hyperfine energy level resulting from interaction of an unpaired electron with varying numbers of equivalent protons

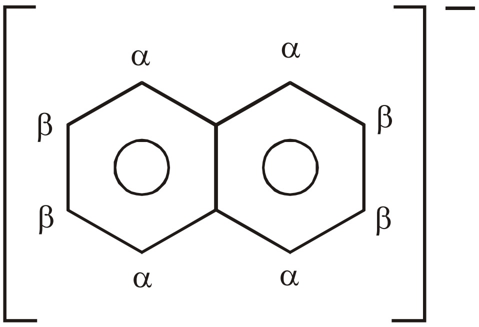
- In general, the total No. of peaks expected for an electron delocalised Caused over n **"equivalent protons'"** is given by **n+1** (i.e. **2n I+1**) and the relative intensities of peaks given by the coefficients of binomial expansion. **(i.e. restricted strictly to the equivalent protons).**

- ⇨ When signal is split by 2 equivalent protons, total m_I for three levels has $\sum m_I = +1,\ 0,\ -1$

  (m_I=0 can have two values $(+½ - ½, -½ \& ½)$ the centre level is doubly degenerate. Thus 3 peaks observed in the spectrum (Δm_I=0 and Δm_S=1) intensity ratio = 1:2:1

- ⇨ If in case the odd electron is delocalized over two sets of **"nonequivalent protons"**, the number of lines thus expected is the product of number expected **[(2nI$_I$ + 1) (2m I$_J$+1)]**

e.g in case of naphthalene negative ion i.e. prepared by adding sodium to naphthalene contains an odd electron which is delocalized over the entire naphthalene ring.



In this case there are two sets of (α & β) of 4 equivalent protons each. A natal of n+1 or 5 peaks expected for an electron delocalized on either of 4 equivalent protons.

i.e. $[(2 \times 2+1) \times (2 \times 2+1)]$

= $[(4+1) \times (4+1)]$

= **25 lines**

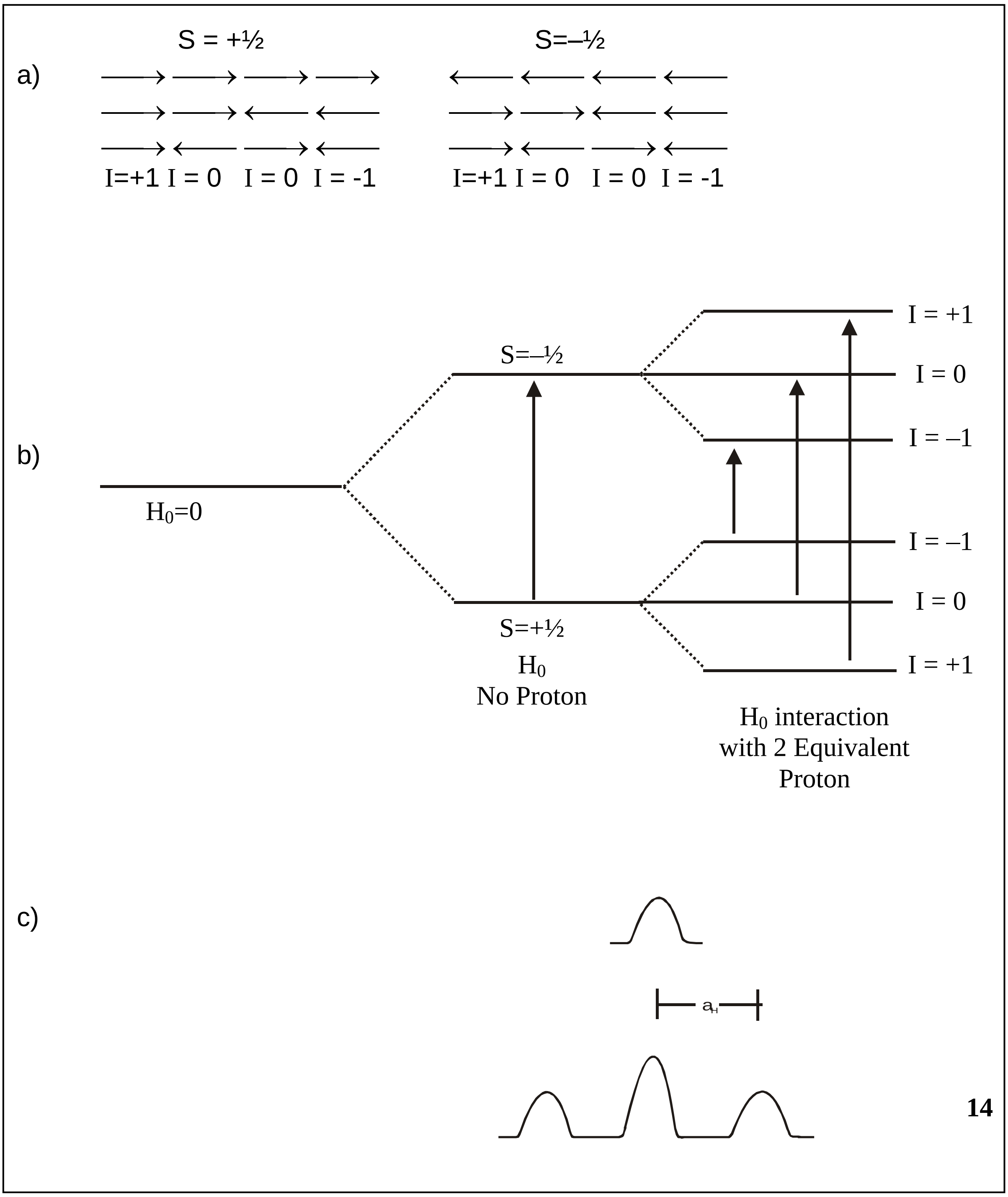
Thus the ESR spectrum would show 25 lines.

- ⇨ **The above rules and examples are for the nuclei with I = ½. But if the electron is delocalized on nuclei with spin greater than ½ i.e. I > ½, other rules apply.**

For eg. Interaction with a single nitrogen nucleus (N^{14}). **I = 1**, will cause a splitting (2I +1) = **2 x 1 + 1 =3**
i.e. 3 lines (triplet) of equal intensity i.e. **1:2:1** is observed.

The above is if the electron is delocalized over equivalent nuclei.

Interaction of unpaired Electron with two equivalent Protons



BIBLIOGRAPHY

1. Russel, S. Drago, Physical Methods in Inorganic Chemistry, East West Press, New York, 1971.

2. D.F. Shriver & Atkins, Inorganic Chemistry, Oxford University Press, 3rd Ed., 1999.

3. B.K. Sharma, Instrumental Methods of Chemical Analysis, Meerut, 20th Ed; 2001.

4. Gurdeep Chatwal & Sham Anand; Instrumental Methods of Chemical Analysis, Himalaya Publishing, Bombay; Ed., 1996.

5. Puri, Sharma & Pathania, Principles of Physical Chemistry, Vishal Publishing Co., Ed., 2004.

6. Bodie Douglass; “Concepts & Models of Inorganic Chemistry”, John Wiley & Sons, Singapore, 3rd Edition.

7. P.F. Knowles, D. Marsh & H.W.E. Rattee “Magnetic Resonance of Biomolecules”, John Wiley & Sons, London, 1976.

8. M.C.R. Symons, “Chemical & Biochemical, Aspects of Electron-Spin Resonance Spectroscopy, Van Nostrand, Reinhold, New York (1978).

9. Pure & Appl. Chem., Vol. 62, No. 6 pp. 1051-1054, 1990. Printed in Great Britain.

10. Kurt Warncke, Jennifer C. Schmidt and Shyue-Chuke, J.A.C.S., 2001-123, 3358.