# Electron Spin Resonance Spectroscopy

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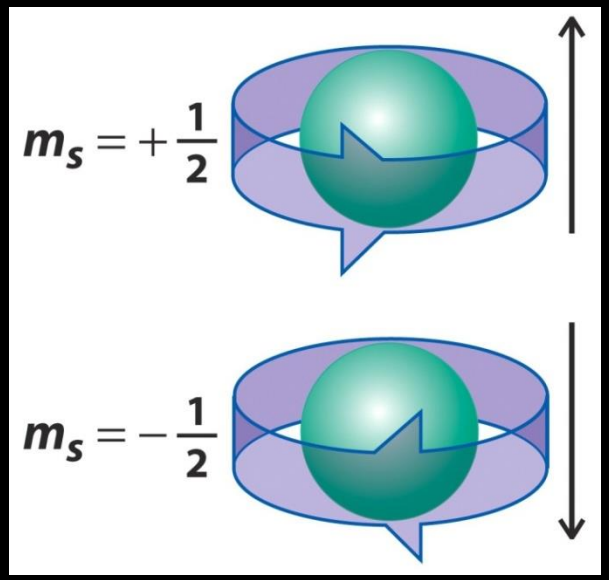
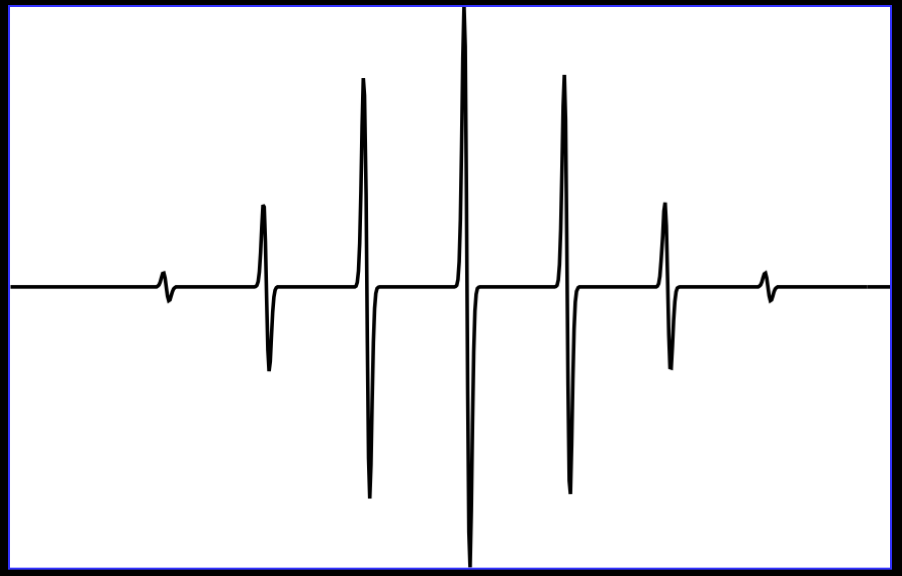


**Invented by Zavoisky-1994**

# What is the ESR?

# EPR = ESR

E Electron –study of unpaired electron spins, and their interaction with their environment.

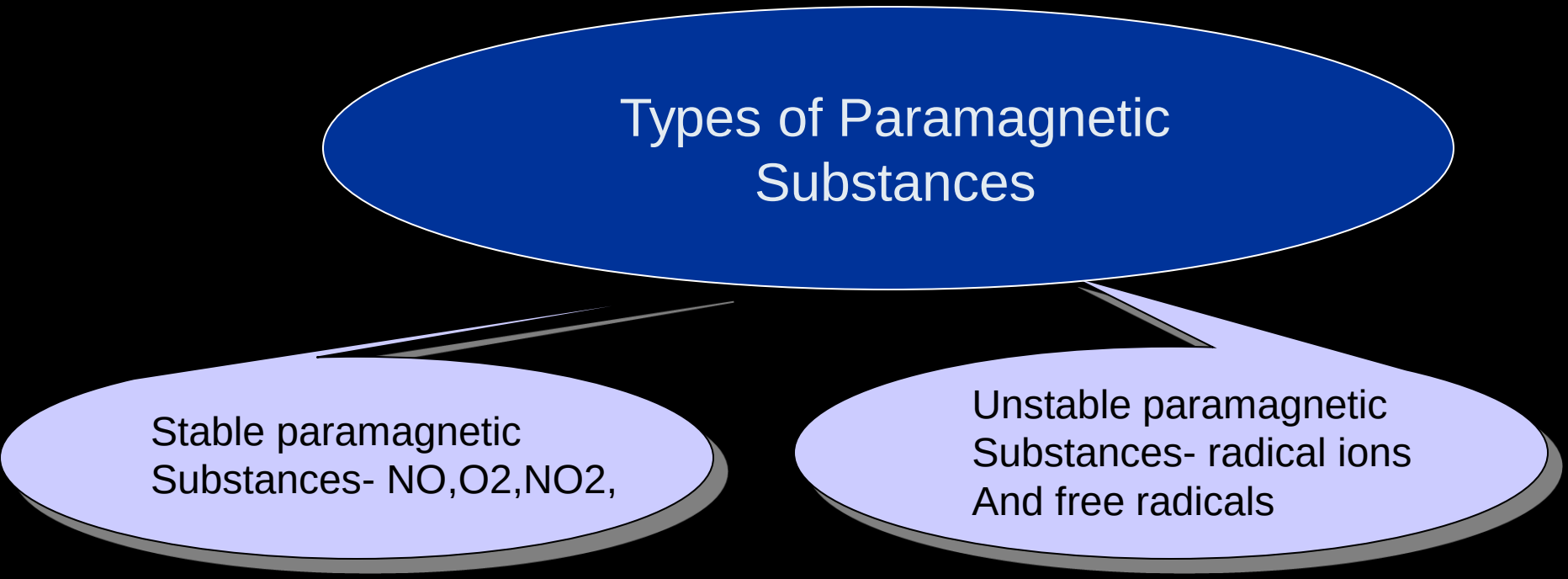
S Spin – Electron spin is a quantum mechanical phenomenon. It is represented by $m_s$, one of the 4 quantum numbers: n, l, m, $m_s$

ms can have one of only 2 values, + ½ and – ½

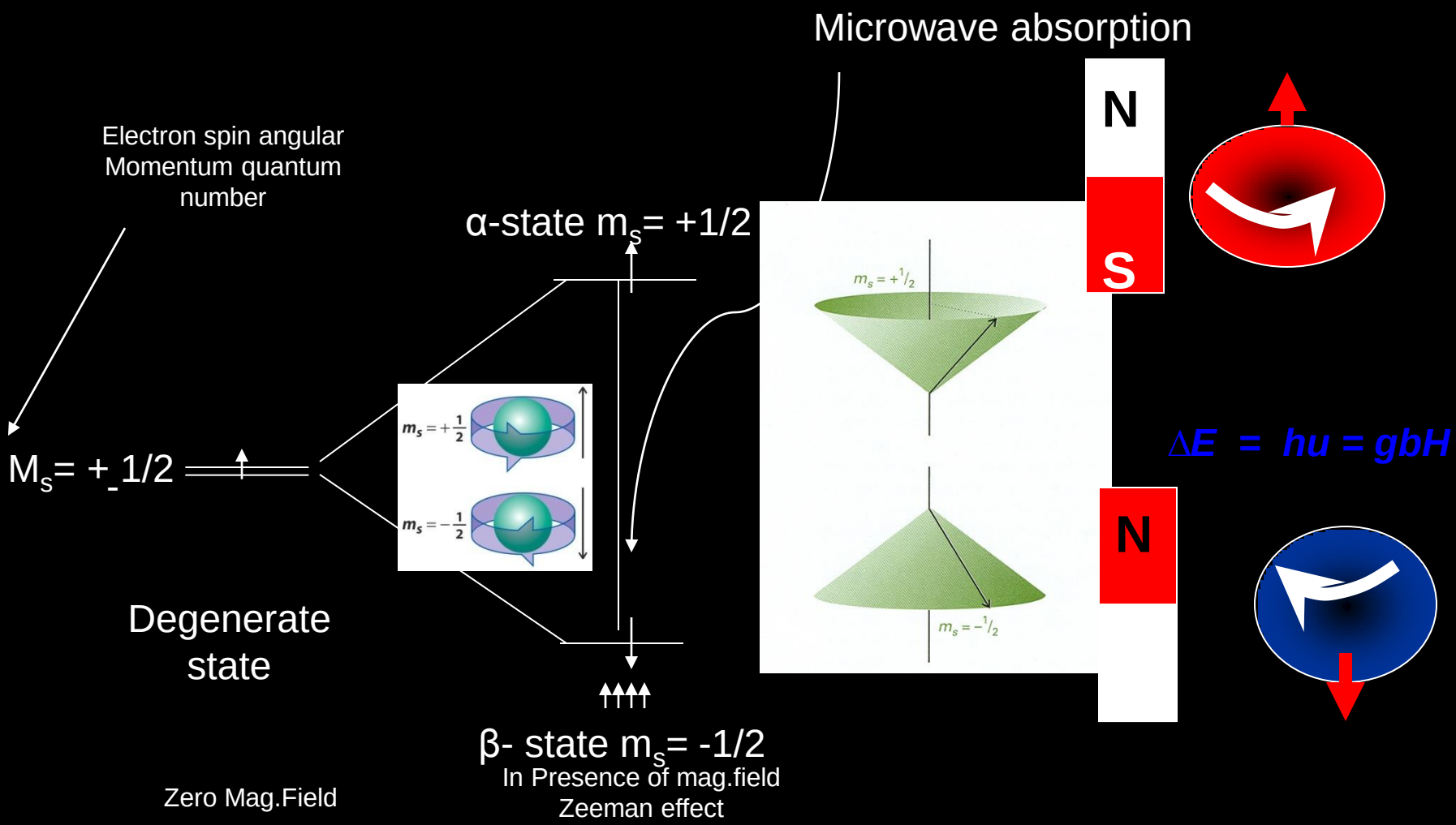
In the language of quantum mechanics, this fundamental property of an isolated electron is an angular momentum. It can be described in a classical physics model as if it were a spinning electric charge, so it is called electron spin. However, this is just a mnemonic model, and does not mean that the electron is really a spinning charge.

P Paramagnetic – The general term paramagnetic is used to describe materials that are attracted to a magnetic field. There are two major contributions to paramagnetism: spin and orbital angular momentum. Since the term paramagnetic is more general, and no free radical has only spin angular momentum without orbital angular momentum, EPR is a more precise term than is ESR.

R Resonance – This may be the most important term of the 3 in EPR. The concept of resonance is central to the power of magnetic resonance techniques.


Types of Paramagnetic Substances
Stable paramagnetic Substances- NO,O2,NO2,
Unstable paramagnetic Substances- radical ions And free radicals

# Zeeman Energy Level Splitting




Zeeman energy level splitting for an electron in a magnetic field. The energy separation is linearly proportional to magnetic field strength, B. Transitions between the two electron energy levels are stimulated by microwave radiation when h $\nu$ = g $\beta$ B. If the line shape is due to relaxation, it is Lorentzian.

**The equation describing the absorption (or emission) of microwave energy between two spin states is**

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

**where:**

***ΔE*** **is the energy difference between the two spin states**
***h*** **is Planck's constant**
**υ is the microwave frequency**
**β is the Bohr magneton**
**H is the applied magnetic field.**

It is function of electron's environment

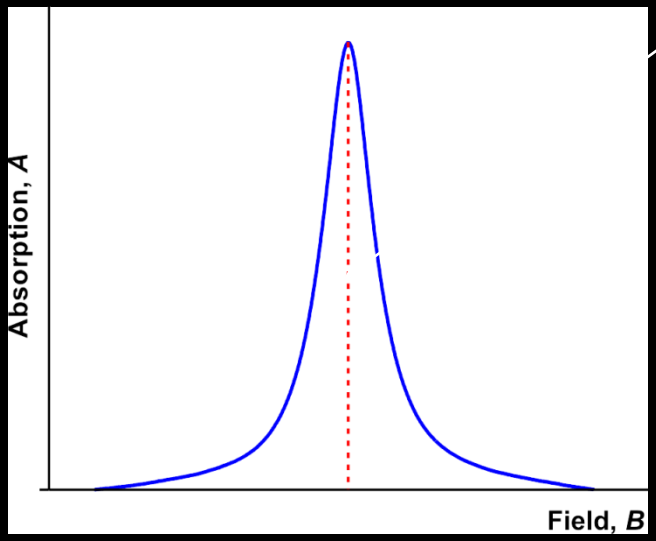
***Proportionality constant/factor***
***Spectroscopic splitting factor***
***Lande's splitting factor***

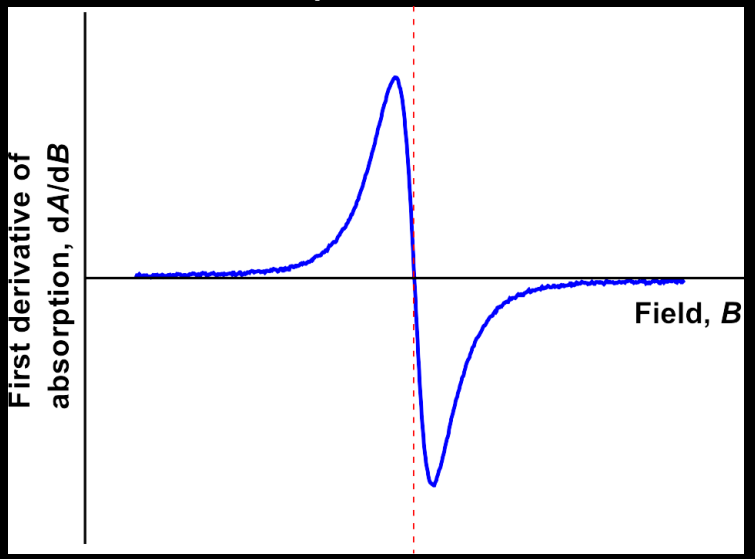
g is characteristic of the radical, and is ≈ 2

Sample calculation for ν = 1 GHz

# Spectra

Area-number of unpaired electrons

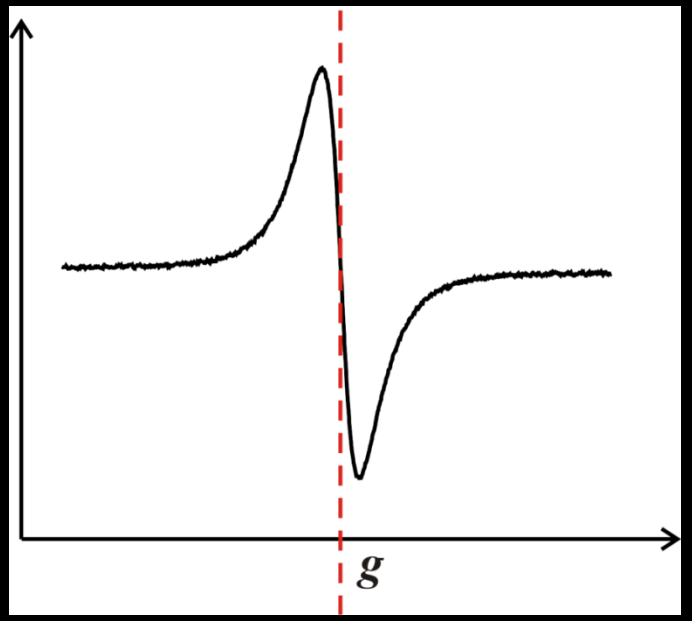



When phase-sensitive detection is used, the signal is the first derivative of the absorption intensity

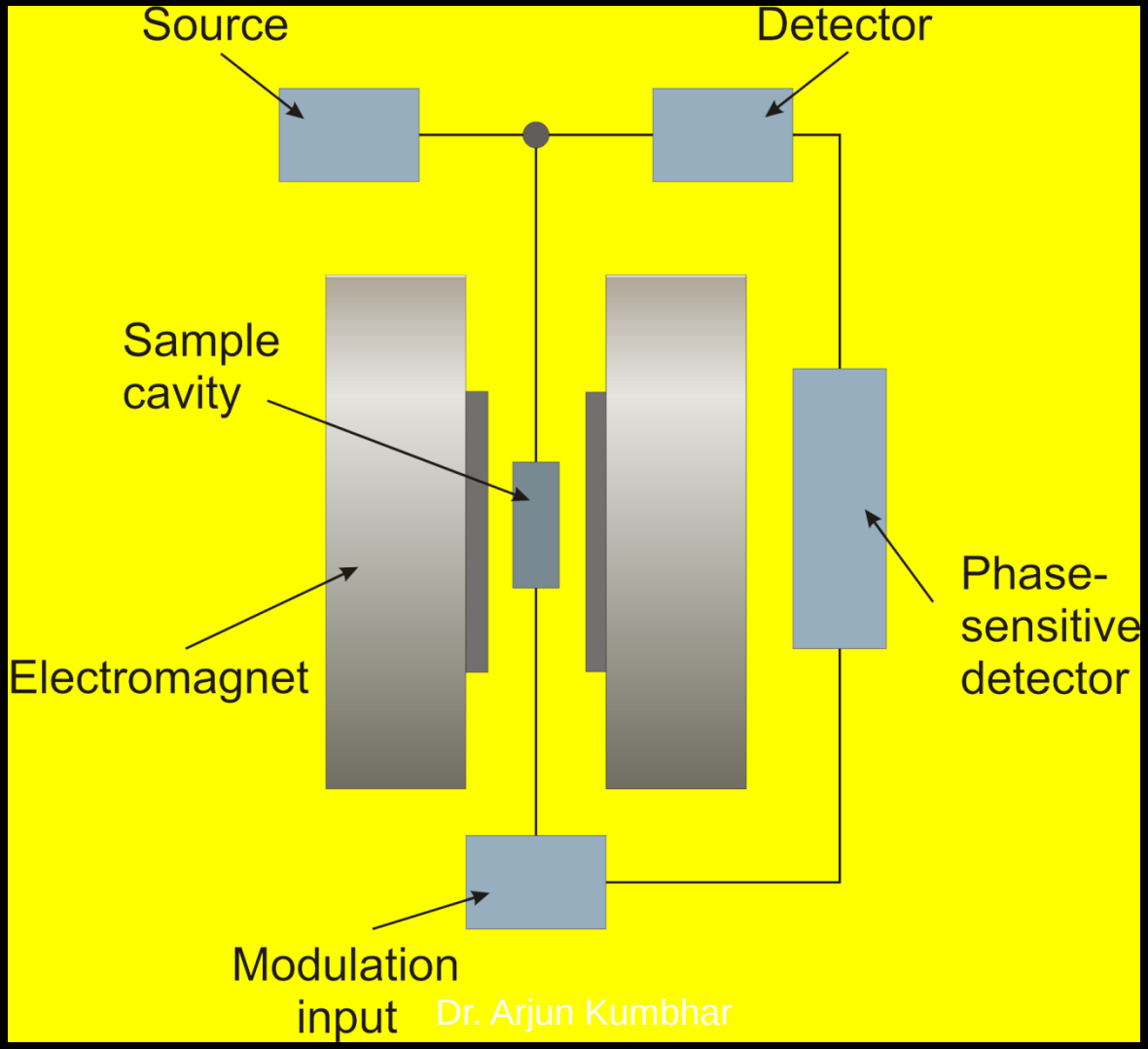
# Proportionality Factor

| | |
|---|---|
| $MoO(SCN)_5^{2-}$ | 1.935 |
| $VO(acac)_2$ | 1.968 |
| $e^-$ | 2.002 |
| $CH_3$ | 2.002 |
| $C_{14}H_{10}$ (anthracene) cation | 2.002 |
| $C_{14}H_{10}$ (anthracene) anion | 2.002 |
| $Cu(acac)_2$ | 2.13 |




Measured from the center of the signal

# How does the spectrometer work?



# ESR spectra of single electron

Electron spin angular Momentum quantum number

α-state $m_s = +1/2$

$m_s = +1/2$

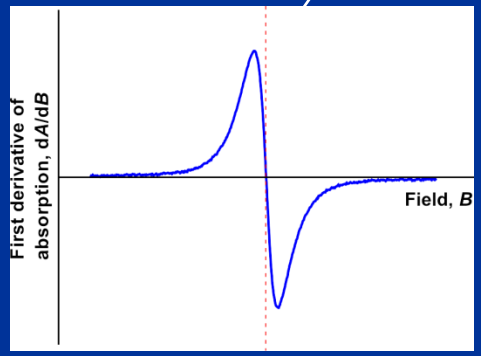
Degenerate state

β- state $m_s = -1/2$

H = 0

H ≠ 0

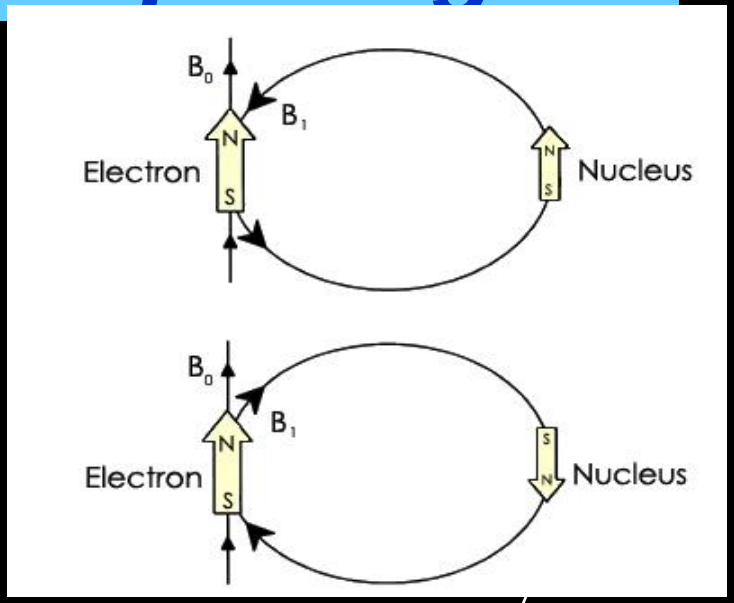
singlet



# A - the hyperfine splitting

Splitting of signals due to interaction

Of spinning electron with adjacent spinning Magnetic nuclei is called hyperfine splitting




Signal splitting ( Multiplicity) = 2 I + 1

Spin quantum number of the nucleus

If single electron interact with n equivalent nuclei of equal spin I

**No of lines in esr = ( 2nI + 1 )**

If single electron interact with set of
n equivalent nuclei of equal spin of spin Ij,
m equivalent nuclei of equal spin of spin Ij,
and p equivalent nuclei of equal spin of spin Ij,

**No of lines in esr = ( 2nIj + 1 ) ( 2mIj + 1) ( 2pIj + 1 )**

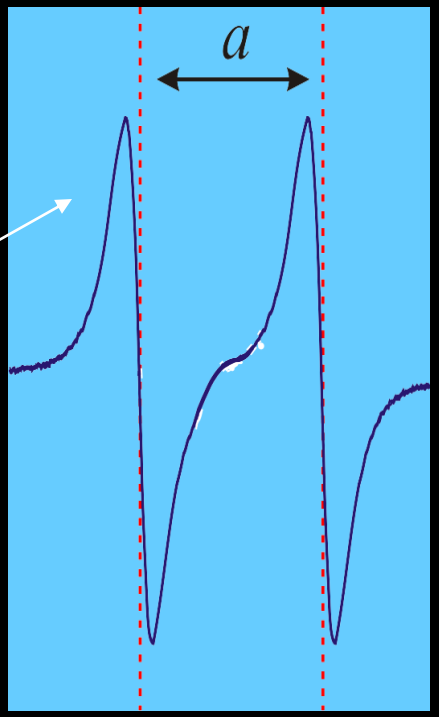
# EPR of H-atom

Electron with s = 1/2

Nucleus with
I = 1/2

Multiplicity = 2I + 1
= 2 x1/2 + 1
= 2

Doublet



Nuclear spin angular momentum quantum Number
mI = o,± ½.

Electron spin angular Momentum quantum number

α-state $m_s$= +1/2

β- state $m_s$= -1/2

$m_s$= ± 1/2

mI= +1/2

mI= -1/2

mI= -1/2

mI= +1/2

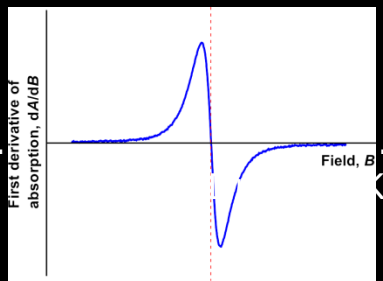
Degenerate state

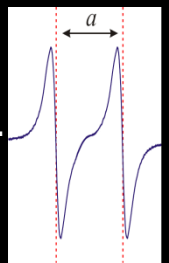
H = 0

H ≠ 0
HFS = 0

H ≠ 0
HFS ≠ 0

Selection Rule
Δms= ± 1
ΔmI= ± 0



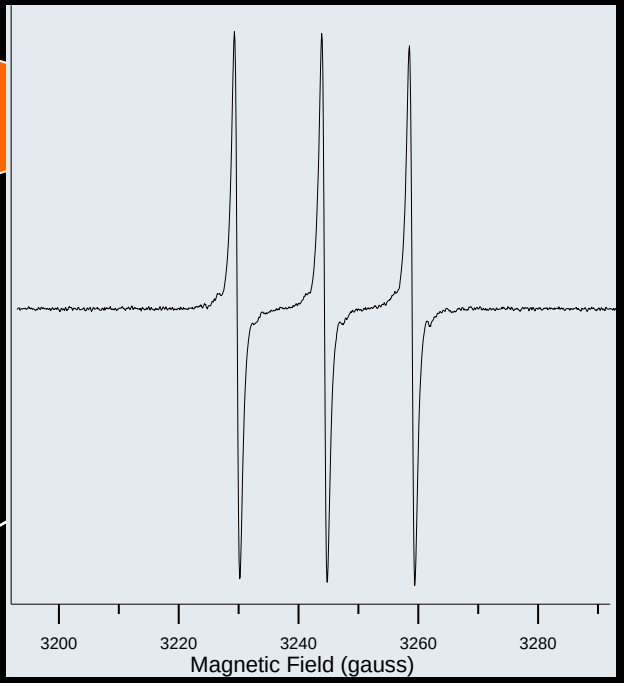



# EPR of D-atom

Electron with s = 1/2

Nucleus with
I = 1

Multiplicity = 2I + 1
= 2 x1 + 1
= 3




Triplet

Nuclear spin angular momentum quantum Number
mI = o,± ½.

Electron spin angular Momentum quantum number

α-state $m_s$= +1/2

β- state $m_s$= -1/2

$m_s$= ± 1/2

mI= +1

mI= 0

mI= -1

mI= -1

mI= 0

mI= +1

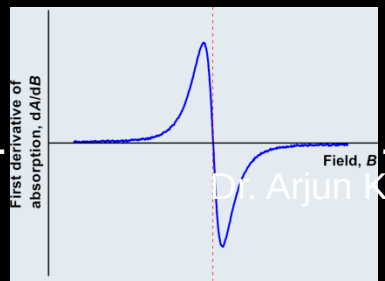
Degenerate state

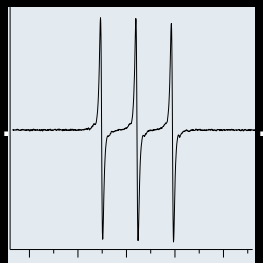
H = 0

H ≠ 0
HFS = 0

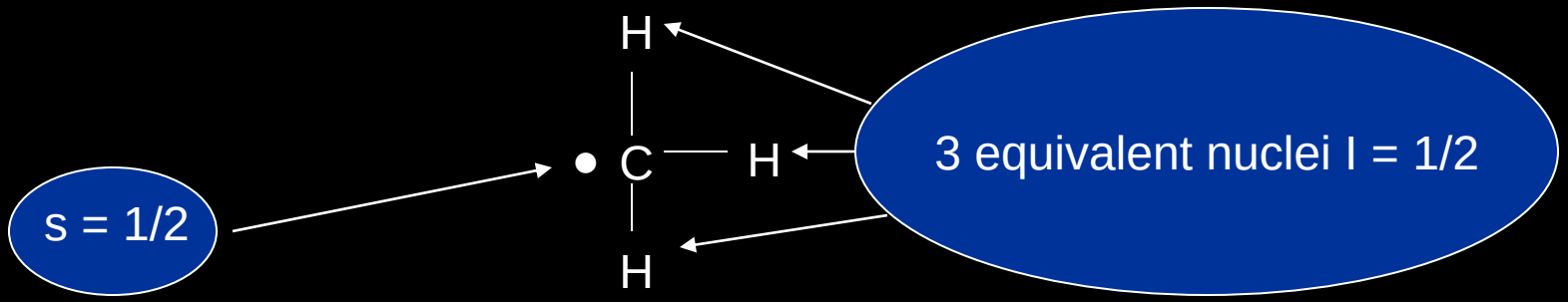
H ≠ 0
HFS ≠ 0

Selection Rule
Δms= ± 1
Δml= ± 0



# EPR of CH3 radical




Multiplicity = (2nI +1) (2nI +1)
= (2 x3x1/2 + 1)(2x1x0+1
= 4


Triplet

Nuclear spin angular momentum quantum Number
mI = o,± ½.

Electron spin angular Momentum quantum number

α-state $m_s$= +1/2

$m_s$= ± 1/2

mI= +32

mI= + 1/2

mI= -1/2

mI= -3/2

mI= -3/2

mI= -1/2

mI= +1/2

mI= +3/2

Degenerate state

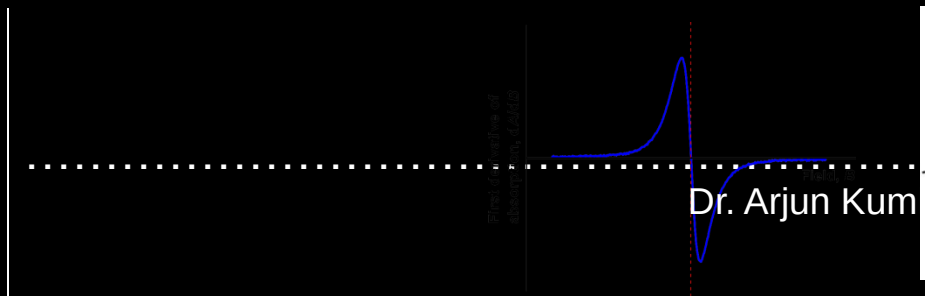
β- state $m_s$= -1/2

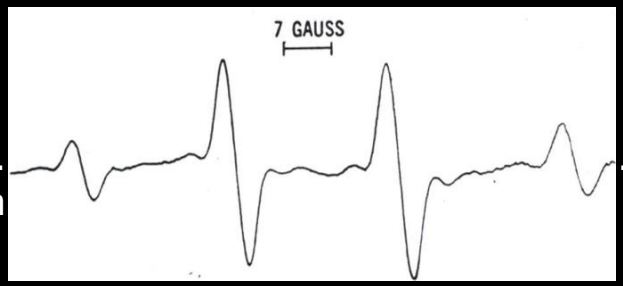
H = 0

H ≠ 0
HFS = 0

H ≠ 0
HFS ≠ 0

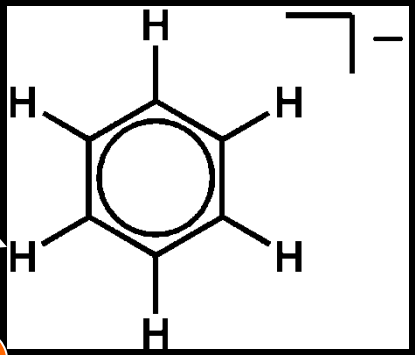
Selection Rule
Δms= ± 1
ΔmI= ± 0



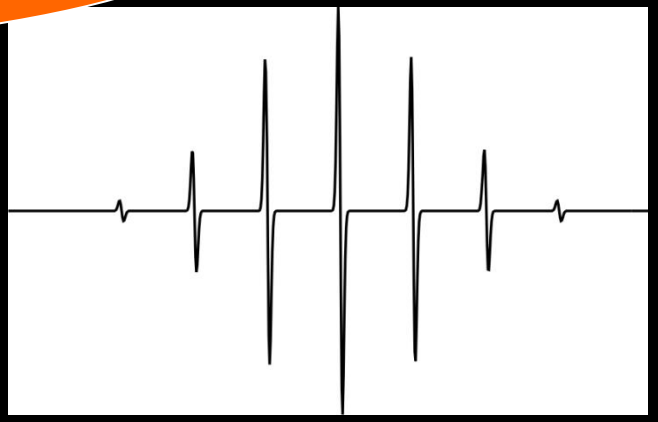


# EPR spectrum of Benzene Radical Anion

6 equivalent nuclei I = 1/2




Multiplicity = (2nI +1) (2nI +1)
= (2 x6x1/2 + 1)(2x1x0+1
= 7



Nuclear spin angular momentum quantum Number
mI = 0,± ½.

Electron spin angular Momentum quantum number

α-state $m_s$= +1/2

$m_s$= ± 1/2

mI= +5/2
mI= +3/2
mI= +1/2
mI= 0
mI= -1/2
mI= -3/2
mI= -5/2
mI= -5/2
mI= -3/2
mI= -1/2
mI= 0
mI= +1/2
mI= +3/2
mI= +5/2

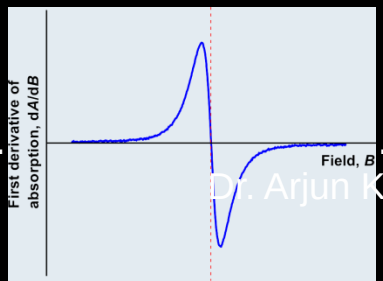
Degenerate state

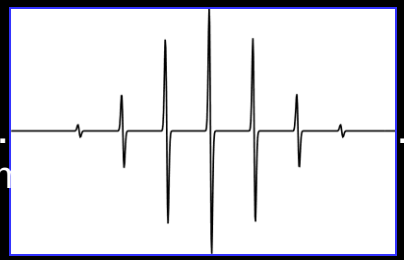
β- state $m_s$= -1/2

H ≠ 0

HFS = 0

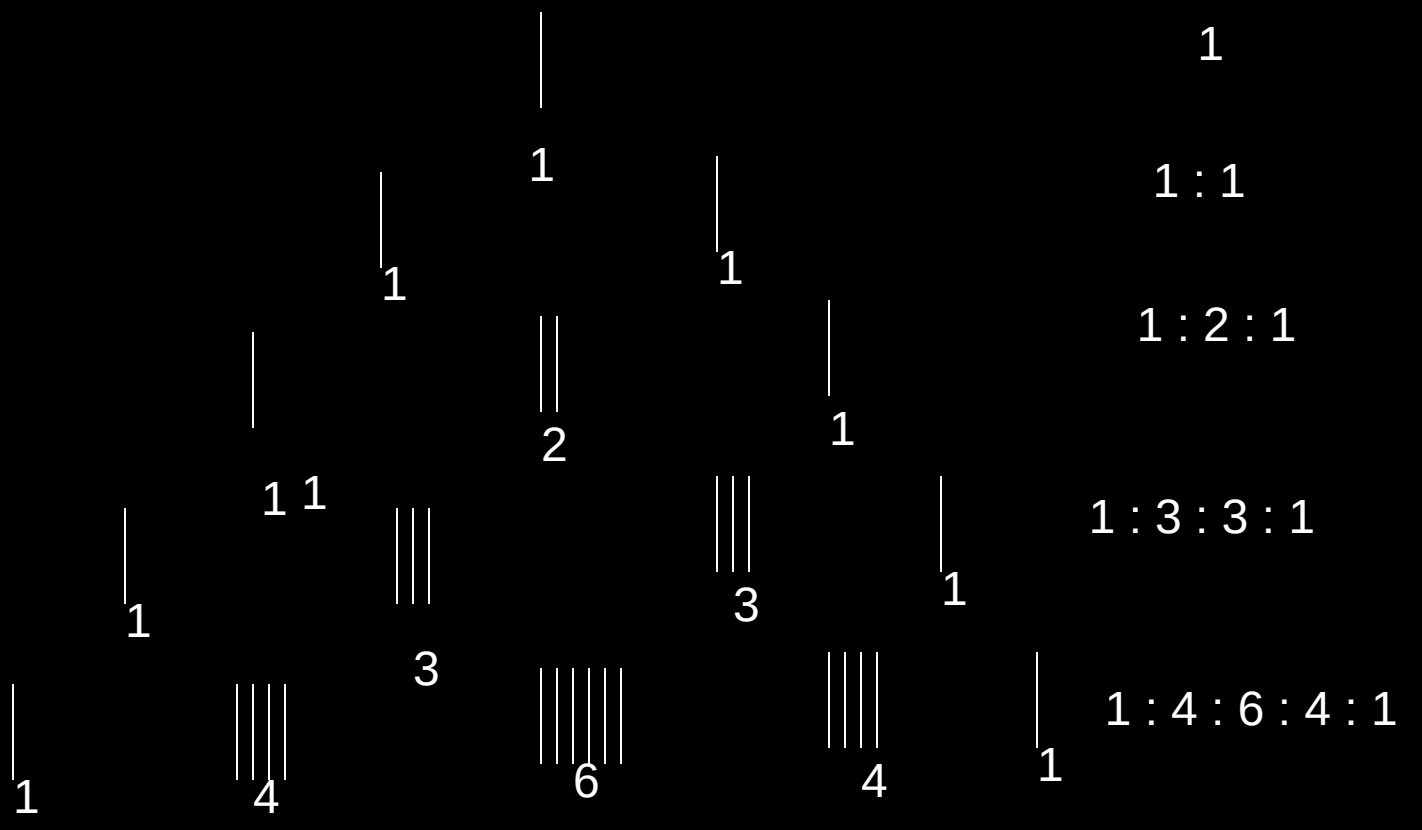
H = 0



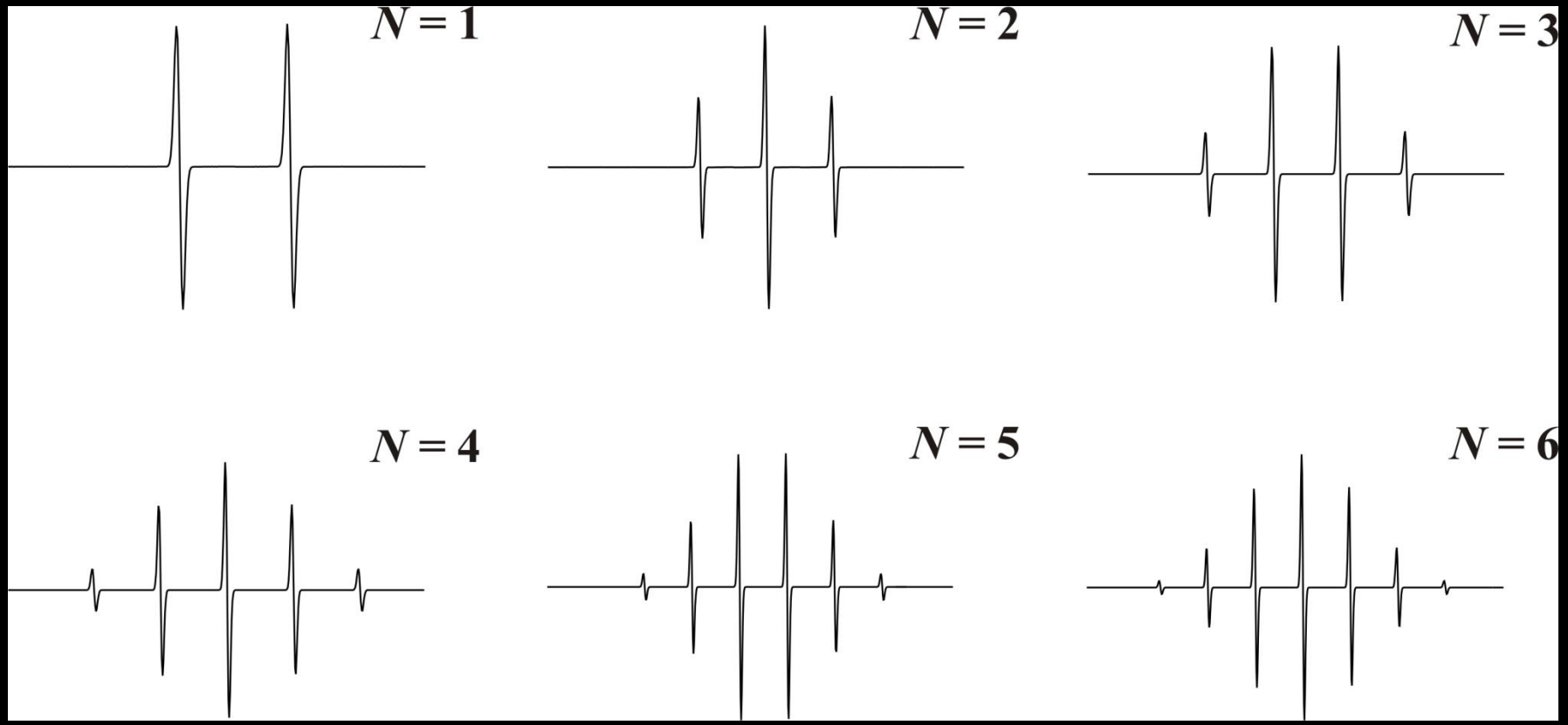



# Stick diagram -Relative Intensities for $I = ½$

| $N$ |
|---|
| 0 |
| 1 |
| 2 |
| 3 |
| 4 |
| 5 |
| 6 |



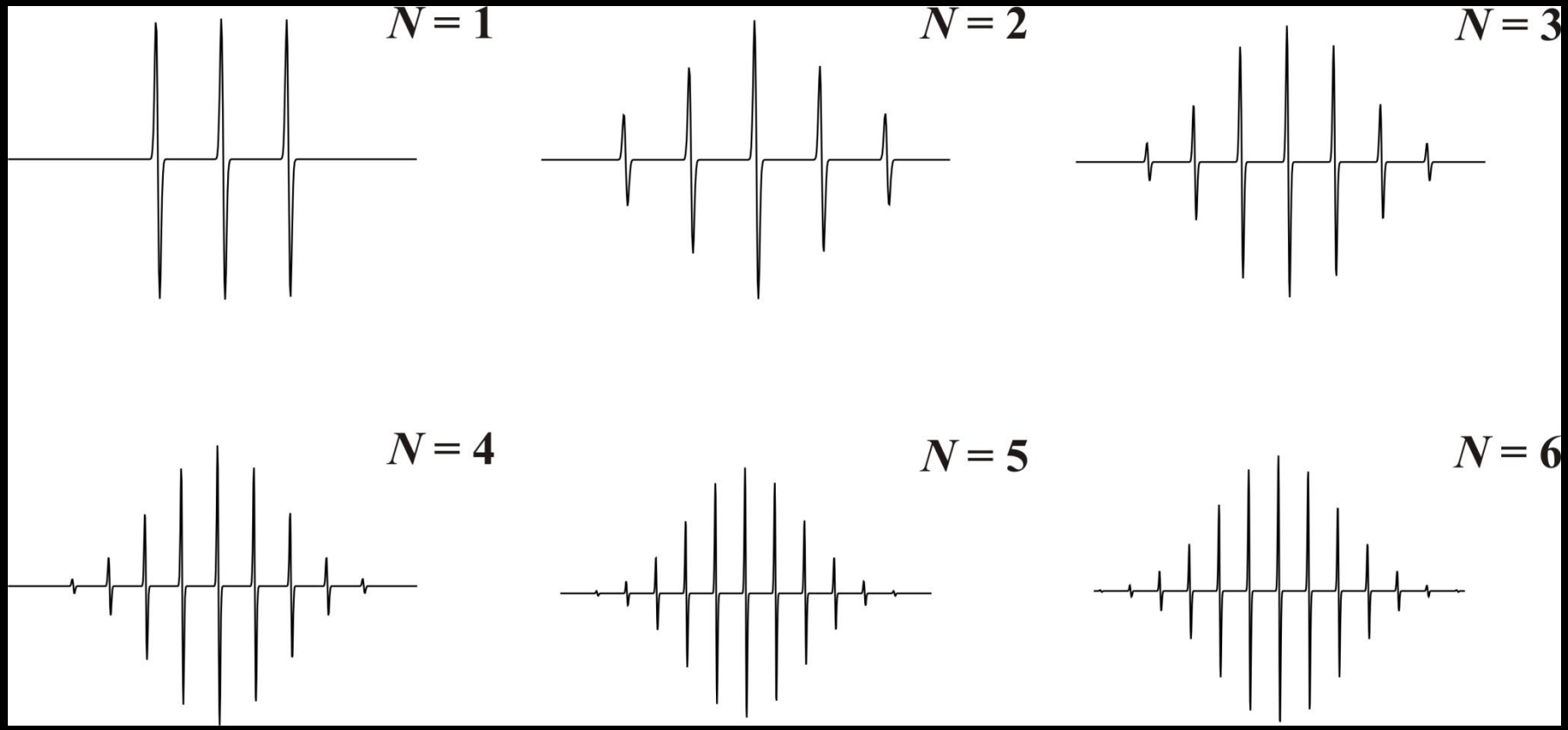
# Relative Intensities for $I = ½$



# Relative Intensities for $I = 1$

| $N$ | Relative Intensities |
|---|---|
| 0 | 1 |
| 1 | 1 : 1 : 1 |
| 2 | 1 : 2 : 3 : 2 : 1 |
| 3 | 1 : 3 : 6 : 7 : 6 : 3 : 1 |
| 4 | 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1 |
| 5 | 1 : 5 : 15 : 20 : 45 : 51 : 45 : 20 : 15 : 5 : 1 |
| 6 | 1 : 6 : 21 : 40 : 80 : 116 : 141 : 116 : 80 : 40 : 21 : 6 : 1 |

# Relative Intensities for $I = 1$

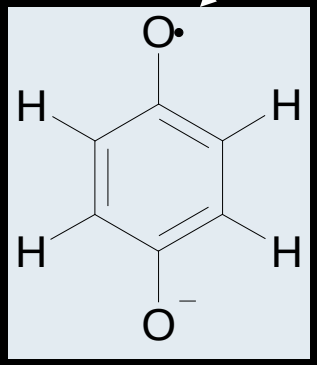


# EPR spectrum of Benzoquinone Radical Anion

4 equivalent nuclei I = 1/2

Multiplicity = (2nI +1) = (2 x4x1/2 + 1)
= 5
mI= +2,+1,0,-1,-2

S=1/2



Nuclear spin angular momentum quantum Number
mI = o,± ½.

Electron spin angular Momentum quantum number

α-state $m_s$= +1/2

$m_s$= ± 1/2

mI= +2
mI= +1
mI= 0
mI= -1
mI= -2

mI= -2
mI= -1
mI= 0
mI= +1
mI= +2

Degenerate state

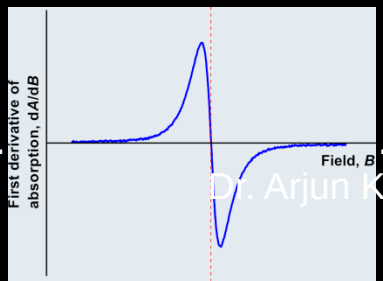
β- state $m_s$= -1/2

H = 0

H ≠ 0
HFS = 0

H ≠ 0
HFS ≠ 0

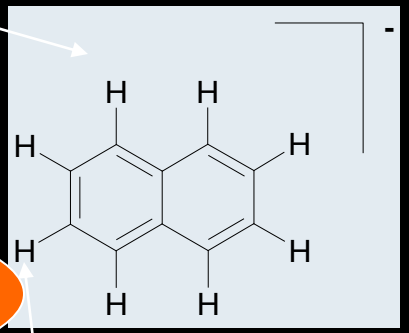
Selection Rule
Δms= ± 1
Δml= ± 0



# EPR spectrum of Naphthalene Radical Anion

S=1/2

4 equivalent alpha nuclei I = 1/2




Multiplicity = (2nI +1) (2nI +1)

= (2 x4x1/2 + 1)(2x4x1/2+1

= 25 mI= +2,+1,0,-1,-2

4 equivalent beta nuclei I = 1/2

# Which nuclei will interact?

- Selection rules same as for NMR
- Every isotope of every element has a ground state nuclear spin quantum number, $I$
  - has value of $n/2$, $n$ is an integer
- Isotopes with even atomic number and even mass number have $I = 0$, and have no EPR spectra
  - $^{12}C$, $^{28}Si$, $^{56}Fe$, …
- Isotopes with odd atomic number and even mass number have $n$ even
  - $^{2}H$, $^{10}B$, $^{14}N$, …
- Isotopes with odd mass number have $n$ odd
  - $^{1}H$, $^{13}C$, $^{19}F$, $^{55}Mn$, …

# Describing the energy levels

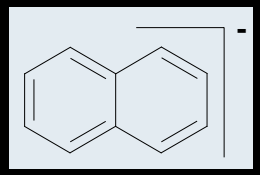
- Based upon the spin of an electron and its associated magnetic moment
- For a molecule with one unpaired electron
  - In the presence of a magnetic field, the two electron spin energy levels are:

$$E = g\mu_B B_0 M_S$$

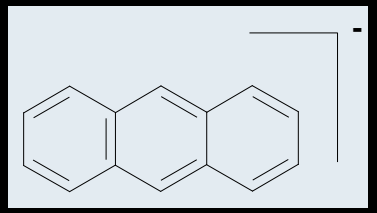
$g$ = proportionality factor $\mu_B$ = Bohr magneton

$M_S$ = electron spin quantum number (+½ or -½) $B_0$ = Magnetic field

# How will you differentiate the following by ESR spectra



A



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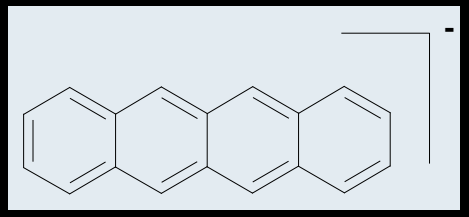
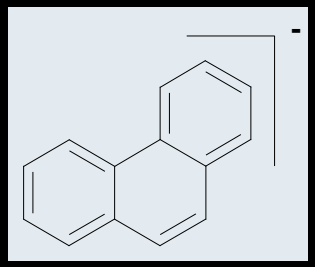


C



D

# Draw and Explain ESR spectra of cycloheptatrienyl radical

# Which of the following system will show ESR spectra

1. **Benzene**
2. **Benzene cation**
3. **Benzene anion**
4. **Cyclopentadienyl cation**

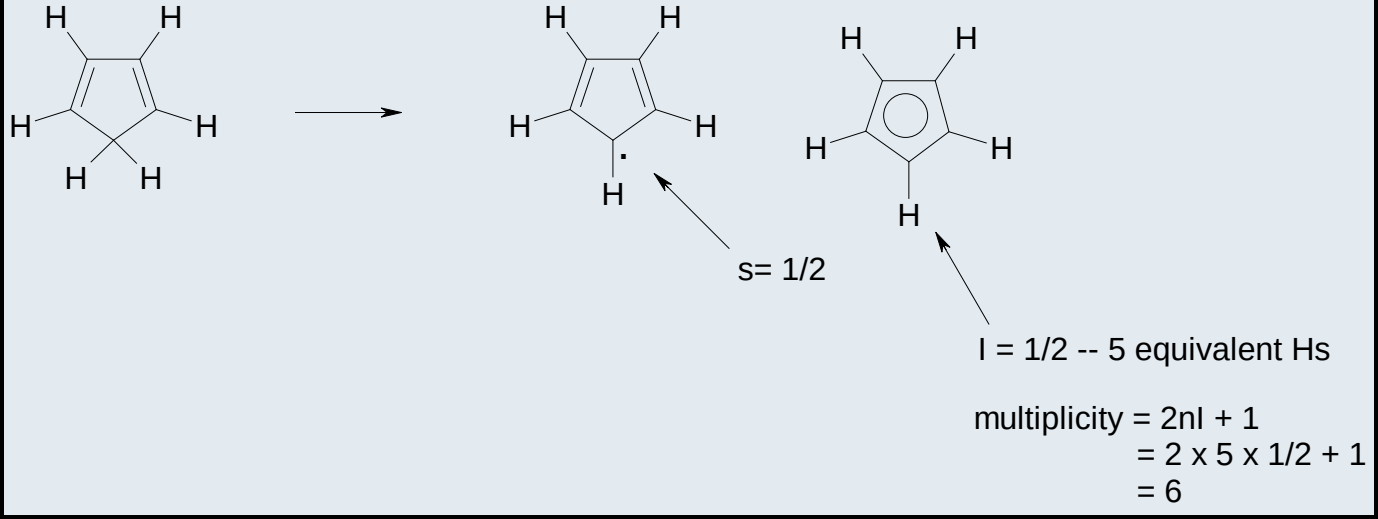
# Which of the following system will show ESR spectra

**1.H**
**2.H2**
**3.Na+**
**4.Cl-**
**5.NO2**
**6.CO2-**

# Draw and Predict the type of ESR spectra to be obtained for 2,3-dichlorobenzoquinone

# Cyclopentadienyl radical shows six lines in esr spectrum.Explain & comment on their intensities

SET-Jan.2006
Marks-06



Nuclear spin angular momentum quantum Number
mI = o,± ½.

Electron spin angular Momentum quantum number

mI= +5/2
mI= +3/2
mI= +1/2
mI= -1/2
mI= -3/2
mI= -5/2
mI= -5/2
mI= -3/2
mI= -1/2
mI= +1/2
mI= +3/2
mI= +5/2

α-state $m_s$= +1/2

$m_s$= ± 1/2

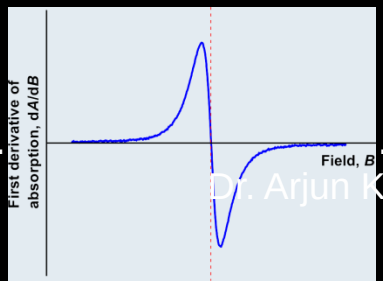
Degenerate state

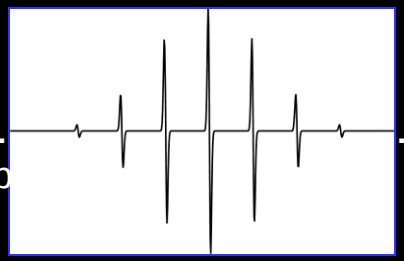
β- state $m_s$= -1/2

H ≠ 0

HFS = 0

H = 0



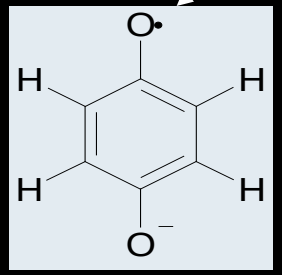
# Differentiate the *ortho& para-isomer* of benzoquinone from esr spectra Of their radicals,viz o/p-benzosemiquinone

**Given I ( 12C)=0, I ( 16O) =0 I ( 1H)=1/2**

SET-Jan-2009
Marks=06

4 equivalent nuclei I = 1/2

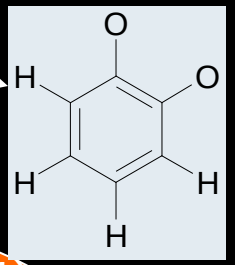
S=1/2




Multiplicity = (2nI +1) = (2 x4x1/2 + 1)
= 5
ml= +2,+1,0,-1,-2

2 set of equivalent nuclei I = 1/2

S=1/2



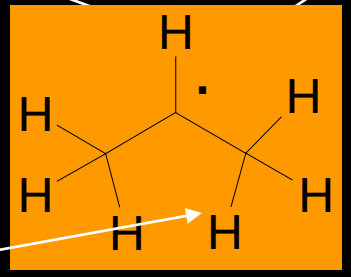

Multiplicity = (2nI +1)(2ml +1) = (2 x2x1/2 + 1) (2 x2x1/2 + 1)
= 9
ml= +4,+3,+2,+1,0,-1,-2,-3,-4

The esr spectrum of free radical C3H7 shows 14-lines with the relative intensity ratio 1:1:6:6:15:15:20:20:20:15:15:6:6:1:1Whether this radical is n-propyl/iso-propyl radical.Explain

Multiplicity = (2nI +1)(2mI +1) = (2 x1x1/2 + 1) (2 x6x1/2 + 1) = 17

1 equivalent nuclei I = 1/2

S=1/2



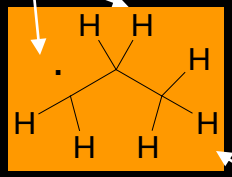

6 equivalent nuclei I = 1/2

Answer- is isopropyl radical

Multiplicity = (2nI +1)(2mI +1) )(2pI +1)
= (2 x1x1/2 + 1) (2 x2x1/2 + 1) (2 x3x1/2 + 1)
= 36

2 equivalent nuclei I = 1/2

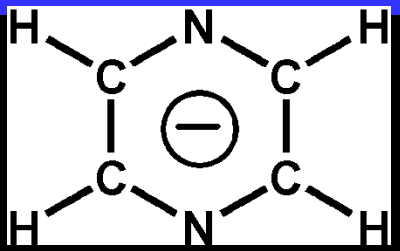
S=1/2




2 equivalent nuclei I = 1/2

3 equivalent nuclei I = 1/2

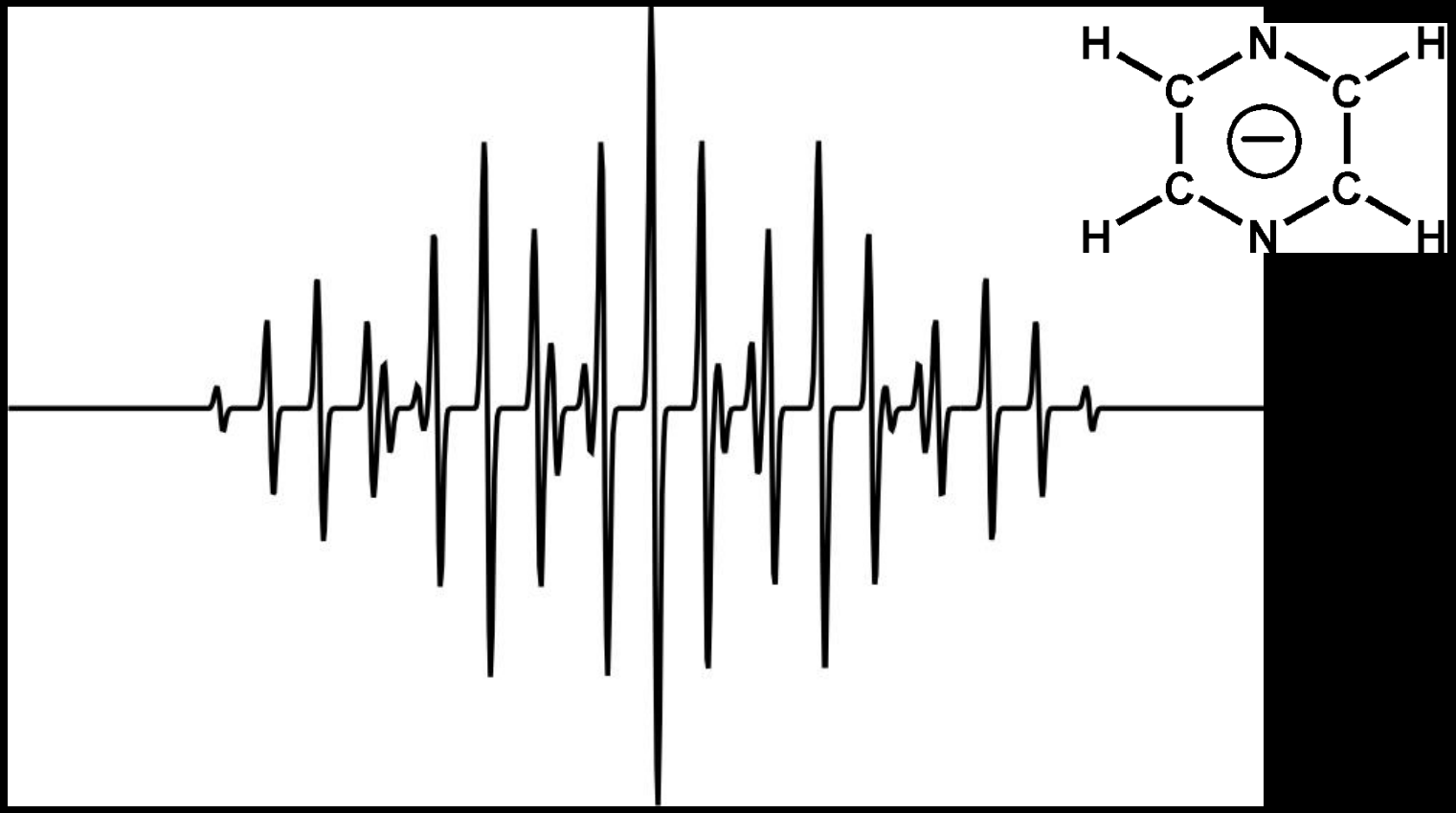
# Hyperfine Interactions




- Example:
  - Pyrazine anion
  - Electron delocalized over ring
    - Exhibits coupling to two equivalent N ($I$ = 1)

      $2NI + 1 = 2(2)(1) + 1 = 5$
    - Then couples to four equivalent H ($I$ = ½)

      $2NI + 1 = 2(4)(1/2) + 1 = 5$
  - So spectrum should be a quintet with intensities 1:2:3:2:1 and each of those lines should be split into quintets with intensities 1:4:6:4:1




EPR spectrum of pyrazine radical anion

# Dec 2012

**36.** The number of lines exhibited by a high resolution EPR spectrum of the species, $[Cu(ethylenediamine)_2]^{2+}$ is [Nuclear spin (I) of Cu = 3/2 and that of N = 1 ]

1. 12 2. 15 3. 20 4. 36

# Dec 2011

**80.** In the EPR spectrum of tetragonal Cu(II) complex, when $g_{\parallel} > g_{\perp} > g_e$ the unpaired electron resides in the orbital:

1. $d_{xy}$
2. $d_{x^2-y^2}$
3. $d_{z^2}$
4. $d_{xz}$.

# June 2012

94. The total numbers of fine and hyperfine EPR lines expected for octahedral high-spin Mn(II) complexes are respectively (I = 5/2 for Mn)

1. 3 and 30 2. 5 and 33 3. 5 and 30 4. 4 and 24