Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Third Year)

Subject: Chemistry

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Paper Title: Physical Chemistry

Unit: Unit 4 Molecular Spectroscopy II

Module Name: Hyperfine Structure

Module No: 33

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Notes

Introduction:

The hyperfine splitting is a special feature of Electron Spin Resonance (ESR) caused by the interaction of electron spins with the magnetic nuclei in the sample. When a single electron interacts with one nucleus, the number of splitting will be equal to (2I +1), where I is the spin quantum number of the nucleus.

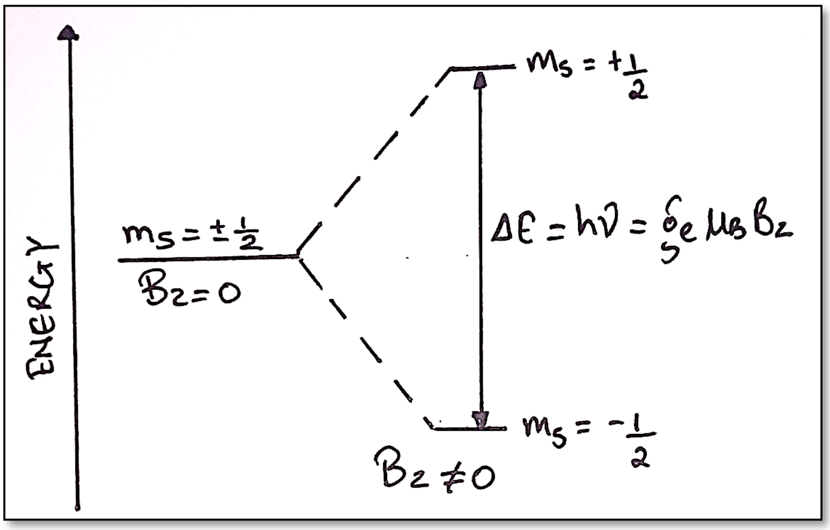
For example, ^{1}H and ^{14}N will cause double and triple splitting respectively.

For ^{1}H, I = ½	For ^{14}N, I = 1
2I + 1 = (2 x ½) + 1	2I + 1 = (2 x 1) + 1
= 2	= 3

In general, if a single electron interacts magnetically with *n* equivalent nuclei, the electron signal is split up into a (2nI + 1) multiplet.

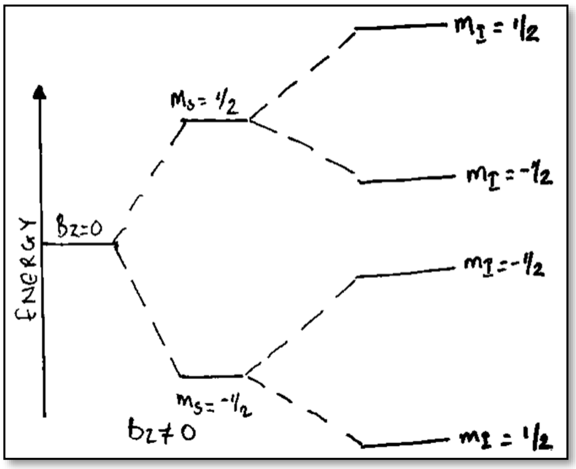
Hyperfine splitting in hydrogen atom:

Let us illustrate the hyperfine splitting by considering an example of a hydrogen atom having one proton and one electron (I = ½ for proton). In the absence of a magnetic field, the single electron of spin (s = ½) gives rise to a doubly degenerate spin energy state. When a magnetic field is applied, the degeneracy is removed and two energy levels will be obtained.



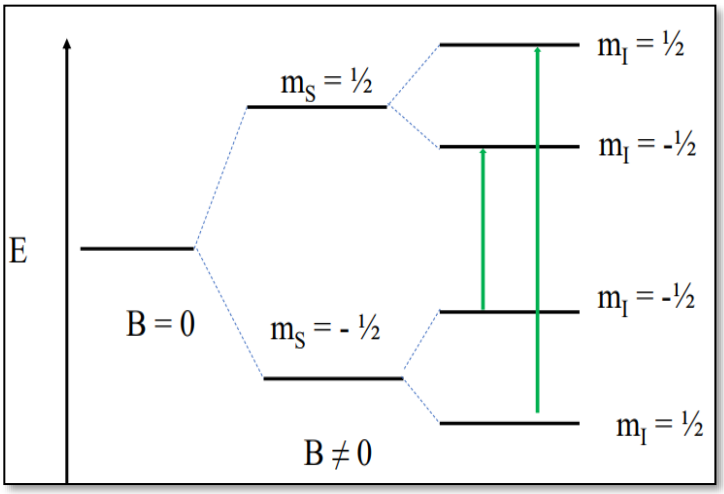
The energy level corresponding to m_s = - ½ is aligned with the magnetic field and the one corresponding to m_s = ½ is aligned opposing the field. The spectrum of a free electron would consist of a single peak corresponding to a transition between these energy levels.

When the interaction between the two energy states and the nuclear spin due to proton is considered, each energy state is further split into two energy levels corresponding to m_I values of, -1/2 and + 1/2 where m_I is the nuclear spin angular momentum quantum number.



The selection rules in ESR are,

$$\Delta mI = 0 \; and \; \Delta ms = \pm 1$$



It means that ESR spectrum of hydrogen atom would consists of two peaks corresponding to the two transitions shown by two arrows.

<u>Hyperfine splitting in methyl radical:</u>

Now let us illustrate the hyperfine splitting by considering an example of a methyl radical having three equivalent protons and one electron (I = ½ for proton). In the absence of a magnetic field, the single electron of spin (s = ½) gives rise to a doubly degenerate spin energy state. When a magnetic field is applied, the degeneracy is removed and two energy levels will be obtained.

When the interaction between the two energy states and the nuclear spin due to proton is considered, each energy state is further split into four energy levels corresponding to m_I values of + 3/2, + 1/2, -1/2 and -3/2 where m_I is the nuclear spin angular momentum quantum number.

For ^{1}H, I = ½

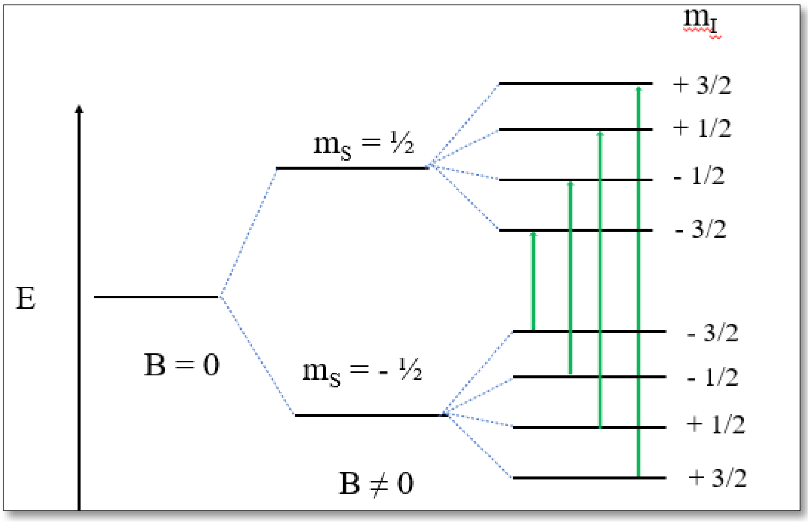
2nI + 1 = (2 x 3 x ½) + 1

= 3 + 1

= 4

The selection rules in ESR are,

$$\Delta mI = 0 \; and \; \Delta ms = \pm 1$$



It means that ESR spectrum of methyl radical would consists of four peaks corresponding to the two transitions shown by two arrows.

Number of hyperfine lines in simple organic radicals:

- $2nI + 1$

$\cdot CH_3$

For ^{1}H, I = ½

2nI + 1 = (2 x 3 x ½) + 1

= 3 + 1

= 4

$\cdot C_6H_6$

For ^{1}H, I = ½

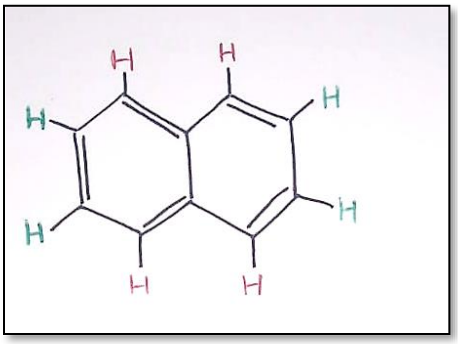
2nI + 1 = (2 x 6 x ½) + 1

= 6 + 1

= 7

- $(2nI + 1)x(2n1I + 1)\ x(2n2I + 1)$

- Naphthalene radical ion



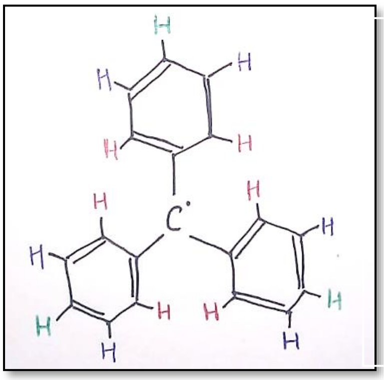
For ^{1}H, I = ½

[(2 x 4 x ½) + 1] x [(2 x 4 x ½) + 1]

= 5 x 5

= 25

- Triphenylmethyl free radical



For ^{1}H, I = ½

[(2 x 6 x ½) + 1] x [(2 x 6x ½) + 1] x [(2 x 3 x ½) + 1]

= 7 x 7 x 4

= 196