Hyperfine coupling constant

- Hyperfine interaction usually results in splitting of lines in an ESR spectrum.
- The interaction energy between the electron spin and a magnetic nucleus is characterized by the **hyperfine coupling constant**
- *This is represented by*
  - **A** with units of energy (Joule)
  - **a** with unit of Magnetic Field (Gauss, Tesla)

Interactions of Single Proton

I=½, M_I=±½

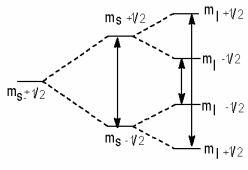
- At the electron there will be one of the two local fields contributed by the proton. For each value of electron spin angular momentum quantum number M_S, the nuclear spin angular momentum quantum number M_I can have the values ±½ giving rise to four different energy levels. The ESR spectrum of hydrogen atom will therefore contain two peaks.

E= gβHMs+aM sM I

- Allowed Transitions are

ΔMS = ±1, Δ MI=0

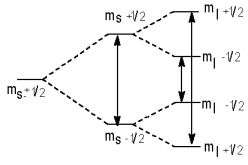
$E_{+½,+½}$= ½gβH+¼a
$E_{+½,-½}$= ½gβH-¼a
$E_{-½,-½}$= -½gβH+¼a
$E_{-½,+½}$= -½gβH-¼a

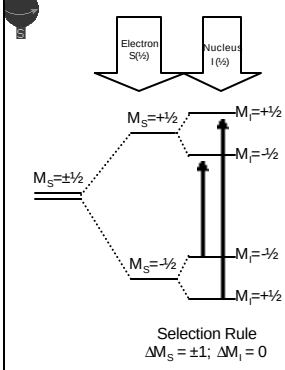


Interactions of Single Proton

From the quantitative expressions for the energy levels of hydrogen atom, in a magnetic field three things are evident

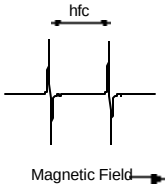
- The equality of splitting of each M_S=±½ states.
- The ordering of the M_I levels is reversed in the lower set of levels as compared to the upper set.
- Transitions occur between same values of M_I.





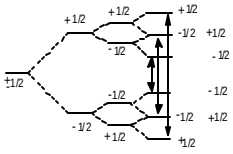
Hyperfine Coupling

S=½;
I=½
Doublet



Hyperfine Interactions In Radical Having Single Set Of Equivalent Protons

- e.g.: $^{\bullet}CH_2OH$ (at low pH, OH will not interact since there is rapid exchange of H)

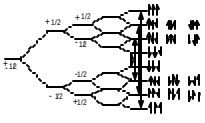


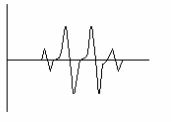
- The spectra will comprise of three lines of the intensity ratio 1:2:1

Hyperfine splitting with a set of three equivalent protons

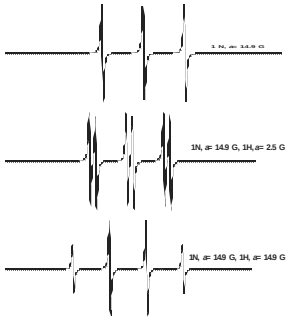
e.g. methyl radical ($^{\bullet}CH_3$)

- The example of a system having S= ½ and I= 3/2 is the methyl radical in which the unpaired electron interacts with three protons.
- There will be four values of M_I corresponding to M_S= +½ and four values for M_S= -½.
- The resultant derivative spectrum will comprise of four lines with the intensity ratio 1:3:3:1.





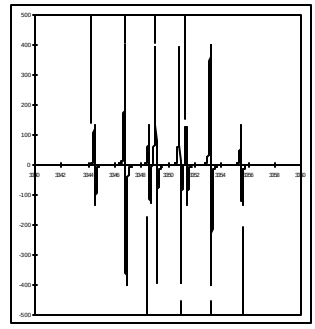
Hyperfine splittings are additive



ESR Spectral analysis

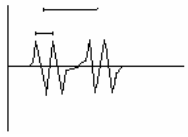
$^{13}CH_3^-$

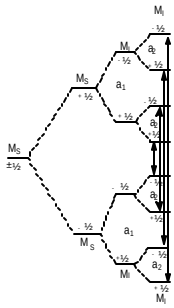
- *Two quartets*
- *Two* coupling constants
- a_H = 2.3 mT
- a_C = 4.1 mT



Radical containing multiple set of equivalent protons

- ***e.g. HO-˙CH-COOH***
- **Here a_1 = 17.13G**
- **a_2 = 2.56G**

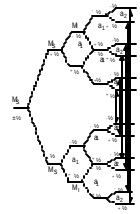


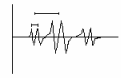


System having three protons, two of which are equivalent

- e.g. .CH_2OH at high pH
- In general if there are sets of **m** and **n** equivalent protons in a molecule, then the maximum number of lines in the spectrum will be given by the formula (n+1)(m+1). For different nuclei, the general rule is (2nI+1)(2mI+1).

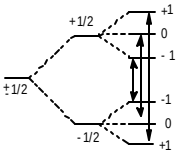
Here a_1=17.4G
a_2=1.15G



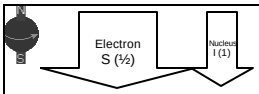


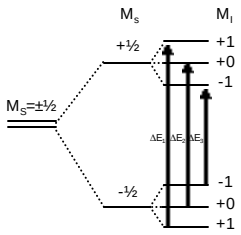
Hyperfine Interactions In Deuterium (S=½, I=1)

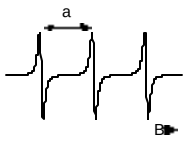
- The deuterium atom is a simple example of a system with S=½ and I=1.
- There are now six spin states.
- By virtue of selection rules $\delta M_S = \pm 1$ and $\delta M_I = 0$, there are three allowed transitions
- Thus three lines corresponding to these transitions.
- These lines will be of equal intensity since there is no coincidence of states.



Hyperfine Coupling







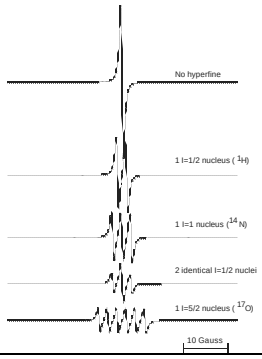
"triplet"

$E = g\beta BS_z + (hA_0)S_zI_z$
$E = g\beta BS_z + (a)S_zI_z$
(hA_0 (Hz) -> a (G) via g-factor)

Selection Rule
$\Delta M_S = \pm 1$ (electron)
$\Delta M_I = 0$ (nuclear)

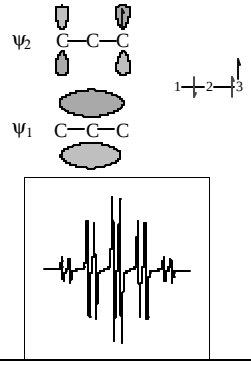
$\Delta E_1 = g\beta B + a$
$\Delta E_2 = g\beta B$
$\Delta E_3 = g\beta B - a$

Hyperfine Splittings



Allyl Radical

- Unpaired electron in non-bonding MO
- So e interacts only with 4 terminal Hs *not* central H
- But from ESR spectrum
  - a(terminal H) = (-) 1.39 mT
  - a(central H) = (+) 0.40 mT
- Enhanced unpaired spin at terminals *and* at central H



Direct ESR analysis of a radical

- Radical cannot be diatomic
- Radical must be available at a detectable concentration
  - At least metastable
  - Frozen solution to greatly decrease radical decay
    - Can greatly complicate the spectrum due to anisotropy
  - Continuous formation inside resonator
    - Enzymatic radical formation
    - Flow experiment
- Radical characterized by hyperfine analysis