EPR Course
NTU Fall 2001
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November 7, 2001
Lecture 5

EPR of Organic Radicals in solution

$\mathcal{H}_S$ = Spin hamiltonian

$$= \mathcal{H}_Z + \mathcal{H}_{\text{nuclear hyperfine couplings}}$$

$$= -\vec{\mu}_S\cdot\vec{H} - \vec{\mu}_L\cdot\vec{H} + \sum_N a_N \vec{I}_N\cdot\vec{S}$$

$$+ \sum_N (-g_S g_N \beta\beta_N)\left\{\frac{\vec{I}_N\cdot S}{r_N^3} - \frac{3(\vec{I}_N\cdot\vec{r}_N)(\vec{S}\cdot\vec{r}_N)}{r_N^5}\right\}$$

$$- \sum_N \vec{\mu}_N\cdot\vec{H}$$

$$= +g_S\beta\vec{S}\cdot\vec{H} + \sum_N a_N\vec{I}_N\cdot\vec{S} - \sum_N g_N\beta_N \vec{I}_N\cdot\vec{H}$$

$\sum_N$ sum over all magnetic nuclei

Note $\langle\vec{\mu}_L\rangle = 0$

$\mathcal{H}_{\text{Dipolar}} = 0$ for radical in solution

$$\mathcal{H}_{\text{Dipolar}} = \sum_N [I_x^N, I_y^N, I_z^N]\begin{bmatrix} \frac{r_N^2-3x_N^2}{r_N^5} & -\frac{3x_Ny_N}{r_N^5} & -\frac{3x_Nz_N}{r_N^5} \\ -\frac{3x_Ny_N}{r_N^5} & \frac{r_N^2-3y_N^2}{r_N^5} & -\frac{3y_Nz_N}{r_N^5} \\ -\frac{3x_Nz_N}{r_N^5} & -\frac{3y_Nz_N}{r_N^5} & \frac{r_N^2-3z_N^2}{r_N^5} \end{bmatrix}\begin{bmatrix} S_x \\ S_y \\ S_z \end{bmatrix}$$

Due to rapid tumbling of radical in solution, each term in 3×3 matrix vanishes

$$\mathcal{H}_S = +g_S\beta S_z H_0 + \sum_N a_N I_z^N S_z - \sum_N g_N\beta_N I_z^N H_0$$

electron spin Zeeman

isotropic nuclear hyperfine

nuclear Zeeman

Energy levels

$$\boxed{W = g_S\beta m_S H_0 + \sum_N a_N m_I^N m_S - \sum_N g_N\beta_N m_I^N H_0}$$

Selection rules for EPR transitions:

$$\Delta m_S = \pm 1$$
$$\Delta m_I^N = 0$$

$$\boxed{h\nu = g_S\beta H_0 + \sum_N a_N m_I^N}$$

frequency swept spectrum at fixed H_0

or

$$\boxed{h\nu_0 - \sum_N a_N m_I^N = g_S\beta H_{resonance}}$$

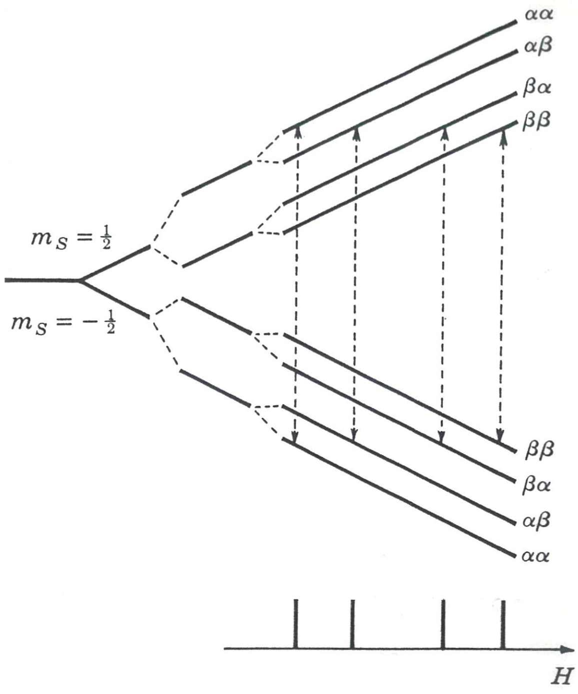
field swept spectrum at fixed frequency ν_0

Examples

1) Unpaired electron coupled to 2 protons with inequivalent hyperfine couplings a_1 and a_2, both assumed positive

$$h\nu_0 - a_1 m_1 - a_2 m_2 = g_S\beta H_{resonance}$$

where $m_1 = m_I^1$
$m_2 = m_I^2$



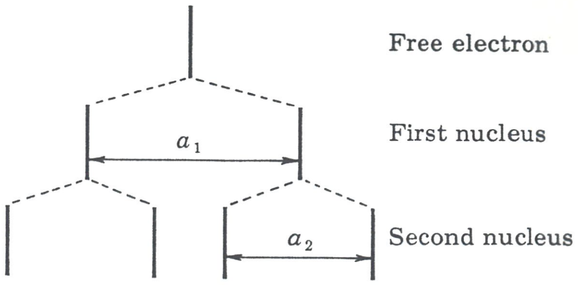
← proton spin $m_1\ m_2$

Hyperfine energy levels and transitions for two protons

$a_1,\ a_2 > 0$

There are four transitions, and since each nuclear spin state is equally probable, four equally intense absorption lines are obtained. Each line may be identified by the values of m_1 and m_2.

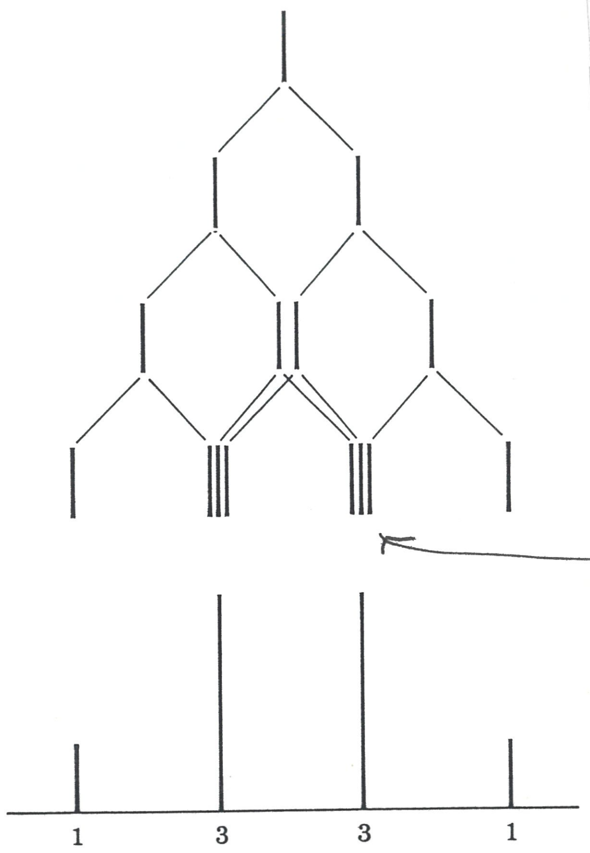
A simple way of describing the two proton spectrum is to say that proton 1 splits the original single line due to the electron spin into a doublet, each line being split into a further two lines because of the interaction with proton 2



. Origin of the four-line hyperfine spectrum from two protons.

2) Coupling to sets of equivalent protons.

$$a_1 = a_2 = a_3 \cdots = a_N = a$$



Hyperfine pattern for three equivalent nuclei.

hyperfine lines associated with different m_I^N's can become coincident !

(same resonance fields)

Return to 2 protons with $a_1 = a_2 = a$

Then

$$h\nu_0 - a_1 m_1 - a_2 m_2 = g_s \beta H_{resonance}$$

or $$h\nu_0 - a(m_1 + m_2) = g_s \beta H_{resonance}$$

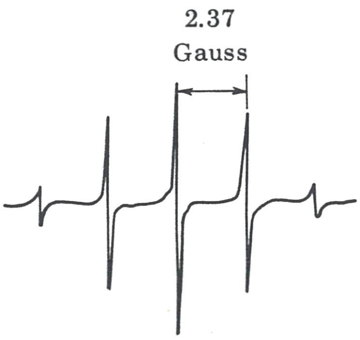
Resonance fields	$(m_1 + m_2) = M$	Nuclear spin states
$h\nu_0 - a$	1	$\alpha\alpha$
$h\nu_0$	0	$\alpha\beta,\ \beta\alpha$
$h\nu_0 + a$	-1	$\beta\beta$

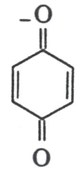
For interaction of the odd electron with $\underline{n}$ equivalent protons ($I = \frac{1}{2}$), the spectrum consists of $2\underline{n}+1$ lines whose relative intensities are proportional to the coefficients of the binomial expansion of $(1+x)^{\underline{n}}$. The results for $\underline{n}=1$ to $\underline{n}=8$ are as follows:

electron	1
1 proton	1 1
2	1 2 1
3	1 3 3 1
4	1 4 6 4 1
5	1 5 10 10 5 1
6	1 6 15 20 15 6 1
7	1 7 21 35 35 21 7 1
8	1 8 28 56 70 56 28 8 1

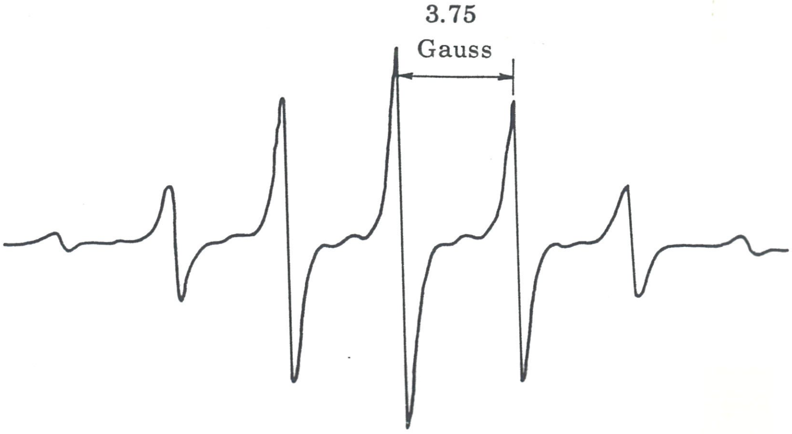
(3) Specific examples

(a)



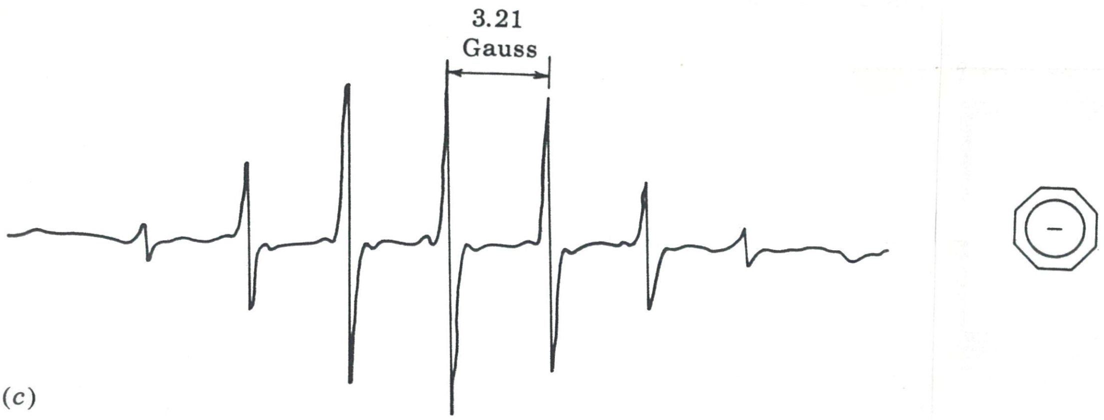


Negative ion of p-benzosemiquinone



(b)

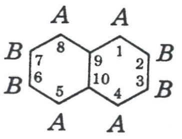
Negative ion of benzene



Negative ion of cyclooctatetraene

(4) A more complicated example

EPR spectrum of naphthalene negative ion, where the unpaired electron interacts with four A-type protons and four B-type protons



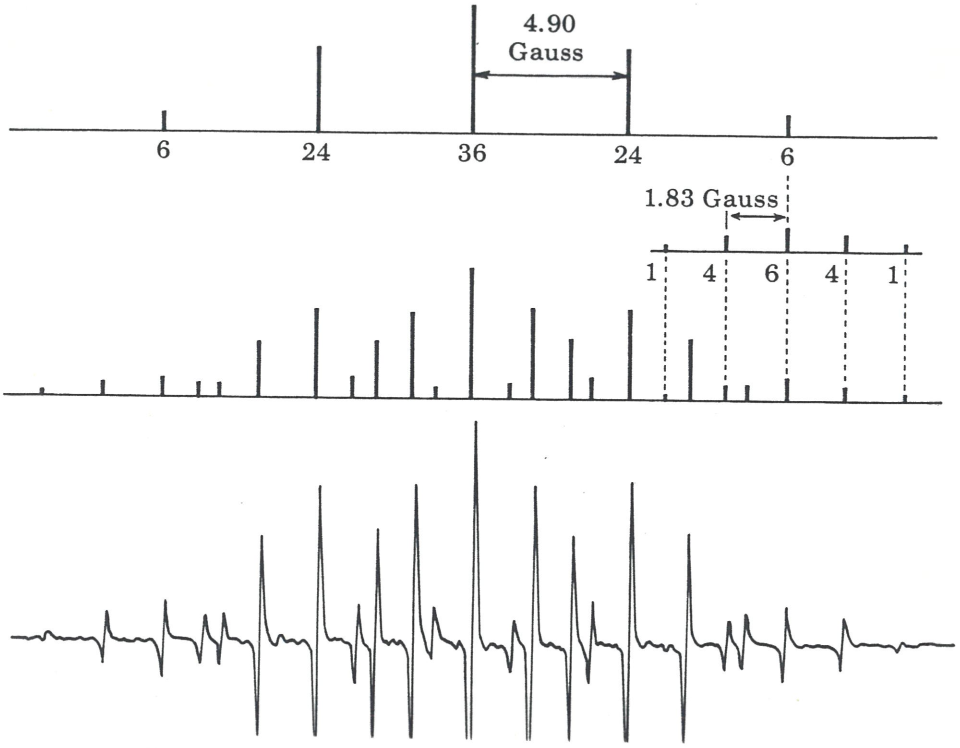
$$a'_A = 4.90 \text{ Gauss}$$

$$a'_B = 1.83 \text{ Gauss}$$

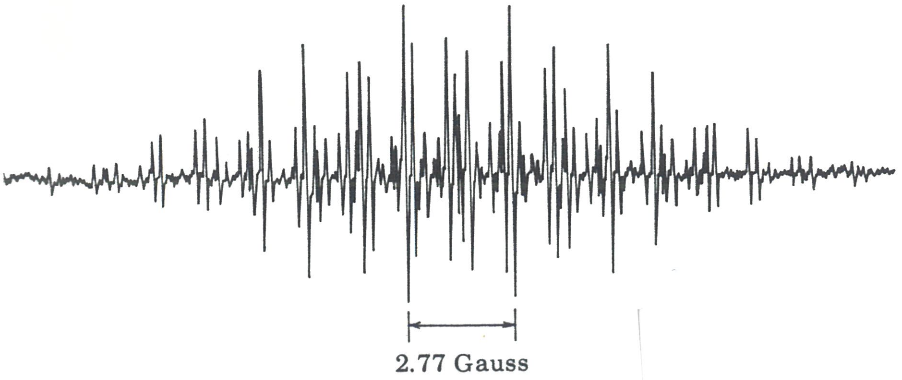
$$a' = \frac{a}{g_s \beta}$$

Interaction with the four A protons alone would give rise to a pattern of five lines with relative intensities 1:4:6:4:1. However, each of these lines is split into a further quintet due to interactions with the B protons. Hence, the complete spectrum contains 25 lines and its analysis yields the two coupling constants a'_A and a'_B. The resultant spectrum is a superposition of 5 quintets with relative intensities

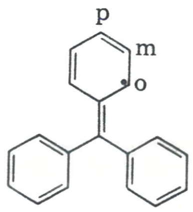
1, 4, 6, 4, 1
4, 16, 24, 16, 4
6, 24, 36, 24, 6
4, 16, 24, 16, 4
1, 4, 6, 4, 1



(5) A <u>very</u> complex spectrum



Electron resonance spectrum of triphenylmethyl.



196 lines from coupling to 3 kinds of equivalent protons, six <u>ortho</u>, six <u>meta</u>, & 3 <u>para</u>

$\boxed{a_o' = 2.53,\ a_m' = 1.11,\ a_p' = 2.77 \text{ gauss}}$

(6) Coupling to other nuclei

a) Example : Methyl radical

Spectrum is a superposition of EPR of $^{12}CH_3$ (98.9%) and $^{13}CH_3$ (1.1%)

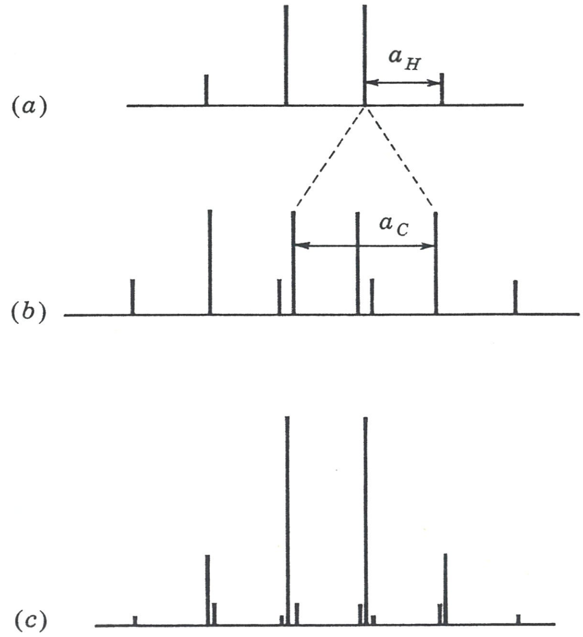
$\uparrow$

$a'_H = 23.04g$

$\nearrow$

$a'_{13C} = 41$ gauss

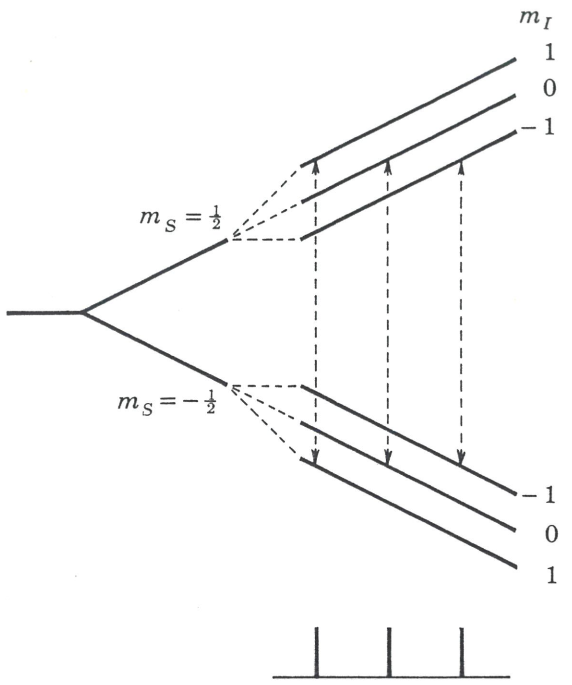
$a'_H = 23$ gauss



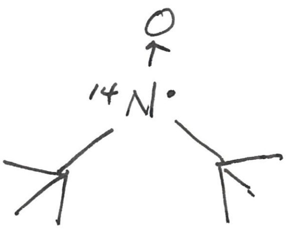
Carbon 13 splittings in the methyl radical. (a) Protons in $C^{12}H_3$; (b) spectrum of $C^{13}H_3$; (c) natural mixture of C^{12} and C^{13}. Splittings are $a'_H = -23$ gauss, $a'_C = +41$ gauss.

b) $I = 1$

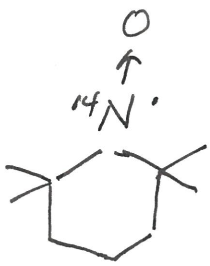
Nuclei with spin $I = 1$ are frequently encountered, common examples being ^{14}N and ^{2}H. A nucleus with $I = 1$ has three allowed spin orientations with components in the z-direction corresponding to m_I values of $+1$, 0 and -1. Hence interaction of an unpaired electron with one ^{14}N nucleus gives rise to three equally intense, equally spaced lines



. Hyperfine levels and transitions for a single nucleus of spin $I = 1$ with positive coupling constant.



DTBN



TEMPO

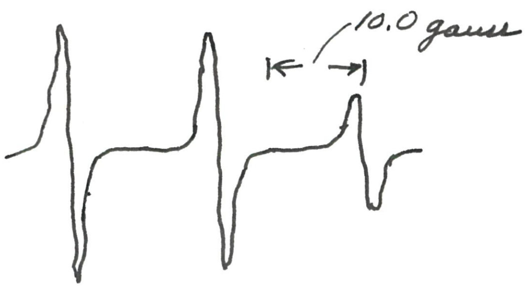
Identity of nuclei and spin could be confirmed by isotope substitution

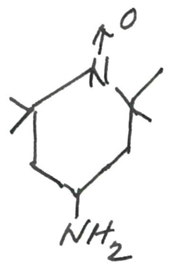
$$^{14}N \longrightarrow {}^{15}N$$

$I = 1$ (three lines) → $I = \frac{1}{2}$ (two lines)

$$\frac{g_{^{15}N}}{g_{^{14}N}} = \frac{-0.567}{0.403}$$

Note change in sign of a!





EPR of TEMPAMINE in 1,3-propanediol

ESR spectrum could also be simplified by deuteration.

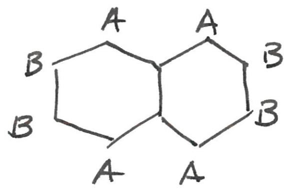
$^1H \longrightarrow {}^2H$

$I = 1/2$ $\qquad$ $I = 1$

two lines (doublet) $\qquad$ three lines (triplet)

$g_{1H} = 5.585$ $\qquad$ $g_{2H} = 0.857$

$$\frac{g_D}{g_H} = 0.1531$$



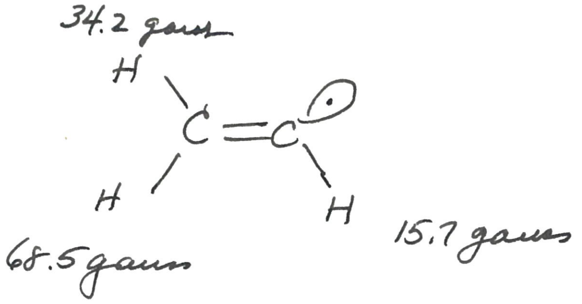
$a'_A = 4.90$ gauss

$a'_B = 1.83$ gauss

The EPR spectrum of naphthalene negative ion could be assigned by recording the spectrum of the deuterated naphthalene negative ion in which the B protons have been replaced by deuterons. Original splittings due to these protons collapse to broadened singlets (triplet unresolved; within linewidth)

Mechanism of Hyperfine Coupling

Consider the $\boxed{\sigma\text{- radical}}$ in vinyl radical obtained by H. abstraction



Unpaired electron occupying a $\underline{\underline{\sigma}}$ MO (symmetrical about plane of molecule)

Recall $$\frac{a}{h} = \frac{8\pi}{3} g_s\beta g_N\beta_N |\psi(0)|^2 = 1420\,\text{MHz}$$ for atomic hydrogen

$$a' = \frac{a}{g_s\beta} = 506.8 \text{ gauss}$$

Does the above result mean the following:

There is $\frac{34.2}{506.8}$ of unpaired electron spin at cis methylene proton

$\frac{68.5}{506.8}$ " " " " at trans methylene proton

$\boxed{0.135} \rightarrow$

and $\frac{15.7}{506.8}$ " " " " at vinyl C-H proton

or odd electron spends 0.135 of the time at trans methylene hydrogen of the radical? $\boxed{\text{No!}}$

This picture is over-simplified!

Actually, all the electrons are involved, including e⁻'s in half-filled molecular orbital containing the odd electrons, as well as the filled molecular orbitals that are filled by a pair of electrons!

Should write the $\mathcal{H}_C$ or Fermi-contact interaction

$$\mathcal{H}_C = \frac{8\pi}{3} g_s \beta g_N \beta_N \sum_{\substack{k \\ \text{all electrons}}} \delta(\vec{r}_k - \vec{r}_N)\vec{S}_k \cdot \vec{I}_N$$

$$= a\, \vec{S} \cdot \vec{I}_N \qquad \text{for many-electron system}$$

where $a = \frac{4\pi}{3} g_s \beta g_N \beta_N \rho(r_N)$

and $\rho(\vec{r}_N) = \int \psi^* \sum_k 2S_{kz}\, \delta(\vec{r}_k - \vec{r}_N)\, \psi \, d\tau$

$\rho(\vec{r}_N)$ is simply the difference between the average number of electrons at the nucleus which has spin α and the number with spin β

The operator $2S_{kz}$ gives a factor of ±1 depending on the spin (α or β), and the δ function ensures that the electron is at the nucleus.

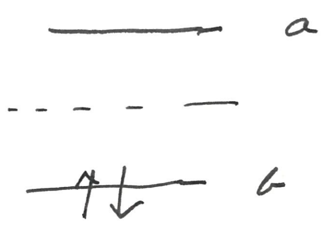
Of course, $\int \psi^* \sum_k 2S_{kz}\, \psi \, d\tau = 1$,

namely, the spin component of the state ψ is $2S_z = 1$ or $S_z = +\frac{1}{2}$.

Perfect Pairing Approximation in Theory of Electronic Structure

To understand what's going on, specifically why we need to rewrite the Fermi-contact Hamiltonian for a many-electron system, let me introduce the "so-called" Perfect Pairing Approximation in the theory of electronic structure.

Consider a molecular system with two Molecular orbitals, one bonding and the other antibonding, and there are two electrons associated with system in neutral molecule.



Typically, one writes the electronic wavefunction of the system as follows:

$$\psi(1,2) = \left(\frac{1}{2!}\right)^{1/2} \begin{vmatrix} \phi_b(1)\,\alpha(1) & \phi_b(1)\,\beta(1) \\ \phi_b(2)\,\alpha(2) & \phi_b(2)\,\beta(2) \end{vmatrix}$$

Slater Determinant

$$= \left(\frac{1}{2}\right)^{1/2} \left[\phi_b(1)\,\phi_b(2)\,\alpha(1)\,\beta(2) - \phi_b(1)\,\phi_b(2)\,\beta(1)\,\alpha(2) \right]$$

$$= \phi_b(1)\,\phi_b(2) \cdot \frac{1}{\sqrt{2}} \left\{ \alpha(1)\,\beta(2) - \beta(1)\,\alpha(2) \right\}$$

Wavefunction for the two MO's same for the two electrons

$\Rightarrow$ Perfect Pairing Approximation

Within this approximation, $\rho(r_N) = 0$

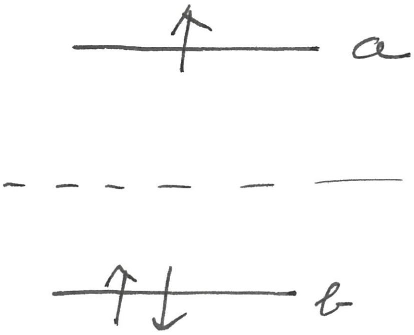
$$\rho(r_N) = \int \psi^*(1,2) \sum_k 2 S_{zk}\, \delta(r_k - r_N)\, \psi(1,2)\, d\tau$$

$$= \sum_{\substack{n \\ \text{MO occupied}}} \int \phi_n^*(r)\left(2\hat{S}_z^{\alpha} + 2S_z^{\beta}\right) \delta(\vec{r} - \vec{r}_N)\, \phi_n(r)\, d\vec{r}$$

$$= \phi_b^*(0)\,\phi_b(0) \cdot \underbrace{(1-1)}_{\text{spin part}} = 0$$

$(\vec{r} - \vec{r}_N)$, i.e., at nucleus "N"

Now, add an extra electron to the system to generate the negative ion or radical.



$$\psi(1,2,3) = \left(\frac{1}{3!}\right)^{1/2} \begin{vmatrix} \phi_b(1)\alpha(1) & \phi_b(2)\alpha(2) & \phi_b(3)\alpha(3) \\ \phi_b(1)\beta(1) & \phi_b(2)\beta(2) & \phi_b(3)\beta(3) \\ \phi_a(1)\alpha(1) & \phi_a(2)\alpha(2) & \phi_a(3)\alpha(3) \end{vmatrix}$$

Again, perfect pairing approximation used.

$$\rho(r_N) = \phi_a^*(0)\,\phi_a(0) \cdot 1 = \phi_a^*(0)\,\phi_a(0)$$

$$\phi_a = \sum_m c_{ma}\, \eta_m$$ (MO = linear combination of atomic orbitals)

so that

$$\rho(r_H) = \phi_a^*(0)\,\phi_a(0) = \phi_a^*(r_H)\,\phi_a(r_H) = c_{Ha}^*\, c_{Ha}\, |1s_H(0)|^2$$

$\neq 0$ only at hydrogens

Recall $\rho(r_H) \equiv$ unpaired electron spin density at the nucleus or probability density measured in electrons/volume

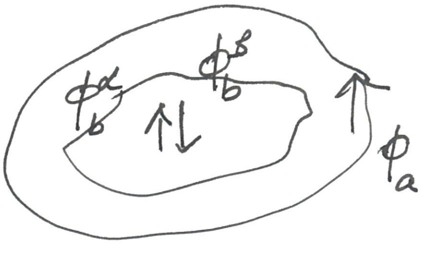
$$a = \frac{4\pi}{3} g_S \beta g_N \beta_N\, c_{Ha}^*\, c_{Ha}\, |1s_H(0)|^2$$

$$= \frac{4\pi}{3} g_S \beta g_N \beta_N\, \rho_H\, |1s_H(0)|^2$$

$\rho_H \equiv$ spin density in an orbital representing the fractional population of unpaired electrons on an atom

More correct interpretation

Include spin polarization of filled MO's by unpaired electron



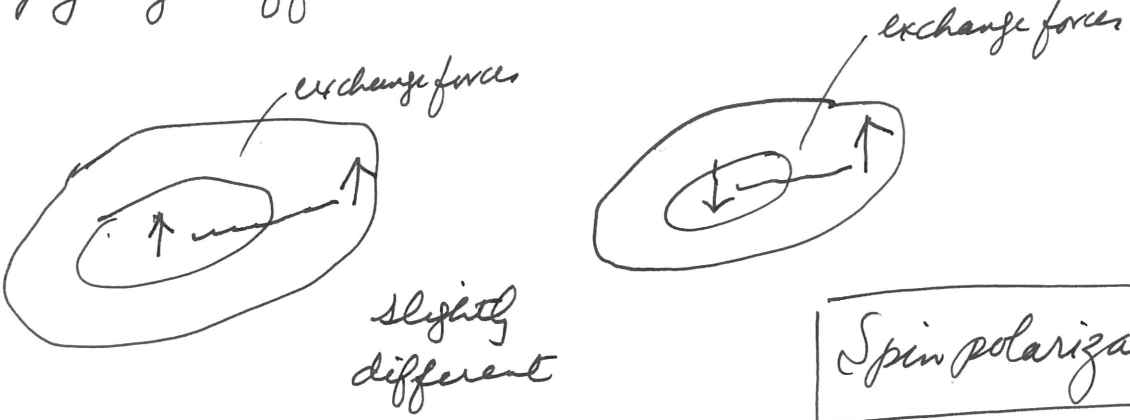
Perfect Pairing approximation

$$\phi_b^\alpha(r) = \phi_b^\beta(r)$$

Strictly speaking

$\phi_b^{\alpha}(r)$ slightly different from $\phi_b^{\beta}(r)$

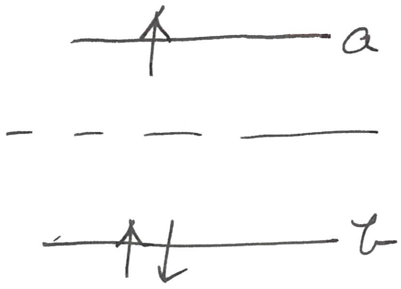
due to different electron repulsion between parallel spins and antiparallel spins occupying different MO's



Spin polarization

Reason for Hund's rule a in atomic structure!

So



More correct to write

$$\Psi(1,2,3) = \left(\frac{1}{3!}\right)^{1/2} \begin{vmatrix} \phi_b(1)\alpha(1) & \phi_b(2)\alpha(2) & \phi_b(3)\alpha(3) \\ \phi_b'(1)\beta(1) & \phi_b'(2)\beta(2) & \phi_b'(3)\beta(3) \\ \phi_a(1)\alpha(1) & \phi_a(2)\alpha(2) & \phi_a(3)\alpha(3) \end{vmatrix}$$

and $\rho(r_N) = C_{Ha}^{*} C_{Ha} \, |1s_H(0)|^2$

$$+ \left(C_{Hb}^{*} C_{Hb} - C_{Hb}'^{*} C_{Hb}'\right) |1s_H(0)|^2$$

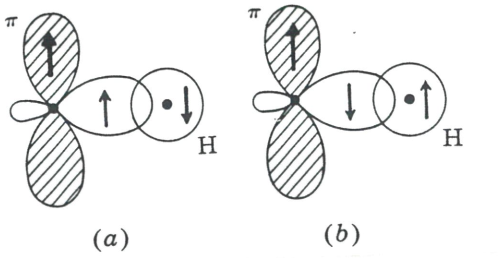
or $\rho_H = C_{Ha}^{*} C_{Ha} + \underbrace{\left(C_{Hb}^{*} C_{Hb} - C_{Hb}'^{*} C_{Hb}'\right)}_{\substack{\text{contribution to spin density} \\ \text{from spin polarization of} \\ \text{filled bonding MO!}}}$

π-radicals

Indirect coupling through a C–H bond

In aromatic radicals, the odd electron occupies a molecular π-orbital delocalized over the carbon atom framework of the molecule. This MO, formed by overlap of carbon $2p_z$ atomic orbitals, has a *node* in the plane of the molecule, where ring hydrogen atoms are. So expect *no* hyperfine coupling to these protons! But they are observed. Again, could be explained by spin polarization.

Within perfect pairing approximation,



(a) (b)

Structures (a) and (b) would be equally important. However, if interaction between σ and π-systems is taken into account, structure (a) is slightly preferred over structure (b) because of the more favorable exchange interaction between the π-electron and the carbon σ-electron, whose spins are parallel. If the odd electron has spin α, there is slight excess α-spin in the carbon σ orbital and corresponding excess β spin in the hydrogen 1s orbital, which gives rise to the isotropic proton splitting. (α-spin in the carbon p_π-orbital induces excess β-spin at proton) Because there is excess β-spin in the hydrogen 1s orbital, $\rho_H < 0$. That is, spin polarization leads to negative spin density at H.

The above offers the valence-bond picture for the problem. An alternative description of the spin polarization is provided by molecular orbital theory.

Normal doublet ground state wavefunction for the C–H fragment would be written as the Slater determinant.

$$\Psi_0 = \frac{1}{\sqrt{6}} \begin{vmatrix} \sigma_b(1)\alpha(1) & \sigma_b(2)\alpha(2) & \sigma_b(3)\alpha(3) \\ \sigma_b(1)\beta(1) & \sigma_b(2)\beta(2) & \sigma_b(3)\beta(3) \\ \pi(1)\alpha(1) & \pi(2)\alpha(2) & \pi(3)\alpha(3) \end{vmatrix}$$

↑ perfect pairing structure

Excited states

$$\Psi_1 = \frac{1}{\sqrt{6}} \begin{vmatrix} \sigma_b(1)\alpha(1) & \sigma_b(2)\alpha(2) & \sigma_b(3)\alpha(3) \\ \sigma_a(1)\beta(1) & \sigma_a(2)\beta(2) & \sigma_a(3)\beta(3) \\ \pi(1)\alpha(1) & \pi(2)\alpha(2) & \pi(3)\alpha(3) \end{vmatrix}$$

$$\Psi_2 = \frac{1}{\sqrt{6}} \begin{vmatrix} \sigma_b(1)\beta(1) & \sigma_b(2)\beta(2) & \sigma_b(3)\beta(3) \\ \sigma_a(1)\alpha(1) & \sigma_a(2)\alpha(2) & \sigma_a(3)\alpha(3) \\ \pi(1)\alpha(1) & \pi(2)\alpha(2) & \pi(3)\alpha(3) \end{vmatrix}$$

& Ψ_3 Ψ_1 with $\pi(1)\beta(1)$ $\pi(2)\beta(2)$ $\pi(3)\beta(3)$

& Ψ_4 Ψ_2 with $\pi(1)\beta(1)$ $\pi(2)\beta(2)$ $\pi(3)\beta(3)$

Spin polarization $\Longrightarrow$ Mix Ψ_0 with a little of

Ψ_1, Ψ_2, Ψ_3 & Ψ_4 or linear combination of Ψ_1, Ψ_2, Ψ_3 + Ψ_4 with same S^2 + S_z, namely $3/4$ + $\pm 1/2$ respectively

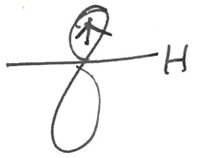
Theoretical calculations provide the following estimate:

A single π-electron induces a negative spin density of about −0.05 in the hydrogen 1s orbital, corresponding to hyperfine splitting of 20-25 gauss $(a < 0)$.

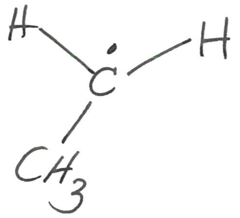
Observed α-proton splittings

a

methyl



−23.04 gauss



ethyl

−22.38 gauss

McConnell's Relation

In aromatic radicals, the odd electron is delocalized. The extent to which the C-H σ-electrons are spin-polarized is directly proportional to the net unpaired electron population, or "π-electron spin density", or

ρ_π on carbon atom.

Mc Connell Relation : $a_H = Q \rho_\pi$

where $Q \cong (-) 22.5$ gauss

TABLE 6.1. Hyperfine Splittings and Spin Distributions in the Cyclic Polyene Radicals C_nH_n

Radical	Spin Density ρ_π	Hyperfine Splitting a_H	Effective Value of Q
CH_3	1	−23.04	−23.04
C_5H_5	1/5	− 5.98	−29.9
$C_6H_6^-$	1/6	− 3.75	−22.5
C_7H_7	1/7	− 3.91	−27.4
$C_8H_8^-$	1/8	− 3.21	−25.7