

## Proposed topics

pg 1

- 1- EPR fundamentals for an isotropic S=1/2 system,
- 2- hyperfine effects on S=1/2,
- 3- anisotropy, effects of spin-orbit coupling, and biradicals.
- 4- a qualitative fly-over of transition metal ions.

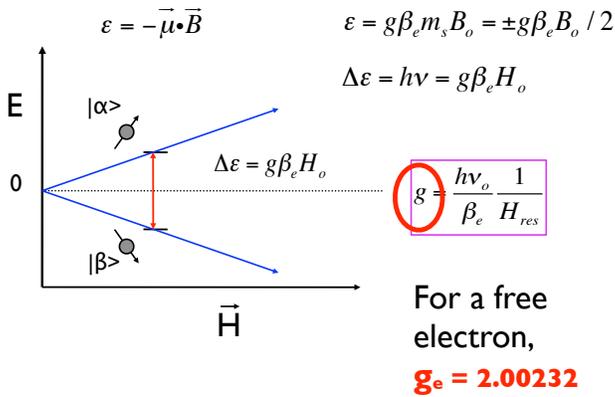
### Today's goals

### Hyperfine coupling

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## REVIEW -1 Information content in $g$

pg 2



In EPR spectra  $g$  can range from **10 to 1** (and beyond).  
5-fold variations vs. ppm variations observed in NMR.  
Range reflects orbital contributions, spin multiplicity and spin-spin coupling.

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## REVIEW -2 Implications for the observed spectrum

pg 3

$$gH = \frac{h\nu_o}{\beta_e}$$

known  $g$ -value standard such as dpph  $g=2.0037 \pm 0.0002$

$$g_x = \frac{g_{std} H_{std}}{H_x}$$

Distortion due to excessive field modulation amplitude

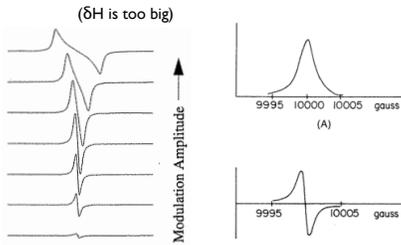


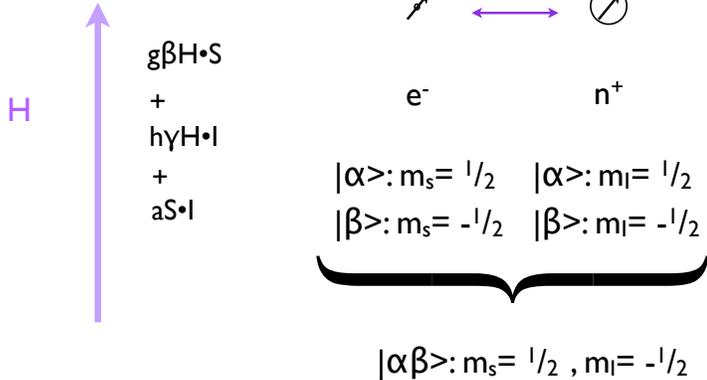
Fig. 2.15, Bruker EPR manual.

Fig. 9.4, Drago 1992

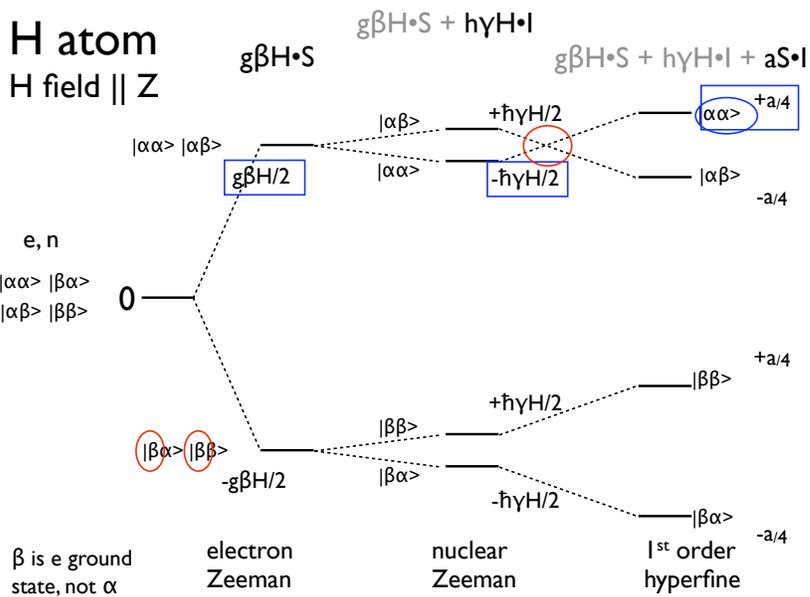
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Hyperfine coupling:  
simplest case = 1 electron interacting with one proton.

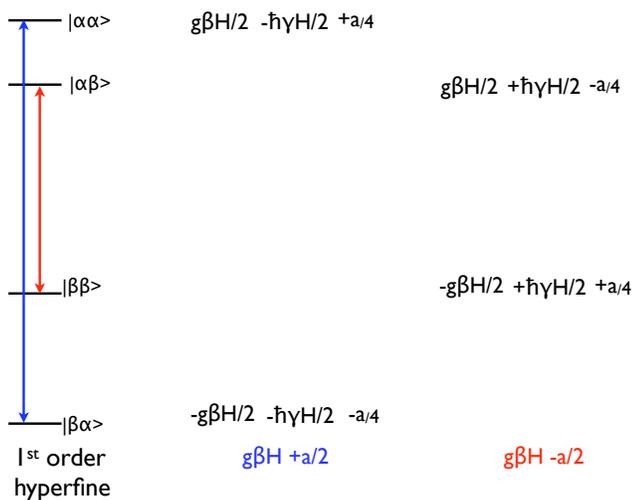
# H atom (what else ?)



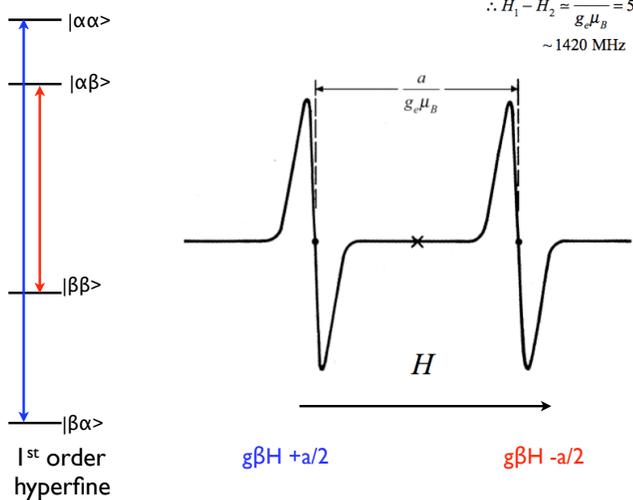
## H atom H field || Z



$$g\beta H \cdot S + \hbar\gamma H \cdot I + aS \cdot I$$



$$g\beta H \cdot S + \hbar\gamma H \cdot I + aS \cdot I$$



$$g_e \mu_B H_1 + \frac{a}{2} = g_e \mu_B H_2 - \frac{a}{2}$$

$$\therefore H_1 - H_2 = \frac{a}{g_e \mu_B} = 506.7 \text{ G}$$

$$\sim 1420 \text{ MHz}$$

A number of proxies are used (misused) for energy

$1/\lambda$	$c/\lambda = \nu$	$\text{cm}^{-1} \times 2.99793 \times 10^{10} \text{ cm/s} = \text{Hz}$ or $\text{cm}^{-1} \times 29.9793 \text{ cm/ns} = \text{GHz}$
$\nu$	$\nu \cdot h = \epsilon$	$\text{Hz} \times 6.63 \times 10^{-34} \text{ Js} \times (6.2 \times 10^{23} \text{ mole}^{-1}) = \text{J/mole}$ $\text{Hz} \times 4.1 \times 10^{-10} \text{ Js/mole}^{-1} = \text{J/mole}$
$H$	$g\beta H/h = \nu$	$\text{G} \times 2.8 \times 10^6 \text{ G}^{-1} \text{ s}^{-1} = \text{Hz}$ for a free electron
	$g\beta H = \epsilon$	$\text{G} \times 2.8 \times 10^6 \text{ G}^{-1} \text{ s}^{-1} \times 6.63 \times 10^{-34} \text{ Js} \times (6.2 \times 10^{23} \text{ mole}^{-1}) = \text{Hz}$ $\text{G} \times 1.15 = \text{mJ/mol}$ <b>for a free electron</b>

For signals where  $g' \neq g_e$ , use the experimental value for  $g'$ .

Coming clean on symbols, too

Magnetic field in a vacuum:  $B$  (magnetic induction)

Magnetic field in a material:  $H$

Bohr magneton =  $\beta_e = \frac{e\hbar}{2mc} = \beta_e = \mu_B$  (I have used  $\beta$ )

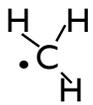
$B = \mu H$  where  $\mu$  is the permeability of a material and  $H$  is the 'auxiliary' magnetic field (in the material). In cgs  $\mu$  is close to 1, and dimensionless. G is cgs, T is SI.

Beware of conversions.

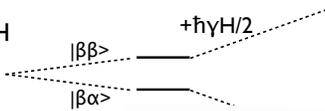
$B = H + 4\pi M$ ,  $M$  is density of magnetization.

Boltzmann's constant  $\beta = k_B$

## Methyl Radical



One H



Three H

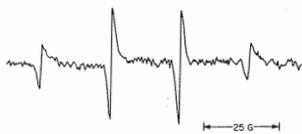
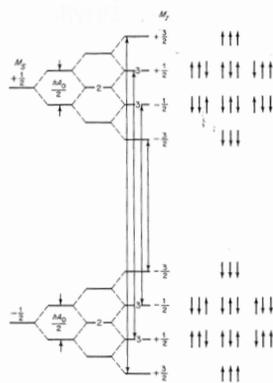
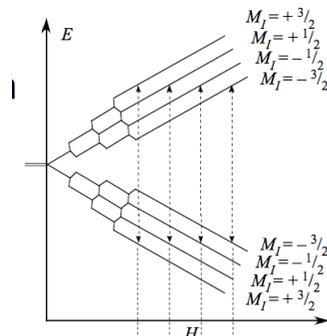
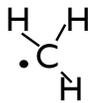


Fig. 4-5 ESR spectrum of the methyl radical ( $\text{CH}_3$ ) at 25°C in aqueous solution. (Spectrum kindly supplied by Mr. Frics Dravnieks.)

Fig 4.2, 4.5 Wertz & Bolton



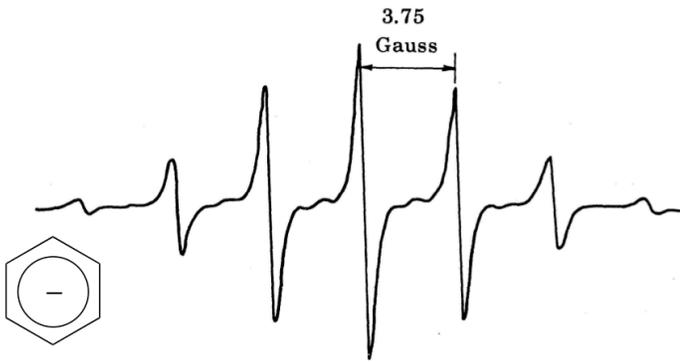
## Methyl Radical



$m_s = -1/2$  manifold is the mirror image of the  $m_s = +1/2$  one, due to the hyperfine interaction's effect.

Fig. 4.9 ESR spectrum of the methyl radical ( $\text{CH}_3$ ) at 25°C in aqueous solution. (Spectrum kindly supplied by Mr. Frics Dravnieks.)

# Benzene Radical Anion



Analysis via Pascal's triangle for identical  $I=1/2$  nuclei  
 one two three four five six  
 1:1 1:2:1 1:3:3:1 1:4:6:4:1 1:5:10:10:5:1 1:6:15:20:15:6

# Butadiene Radical Anion

Five 1:2:1 triplets in accordance with Hückel theory

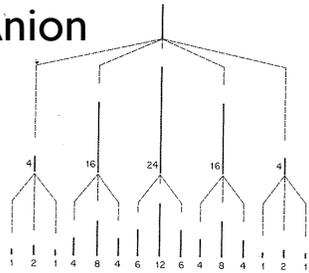
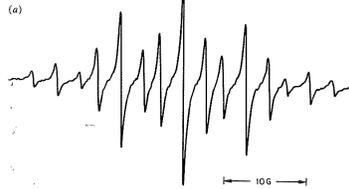


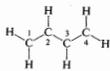
Fig. 4-13 (a) ESR spectrum of the butadiene anion in liquid  $\text{NH}_3$ . [Spectrum kindly supplied by Professor R. J. Myers. See D. H. Levy and R. J. Myers, *J. Chem. Phys.*, **41**:1062 (1964).] (b) Reconstruction of the ESR spectrum of butadiene anion.



W&B 4.13

# Butadiene Radical Anion

Table 5-1 Molecular orbitals and energies of butadiene



$$\begin{aligned} \psi_4 &= 0.371\phi_1 - 0.600\phi_2 + 0.600\phi_3 - 0.371\phi_4; W_4 = \alpha - \left(\frac{\sqrt{5}+1}{2}\right)\beta \\ \psi_3 &= 0.600\phi_1 - 0.371\phi_2 - 0.371\phi_3 + 0.600\phi_4; W_3 = \alpha - \left(\frac{\sqrt{5}-1}{2}\right)\beta \\ \psi_2 &= 0.600\phi_1 + 0.371\phi_2 - 0.371\phi_3 - 0.600\phi_4; W_2 = \alpha + \left(\frac{\sqrt{5}-1}{2}\right)\beta \\ \psi_1 &= 0.371\phi_1 + 0.600\phi_2 + 0.600\phi_3 + 0.371\phi_4; W_1 = \alpha + \left(\frac{\sqrt{5}+1}{2}\right)\beta \end{aligned}$$

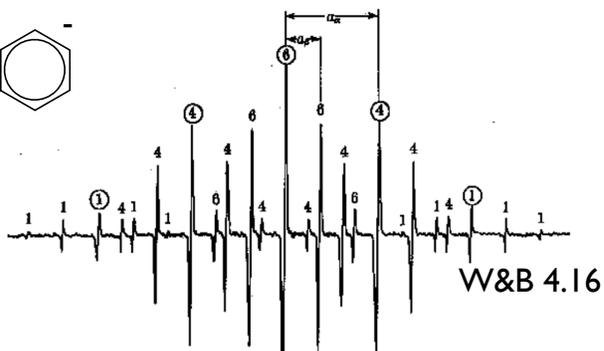
W&B T5.1

Five 1:2:1 triplets in accordance with Hückel theory

Table 5.1 indicates electron densities of the unpaired  $e^-$  of  $\rho_e = 0.36$  for C1 and C4,  $\rho_e = 0.14$  for C2 and C3.

$0.36/0.14 = 2.57$  and the ratio of  $a_1/a_2 = 2.73$ . Thus a scales with  $\rho_e$ .  $a=Q\rho$ , Q is on the order of -20 to -30 G (H. McConnell) (depending on the type of hydrocarbon).

# Naphthalene Radical Anion



$a_1 = 4.90 \text{ G}$     $a_2 = 1.83 \text{ G}$

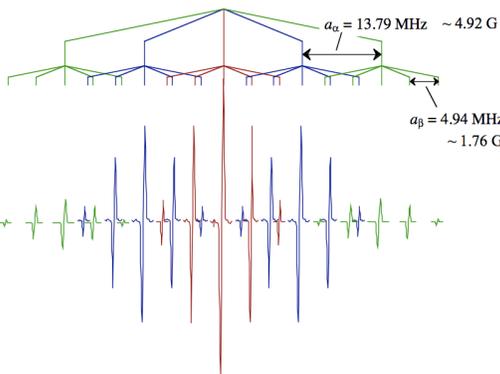
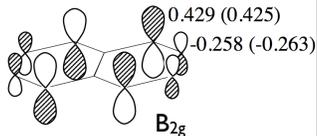
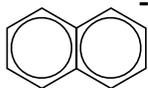
$(n+1)(m+1)$  lines total,  $n$  and  $m$  are the number of each type of H.

Manifolds of  $a_2$  structure from different branches of  $a_1$  may cross.

The separation between the two outer-most lines is the smallest hyperfine splitting.

When one  $a$  is an integer multiple of another, lines will overlay, unexpected intensities will result and the number of lines will be smaller than expected. SIMULATE

# Naphthalene Radical Anion



Coefficients from EPR  
(vs. Hückel)

$.429^2 = .184$ ,  $.258^2 = .067$

# Anthracene Radical Anion

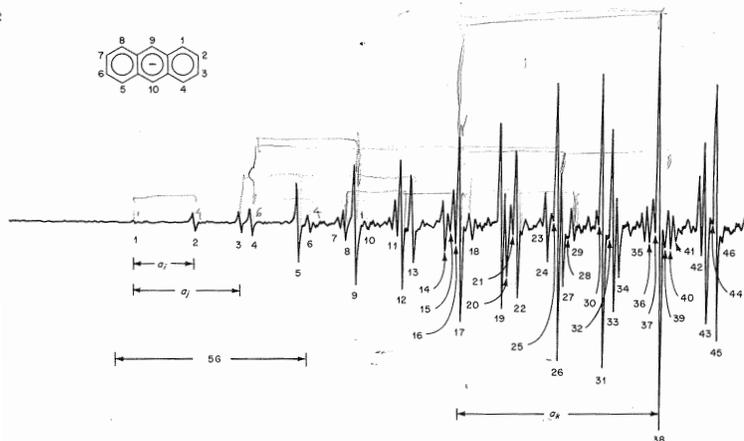
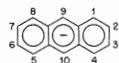


Fig. 4-17 Low-field portion of the ESR spectrum of the anthracene anion. Proton hyperfine lines are numbered; unnumbered lines arise from  $^{13}\text{C}$  splittings. The three proton splitting constants are indicated.

W&B 4.17

# Higher Acene Radicals

Benzene

3.75 G

Naphthalene



1  
2

4.92

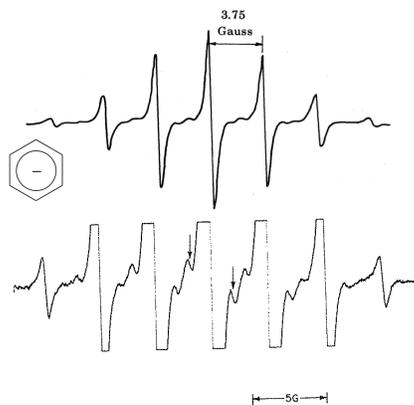
1.76

Table 5-5 Hyperfine splittings in polyacene ions

Molecule	Position	$a_+$ , G	$a_-$ , G
	9	6.53	5.34
	1	3.06	2.74
	2	1.38	1.51
	5	5.05	4.23
	1	1.69	1.54
	2	1.03	1.16
	6	5.08	4.26
	5	3.55	3.03
	1	0.98	0.92
	2	0.76	0.87

W&B T5.5

Hyperfine from other nuclei: natural abundance  $^{13}\text{C}$

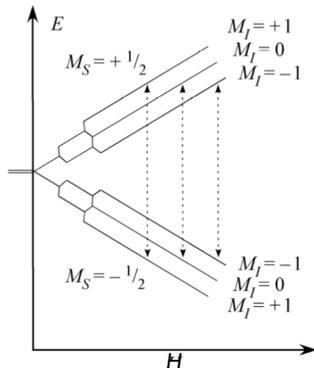
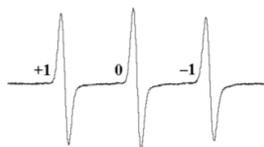
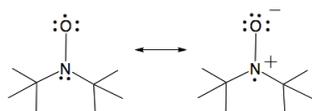


W&B 4.22

$^{13}\text{C}$  satellites have intensity  $6 \times 0.55\% = .033$

$^{14}\text{N}$ ,  $I=1$ :  $m_I = -1, 0, 1$

Split into three lines, but 1:1:1, NOT 1:2:1.  
Three lines because  $3 = 2I + 1$



Why we care about the hyperfine couplings:

$$a = Q\rho_e$$

McConnell's relation says that the coupling to an H is proportional to the unpaired electron density at the C position at which the H is attached. The hyperfine couplings map out electron density distribution of the singly occupied orbital. Moreover this is usually a frontier orbital and therefore directly related to reactivity.

$$a = Q\rho_e,$$

Q is on the order of -20 to -30 G (depending on the type of hydrocarbon).

Thus,  $^1\text{H}$  hyperfine couplings map out the distribution and emphasis of the SOMO.

Knowing which sites have the large 'a' values can tell you which sites are the ones with the most unpaired e density (donors, nucleophiles).

Sites with the smallest hyperfine couplings will be best able to accept electron density.

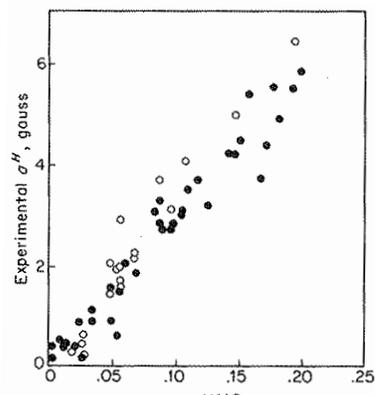


Fig. 5-4 Proton hyperfine splittings vs. HMO unpaired electron densities for a group of aromatic hydrocarbon radical ions. Open circles refer to positive ions and full circles to negative ions. [Taken from I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, 43:2712 (1965).]