Proposed topics

-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

**Information content in $g$**

\[
\epsilon = -\mu \cdot \vec{B} \quad \quad \epsilon = g\beta m_B = \pm g\beta B_o / 2
\]

\[
\Delta \epsilon = h\nu = g\beta H_o
\]

For a free electron, 

\[
g_e = 2.00232
\]

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.

**Implications for the observed spectrum**

\[
gH = \frac{h\nu}{\beta_e}
\]

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

\[
g_x = \frac{g_{\text{add}} H_{\text{add}}}{H_x}
\]

Distortion due to excessive field modulation amplitude

Fig. 2.15, Bruker EPR manual.

Fig. 9.4, Drago 1992
Hyperfine coupling:
simplest case = 1 electron interacting with one proton.

H atom (what else ?)

$|\alpha>: m_s = \frac{1}{2}, |\alpha>: m_l = \frac{1}{2}$

$|\beta>: m_s = -\frac{1}{2}, |\beta>: m_l = -\frac{1}{2}$

$|\alpha\beta>: m_s = \frac{1}{2}, m_l = -\frac{1}{2}$
A number of proxies are used (misused) for energy

\[
\lambda = \frac{c}{\nu}, \quad \frac{c}{\lambda} = \nu
\]

\[
\nu \times h = \varepsilon
\]

\[
H \times g \beta H/h = \nu
\]

\[
g \beta H = \varepsilon
\]

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 = \( \beta = \frac{e\hbar}{2mc} = \beta_e = \mu_B \) (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 \( \beta = k_B \)

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**Methyl Radical**

One H

\( |\beta\beta\rangle \)

\( +\hbar H/2 \)

Three H

\( m_s=\pm \frac{1}{2} \) manifold is the mirror image of the \( m_s=\pm \frac{1}{2} \) one, due to the hyperfine interaction's effect.
Benzene Radical Anion

Analysis via Pascal's triangle for identical I=1/2 nuclei

<table>
<thead>
<tr>
<th>one</th>
<th>two</th>
<th>three</th>
<th>four</th>
<th>five</th>
<th>six</th>
</tr>
</thead>
</table>

Butadiene Radical Anion

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 $\rho_e$.

$\alpha = Q \rho$, Q is on the order of -20 to -30 G (H. McConnell) (depending on the type of hydrocarbon).
Naphthalene Radical Anion

\[ a_1 = 4.90 \text{ G} \quad a_2 = 1.83 \text{ G} \]

(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

\[ a_1 = 13.79 \text{ MHz} \quad a_2 = 4.92 \text{ G} \]

Coefficients from EPR (vs. Hückel):

\[ B_{2g} = 0.429 (0.425) \quad B_{5g} = -0.258 (-0.263) \]

Anthracene Radical Anion

\[ a_1 = 1.429 \text{ G} \quad a_2 = .184, .258^2 = .067 \]
Higher Acene Radicals

Benzene

Naphthalene

<table>
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<tr>
<th>Molecule</th>
<th>Position</th>
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<th>$a_{H^2}$, G</th>
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</table>

W&B T5.5

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

$^{13}$C satellites have intensity $6 \times 0.55\% = 0.33$

W&B 4.22

$^{14}$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, '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 J. C. Lewis and L. S. Singer, J. Chem. Phys., 43, 2712 (1965).]