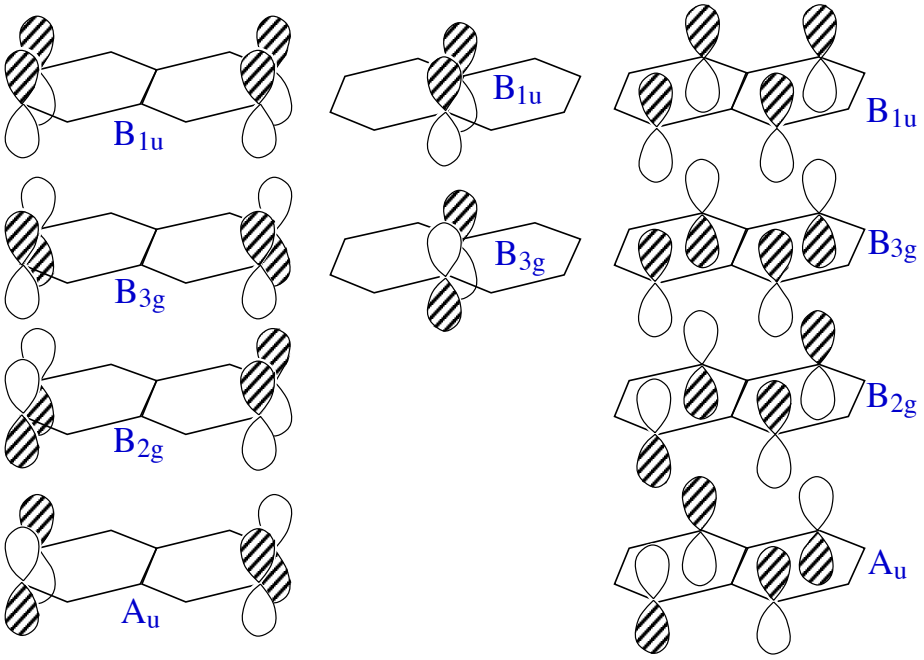
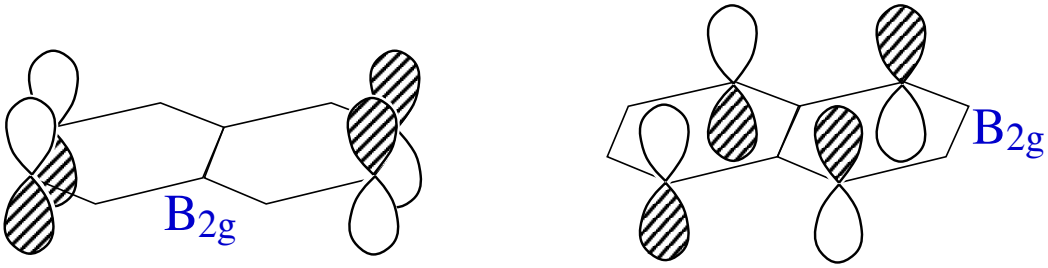
Naphthalene π-Orbital SALCs



Naphthalene B_{2g} SALCs



$$\Phi_1 = \frac{1}{2}\left(\chi_2 + \chi_3 - \chi_6 - \chi_7\right) \qquad \Phi_2 = \frac{1}{2}\left(\chi_1 + \chi_4 - \chi_5 - \chi_8\right)$$

Note: Cotton makes a sign error on p. 173

$$\begin{bmatrix} \alpha + \beta - E_\mu & \beta \\ \beta & \alpha - E_\mu \end{bmatrix} \begin{bmatrix} c_{1\mu} \\ c_{2\mu} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

B_{2g} orbital energies

$$\Phi_1=\frac{1}{2}(\chi_2+\chi_3-\chi_6-\chi_7) \qquad \Phi_2=\frac{1}{2}(\chi_1+\chi_4-\chi_5-\chi_8)$$

$$\begin{vmatrix} \alpha+\beta-E_\mu & \beta \\ \beta & \alpha-E_\mu \end{vmatrix}=0 \quad \Rightarrow \quad E_\mu^2-\beta E_\mu-\beta^2=0$$

(take $\alpha = 0$ - sets the energy zero)

$$E_{bonding}=\frac{\sqrt{5}+1}{2}\beta; \quad E_{antibonding}=\frac{1-\sqrt{5}}{2}\beta$$

MO coefficients? Plug each energy back into the secular eqn:

eg., for antibonding orb.: $\begin{bmatrix} \beta-\frac{1-\sqrt{5}}{2}\beta & \beta \\ \beta & -\frac{1-\sqrt{5}}{2}\beta \end{bmatrix}\begin{bmatrix} c_{1\mu} \\ c_{2\mu} \end{bmatrix}=\begin{bmatrix} 0 \\ 0 \end{bmatrix}$

B_{2g} orbital energies, cont.

For the antibonding orbital, the secular eqn.

yields two eqns with the same solution:

$$\frac{c_2}{c_1}=-\frac{\sqrt{5}+1}{2}$$

Normalization of $\psi_{\text{antibonding}}$ demands $c_1^2+c_2^2=1$

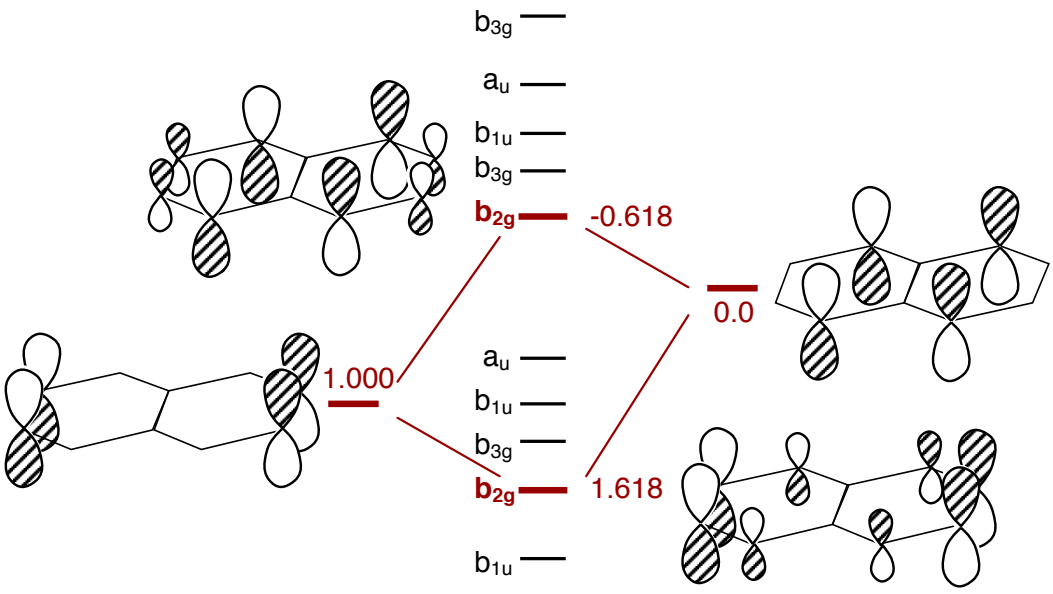
Solving: $c_1=\sqrt{\frac{2}{5+\sqrt{5}}}=0.5257$; $c_2=-0.8507$

Finally, we plug these into: $\psi_{\text{antibonding}}=c_1\Phi_1+c_2\Phi_2$

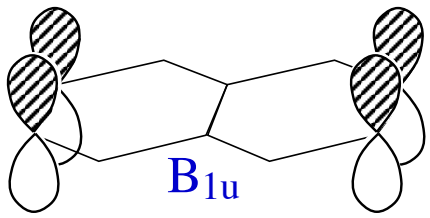
$$\Phi_1=\frac{1}{2}(\chi_2+\chi_3-\chi_6-\chi_7) \qquad \Phi_2=\frac{1}{2}(\chi_1+\chi_4-\chi_5-\chi_8)$$

$$\psi_{\text{antibonding}}=0.2629(\chi_2+\chi_3-\chi_6-\chi_7)$$
$$-0.4253(\chi_1+\chi_4-\chi_5-\chi_8)$$

B_{2g} π Orbital Energies

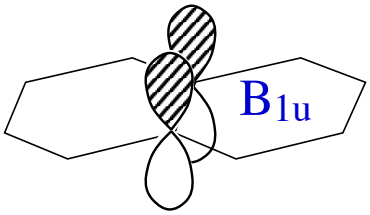


Naphthalene B_{1u} SALCS

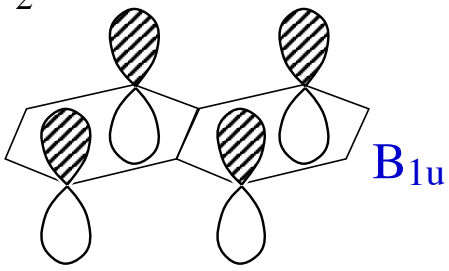


$$\Phi_1 = \frac{1}{2}(\chi_2 + \chi_3 + \chi_6 + \chi_7)$$

$$\Phi_2 = \sqrt{\frac{1}{2}}(\chi_9 + \chi_{10})$$



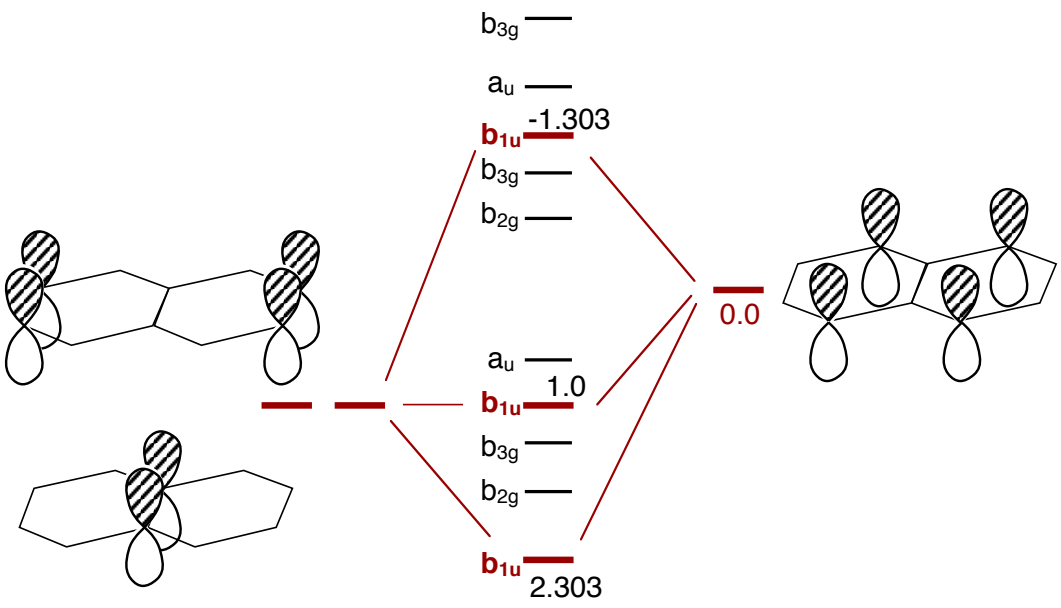
$$\Phi_3 = \frac{1}{2}(\chi_1 + \chi_4 + \chi_5 + \chi_8)$$



B_{1u} Secular Equation

$$\begin{bmatrix} \alpha+\beta-E_\mu & 0 & \beta \\ 0 & \alpha+\beta-E_\mu & \sqrt{2}\beta \\ \beta & \sqrt{2}\beta & \alpha-E_\mu \end{bmatrix} \begin{bmatrix} c_{1\mu} \\ c_{2\mu} \\ c_{3\mu} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

B_{1u} π Orbital Energies



What is ESR (EPR)?

- ESR is the electron-spin analog of NMR.
- For a given applied field strength, ESR transitions occur at ~2000 times higher energy than NMR ($\mu_B/\mu_N = m_p/m_e = 1836.15$)
- Hyperfine splittings of ESR transitions arise from the interaction of the nuclear spins on electron spin transition energy.

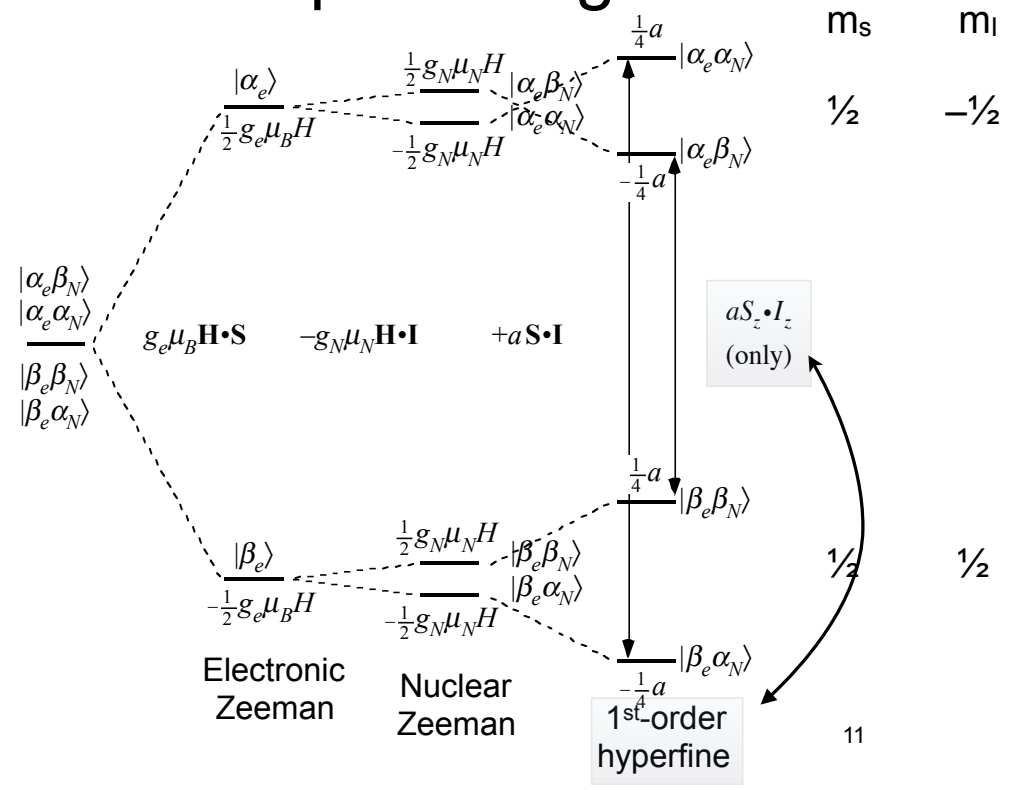
H-atom Spin Hamiltonian

$$\mathcal{H}_{\text{Spin}} = g_e\mu_B\mathbf{H}\bullet\mathbf{S} - g_N\mu_N\mathbf{H}\bullet\mathbf{I} + a\mathbf{S}\bullet\mathbf{I}$$

$$a = \frac{8\pi}{3} g_e\mu_B g_N\mu_N \left|\psi(0)\right|^2$$

- 1st term: electronic Zeeman
- 2nd term: nuclear Zeeman
- 3rd term: Fermi Contact hyperfine (isotropic) – magnitude depends on the electron density of the unpaired electron on the nucleus, $\psi(0)$.

H-atom Spin Energies



$$h\nu_1 = h\nu_2$$

$$E(\alpha_e\alpha_N) - E(\beta_e\alpha_N) = E(\alpha_e\beta_N) - E(\beta_e\beta_N)$$

$$\left(\frac{1}{2}g_e\mu_B H_1 - \frac{1}{2}g_N\mu_N H_1 + \frac{a}{4}\right) - \left(-\frac{1}{2}g_e\mu_B H_1 - \frac{1}{2}g_N\mu_N H_1 - \frac{a}{4}\right)$$

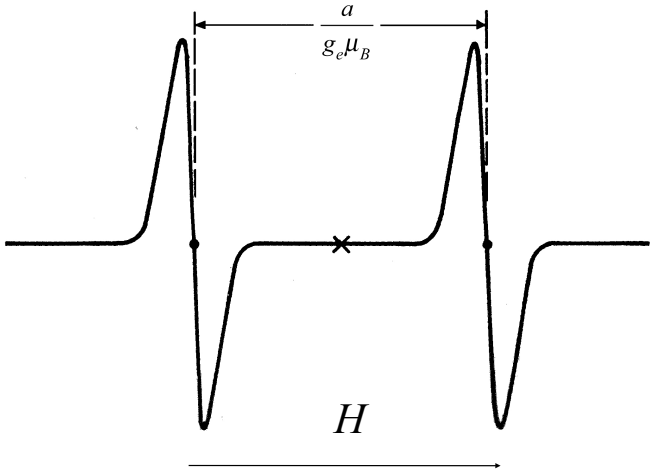
$$= \left(\frac{1}{2}g_e\mu_B H_2 + \frac{1}{2}g_N\mu_N H_2 - \frac{a}{4}\right) - \left(-\frac{1}{2}g_e\mu_B H_2 + \frac{1}{2}g_N\mu_N H_2 + \frac{a}{4}\right)$$

(neglects 2nd-order hyperfine)

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

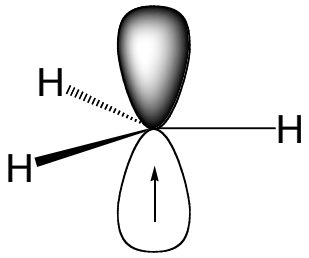
$$\therefore H_1 - H_2 \simeq \frac{a}{g_e\mu_B} = 506.7 \text{ G}$$

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



H-atom Spectrum

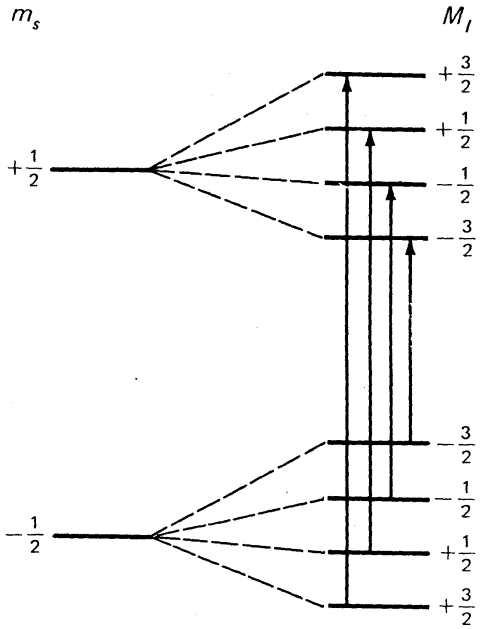
Hyperfine spitting in $CH_3^{\bullet}$



- Origin of proton hyperfine interaction: ***Configuration interaction*** must be accounted for, because at the orbital level π electrons have zero probability at the H-atom nuclei.
- Get a quartet signal due to hyperfine splitting of three ^1H (spin-1/2) nuclei.

Methyl radical splitting diagram

- The four transitions for the methyl radical. $+m_I$ states are lowest for $m_s = -1/2$ and the $-m_I$ state lowest for $m_s = 1/2$, from the **I•S** term.



From Drago, "Physical Methods…" - Fig. 9-7 – corrected.

Methyl radical splitting diagram

- The four transitions for the methyl radical. $+m_I$ states are lowest for $m_s = -1/2$ and the $-m_I$ state lowest for $m_s = 1/2$, from the **I•S** term.

Plotted to reflect the constant-frequency experimental conditions.

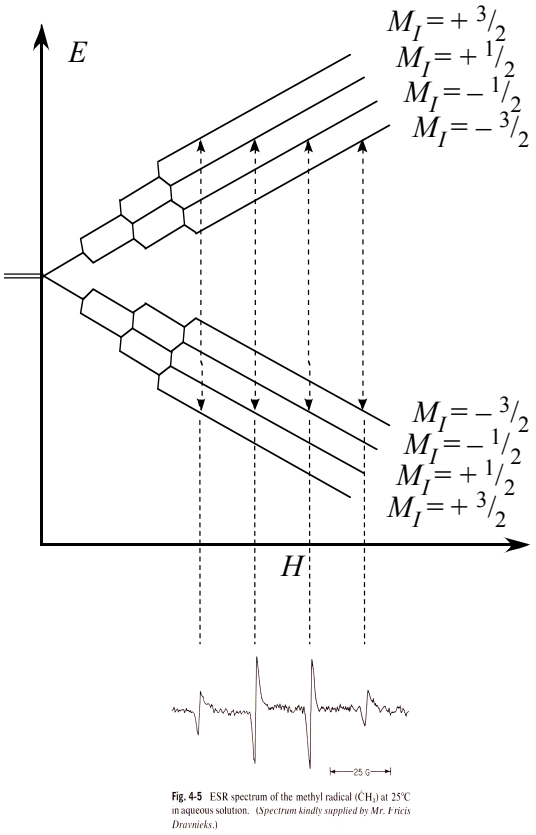
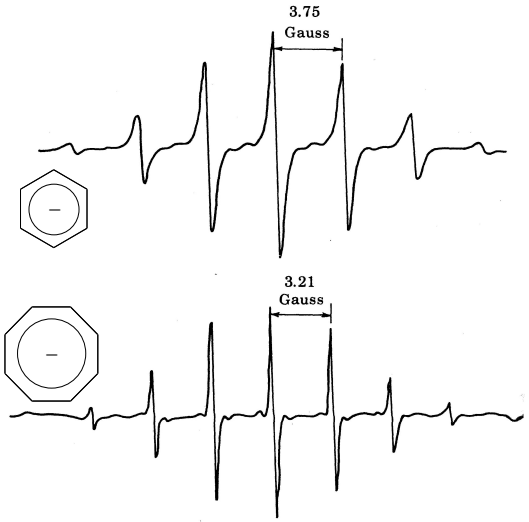
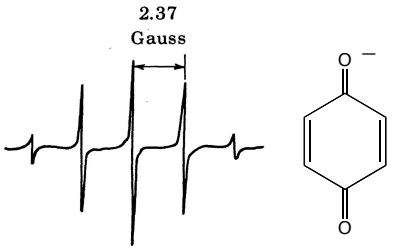


Fig. 4-5 ESR spectrum of the methyl radical ($\dot{C}H_3$) at 25°C in aqueous solution. (*Spectrum kindly supplied by Mr. Fricis Druvnieks.*)

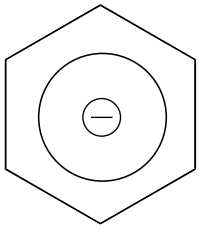
Organic π Radicals

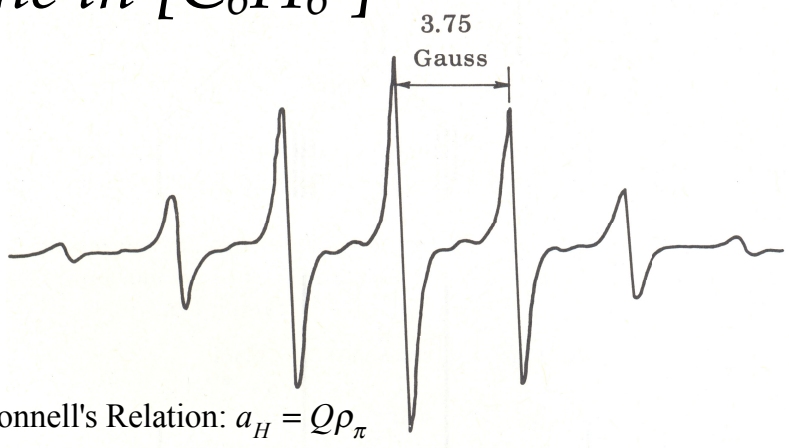




$$a_H = Q\rho_H \;;\; Q \simeq 22.5 \text{ G}$$

Hyperfine in $[C_6H_6^{\bullet}]^-$





McConnell's Relation: $a_H = Q\rho_\pi$

ρ_π is the π electron spin-density on the adjacent carbon,

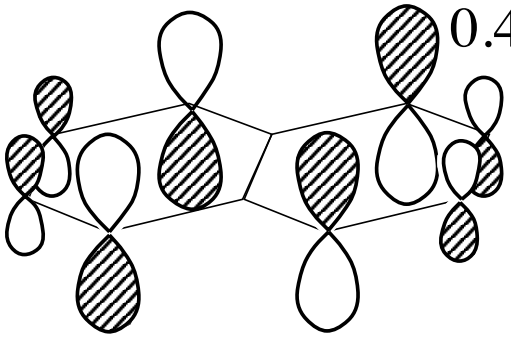
a_H is the measured hyperfine coupling constant for a given proton

$Q \simeq$ -22.5 gauss, is a proportionality constant

- Get a septet signal due to hyperfine splitting of six ^1H (spin-1/2) nuclei.

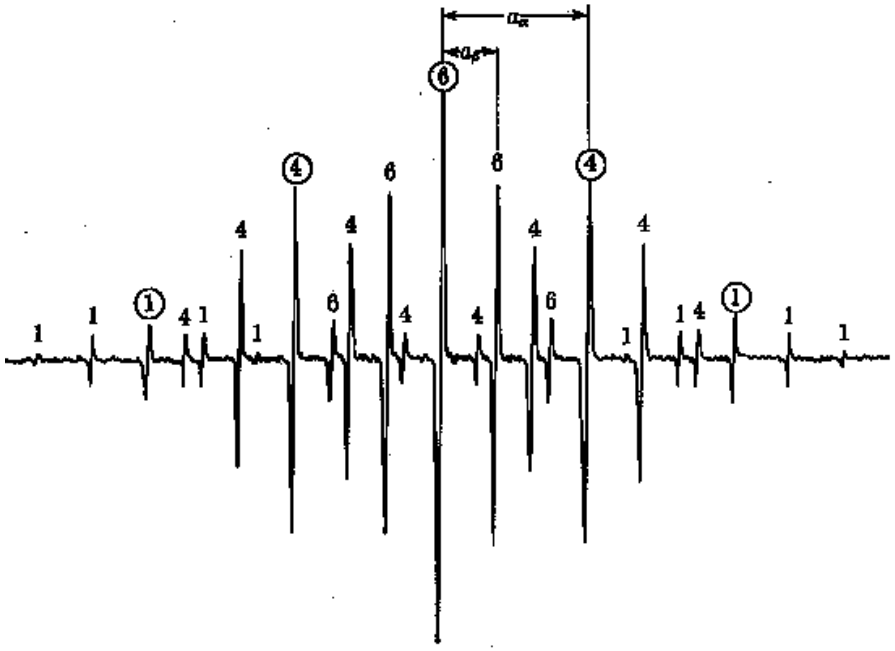
Naphthalide Anion - SOMO

B_{2g}

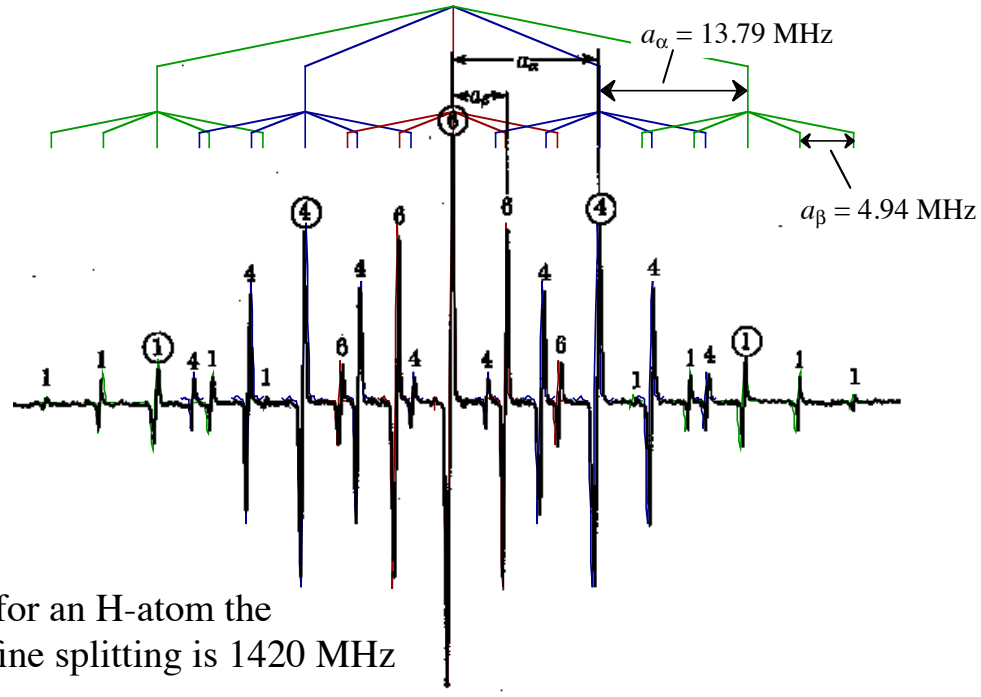


Numbers are coefficients from ESR (Hückel)

ESR Spectrum: Naphthalide Anion



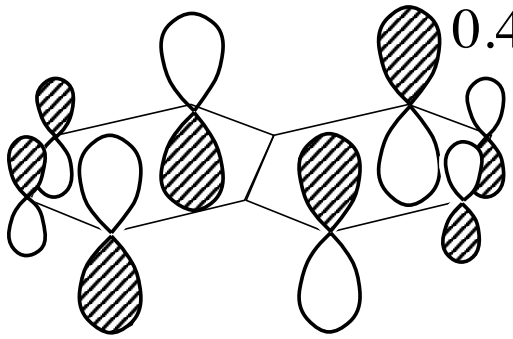
ESR Spectrum: Naphthalide Anion



Note: for an H-atom the hyperfine splitting is 1420 MHz

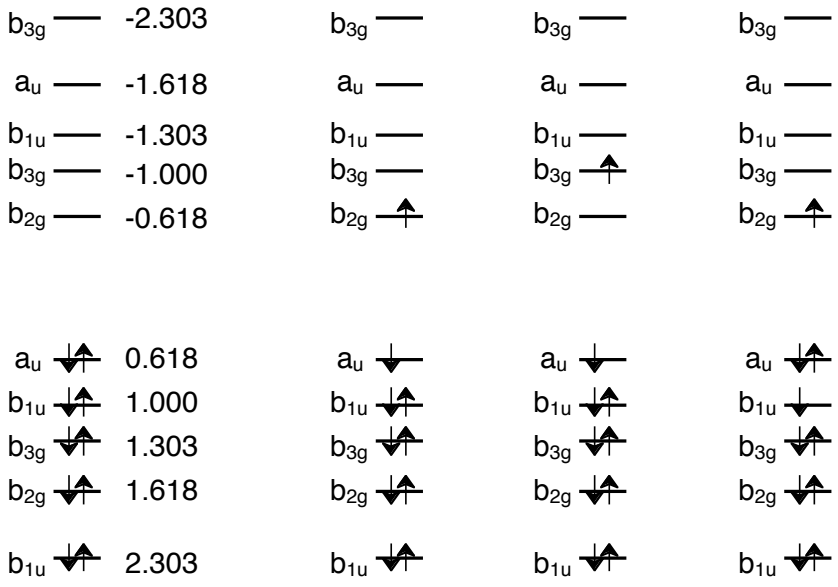
Naphthalide Anion - SOMO

B_{2g}

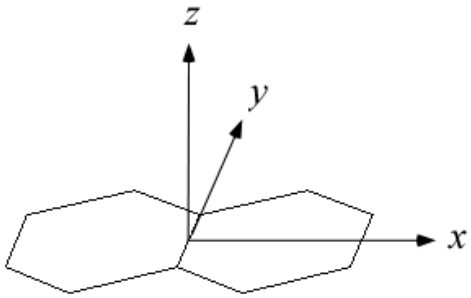


Numbers are coefficients from ESR (Hückel)

Naphthalene MO Energies & Excited States

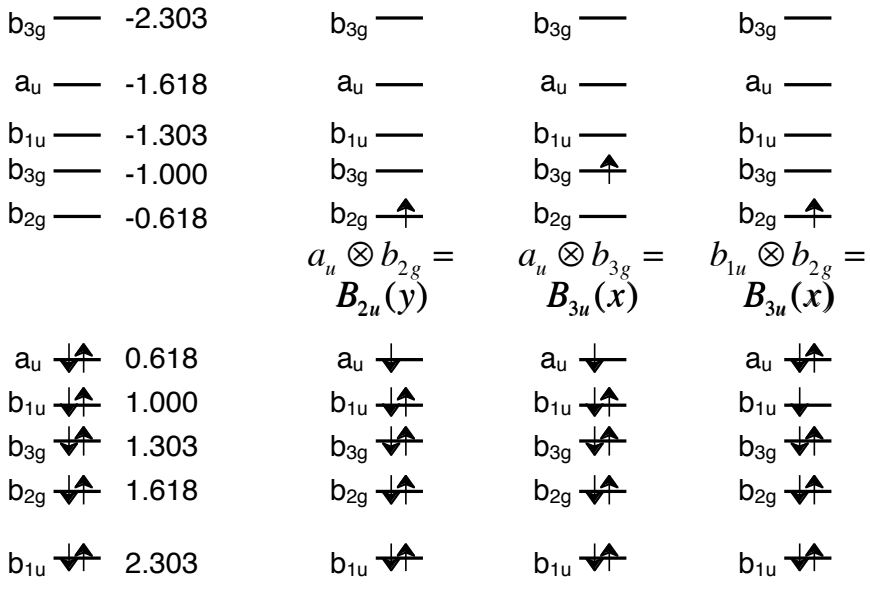


D_{2h} Character Table

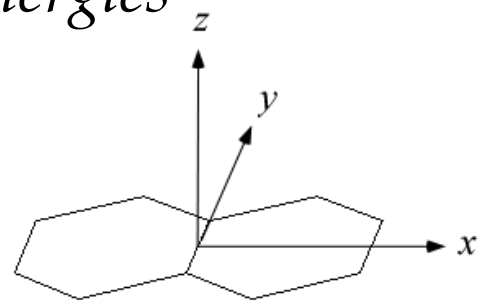


D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

Naphthalene MO Energies & Excited States



Observed Transition Energies



Electronic Transitions - Naphthalene		
E(cm^{-1})	Polarization	Assignment
31,800	Long axis (x)	$^1A_{1g} \longrightarrow {}^1B_{3u}$
34,700	Short Axis (y)	$^1A_{1g} \longrightarrow {}^1B_{2u}$
45,200	Long Axis (x)	$^1A_{1g} \longrightarrow {}^1B_{3u}$