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HYPERFINE SPLITTING IN AROMATIC FREE RADICALS

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The hyperfine structure of the ESR spectra of free radicals is a property of the system of electrons and nuclei which constitute the molecule. It arises from the energy of interaction of the unpaired electrons and nuclear spins which is of the form

$$E_{hf} = \underset{\sim}{I} \cdot \underset{\sim}{T} \cdot \underset{\sim}{J}$$

where $\underset{\sim}{T}$ is a tensor of second rank, $\underset{\sim}{I}$ is the nuclear spin and $\underset{\sim}{J}$ the total electron angular momentum. In other words, a nucleus of spin $\underset{\sim}{I}\hbar$ serves as a probe to the electronic structure of a complex molecular free radical. The measurement of this coupling energy is in general of prime importance, because it permits the direct determination of the electron densities, and its theoretical analysis has therefore received a considerable amount of attention in the literature.

In particular, it is not uncommon for the ESR spectra of free radicals in solutions to possess a hyperfine structure, as shown in Fig. 1 for the p-benzosenicquinone ion and for which the radiation induced transitions in the Paschen-Back high field approximation are governed by the Bohr relationship:

$$h\omega = h\omega_0 + \sum_n A_n I_n^z + \gamma n/h\, I_n^z H^z \;,\; I_n^z = I_n, I_n-1, \text{---} I_n$$

$h\omega_0$ is the energy difference between the electronic Zeeman levels in the absence of the hyperfine interaction and A_n is a constant characteristic of the free radical and the nucleus n, of gyromagnetic ratio γ_n. H^z is the applied external magnetic field. In the aromatic π-electron free radicals, the sigma bonded protons with spin $I = \frac{1}{2}$ are responsible for the observed structure. This experimental evidence has led therefore to the conclusion that the spin polarization is transmitted through a valence bond between the σ- and π-electrons which up to that time were considered as non interacting groups. Weissman[1] and McConnell[2] have brought forthe the idea that as originally proposed by Abragam Horowitz and Pryce[3] in their study of the hyperfine splitting of the ions of the transition metal series, this bonding can be explained in terms of a magnetic moment density matrix in which all the excited configurations contributing to the ground state through the correlation interaction between the two groups would have to be included. This approach, which has been successfully developed and applied to numerous cases in the literature, will now be given in some detail. Use will be made of the density matrix formalism developed by Löwdin[4] and McWeeney.[5]

The Density Matrix Formulation

The electronic system described by "Atoms in Molecules" is given, within the Born-Oppenheimer approximation,[6] in terms of a complete set of atomic orbitals under the restriction that the Pauli principle be obeyed. A directly measurable physicochemical property of this system Ω has then an expectation value,

$$< \Omega > = \int \psi (\underset{\sim}{x}) \Omega (\underset{\sim}{x}) \psi^{*} (\underset{\sim}{x}) d\underset{\sim}{x} \tag{2}$$

where $\Omega (\underset{\sim}{x})$ is a function associated with the observable, and $\psi (\underset{\sim}{x})$ is the wave function which describes the electronic state when $\underset{\sim}{x}$ spans the complete space and spin coordinates $(\underset{\sim}{r}, \underset{\sim}{s})$ of the N electrons $(\underset{\sim}{x} = \underset{\sim}{x}_1, \underset{\sim}{x}_2, \cdots \underset{\sim}{x}_N)$. $\psi (\underset{\sim}{x})$ is expressed, in general, as a superposition of configurations. Thus,

$$\psi (\underset{\sim}{x}) = \sum_K C_K \psi_K (\underset{\sim}{x}) \tag{3}$$

where each $\psi_K(\underset{\sim}{x})$ is given by the antisymmetrized product of the single particle molecular spin-orbitals $\psi_k(\underset{\sim}{x}_i)$, which are in turn linear combinations of the complete set of atomic orbitals $\phi(x_i)$:

$$\psi_k(\underset{\sim}{x}_i) = \sum_{\nu} T_{k\nu} \phi_\nu (\underset{\sim}{x}_i) = \underset{\sim}{T}_k^{+} \phi$$

or (4)

$$\underset{\sim}{\psi} = T^{+} \phi$$

where T is a square matrix which transforms the N-dimensional space of atomic orbitals $\underset{\sim}{\phi}$ into that of molecular orbitals $\underset{\sim}{\psi}$. The atomic orbitals are characterized by the fourfold symbol $\nu = (n, \ell, m, m_s)$, in such a manner that:

$$\phi_\nu (\underset{\sim}{x}) = R_n(r) Y_{\ell m}(\theta, \varphi) f_s(m_s) \tag{5}$$

where (r, θ, φ) are the spherical polar coordinates of the electron with respect to the nucleus ν. $R_n(r)$ depends only on the distance from ν and $Y_{\ell m}(\theta,\varphi)$ is a spherical harmonic, (see for instance Ref. (7) p. 57). Also, ℓ, the azimutal quantum number, indicates the irreducible representation of the spatial symmetry (s, p, d, ...), and m the particular component of the $2\ell + 1$ fold degenerate states of orbital angular momentum, while n, the principal quantum number distinguishes the various states with the same transformation property but with different energy. Finally the spin function f_s, is equal to α or β according to whether $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$.

The Ψ_K are given approximately by either one of the following two conventional expressions†: (see for instance Ref. (7), p. 232):

A. By the Slater-Pauling 'Valence Bond' (VB) Formula (8) (9):

$$\Psi_K = \underset{\sim}{\mathcal{R}}\, \underset{\sim}{\mathcal{A}}\, [\psi_{k1}(\underset{\sim}{x}_1)\bar{\psi}_{k2}(\underset{\sim}{x}_2)\cdots\bar{\psi}_{kN}(\underset{\sim}{x}_N)], = \frac{1}{\sqrt{2^n}} \sum_{\underset{\sim}{R}} (-1)^r\, \underset{\sim}{R}\, D_K \qquad (6a)$$

B. By the "Molecular Orbital" (MO) method developed by Hückel (10) and Mulliken (11):

$$\Psi_K = \underset{\sim}{\mathcal{A}}\, [\psi_{k1}(\underset{\sim}{x}_1)\bar{\psi}_{k2}(\underset{\sim}{x}_2)\cdots\bar{\psi}_{kN}(\underset{\sim}{x}_N)] = D_K, \{\underset{\sim}{\mathcal{A}} = \frac{1}{\sqrt{N!}} \sum_{\underset{\sim}{P}} (-1)^p\, \underset{\sim}{P}\} \qquad (6b)$$

where D_K is the Slater determinant

$$D_K = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k1}(1) & \bar{\psi}_{k2}(1) & --- & \bar{\psi}_{kn}(1) \\ \psi_{k1}(2) & \bar{\psi}_{k2}(2) & --- & \bar{\psi}_{kn}(2) \\ - - & - - & - & - - \\ \psi_{k1}(n) & \bar{\psi}_{k2}(n) & --- & \bar{\psi}_{kn}(n) \end{vmatrix} = ||\psi_{k1}\bar{\psi}_{k2} --- \bar{\psi}_{kn}||$$

The eigenvalue of the spin is indicated by a superscript, a bar for $m_s = -1/2$ and nothing for $m_s = +1/2$.

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† $\underset{\sim}{R}$ interchanges the spin in the n pairs of orbits which are bonded together and $\underset{\sim}{P}$ permutes the electrons among the spin-orbitals, with the corresponding parities r and p. The transformation $\underset{\sim}{T}$ in Eq. (4) in the valence bond, VB method is the unit matrix when hybrid orbitals have been taken into account.

The function $\underset{\sim}{\Omega}(\underset{\sim}{x})$ is in general expanded in terms of zero, one, two, etc. particle operators:

$$\underset{\sim}{\Omega}(\underset{\sim}{x}) = \underset{\sim}{\Omega}_0 + \sum_i \underset{\sim}{\Omega}_1(\underset{\sim}{x}_i) + \frac{1}{2} \sum_{i\,j}{}' \underset{\sim}{\Omega}_2(\underset{\sim}{x}_i, \underset{\sim}{x}_j) + \cdots \tag{7}$$

and according to Eq. (2) its expectation value is:

$$\begin{aligned} \langle \Omega \rangle = \Omega_0 &+ \int [\underset{\sim}{\Omega}_1(\underset{\sim}{x}_1)\, \rho_1(\underset{\sim}{x}_1, \underset{\sim}{x}_1)]_{\underset{\sim}{x}_1 = \underset{\sim}{x}_1}\, d\underset{\sim}{x}_1 \\ &+ \frac{1}{2} \int [\underset{\sim}{\Omega}_2(\underset{\sim}{x}_1, \underset{\sim}{x}_2)\, \rho_2(\underset{\sim}{x}_1, \underset{\sim}{x}_2; \underset{\sim}{x}_1, \underset{\sim}{x}_2)]_{\substack{\underset{\sim}{x}_1 = \underset{\sim}{x}_1 \\ \underset{\sim}{x}_2 = \underset{\sim}{x}_2}}\, d\underset{\sim}{x}_1\, d\underset{\sim}{x}_2 \\ &+ \cdots \end{aligned} \tag{8}$$

where the operation inside the bracket is carried out before the prime sign is eliminated. Here $\rho_1, \rho_2 \ldots \rho_N$ are defined as the one, two, etc. electron density matrices

$$\rho_1(\underset{\sim}{x}_1; \underset{\sim}{x}_1) = N! \int (\underset{\sim}{x}_1, \underset{\sim}{x}_2, \cdots \underset{\sim}{x}_N)\, \psi^*(\underset{\sim}{x}_1, \underset{\sim}{x}_2, \cdots \underset{\sim}{x}_N)(d\underset{\sim}{x}_{\ldots})$$

$$\rho_2(\underset{\sim}{x}_1, \underset{\sim}{x}_2; \underset{\sim}{x}_1, \underset{\sim}{x}_2) = \frac{N!}{(N-2)!} \int \psi(\underset{\sim}{x}_1, \underset{\sim}{x}_2, \cdots \underset{\sim}{x}_N)\, \psi^*(\underset{\sim}{x}_1, \underset{\sim}{x}_2, \cdots \underset{\sim}{x}_N)(d\underset{\sim}{x}_{12})$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\rho_N(\underset{\sim}{x}_1, \underset{\sim}{x}_2, \cdots \underset{\sim}{x}_N; \underset{\sim}{x}_1, \underset{\sim}{x}_2, \cdots \underset{\sim}{x}_N) = N\ \psi(\underset{\sim}{x}_1, \underset{\sim}{x}_2, \cdots \underset{\sim}{x}_N)\, \psi^*(\underset{\sim}{x}_1, \underset{\sim}{x}_2, \cdots \underset{\sim}{x}_N)$$

and

$$d\underset{\sim}{x} = (d\underset{\sim}{x}_1)\, d\underset{\sim}{x} = (d\underset{\sim}{x}_{12})\, d\underset{\sim}{x}_1\, d\underset{\sim}{x}_2, \cdots \tag{9}$$

The importance of the density matrix is due to the physical significance of the diagonal elements. Thus:

$\rho_1(\underset{\sim}{x}_1; \underset{\sim}{x}_1)\, d\underset{\sim}{r}_1$ = number of particles in the system multiplied by the probability of finding one within the volume element $d\underset{\sim}{r}_1$, centered about $\underset{\sim}{x}_1$.

$\rho_2(\underset{\sim}{x}_1, \underset{\sim}{x}_2; \underset{\sim}{x}_1', \underset{\sim}{x}_2')\, d\underset{\sim}{r}_1\, d\underset{\sim}{r}_2$ = 2 x number of pairs in the system multiplied by the probability of simultaneously finding one particle in each of the volume elements $d\underset{\sim}{r}_1$ and $d\underset{\sim}{r}_2$ centered about $\underset{\sim}{x}_1$ and $\underset{\sim}{x}_2$, respectively.

According to Eq. (3) then:

$$\rho_r(1,2,\cdots n|1',2',\cdots n') = \Sigma\, \rho_{K\lambda}\, \rho_n(K\lambda|1,2,\cdots n;\, 1',2',\cdots n') \tag{9}$$

where

$$\rho_{K\lambda} = C_K\, C_\lambda^*$$

$$\rho_n(1,2,\cdots n|1',2',\cdots n') =$$

$$\frac{N!}{(N-n)!} \int \Psi_K(1,2,\cdots n,\cdots N)\, \Psi^*(1',2',\cdots n',\cdots N)(d\underset{\sim}{x}_n')$$

with the relationship between successive density matrices:

$$(N-n)\rho_n(1,2,\cdots n|1',2',\cdots n') =$$

$$\int \rho_{n+1}(1,2,\cdots n,n+1|1',2',\cdots n',n+1)\, d\underset{\sim}{x}_{n+1}$$

For brevity the coordinates are indicated by the particle index. Also the space and spin coordinates may now be separated according to McWeeny:

$$\rho_1(K\lambda|1;1') = p_1(K,\lambda|\overset{\alpha}{1};\overset{\alpha}{1}')\, \alpha(1)\, \alpha^*(1') + p_1(K,\lambda|\overset{\alpha}{1};\overset{\beta}{1}')\, \alpha(1)\, \beta^*(1')$$
$$+ p_1(K,\lambda|\overset{\beta}{1};\overset{\alpha}{1}')\, \beta(1)\, \alpha^*(1') + p_1(K,\lambda|\overset{\beta}{1};\overset{\beta}{1}')\, \beta(1)\, \beta^*(1') \tag{10}$$

where the p_i are spinless density matrices obtained by integrating ρ_i over the spin coordinates. The spin product to which the spatial function belongs is indicated by a raised symbol. In particular, if there exists an axis of quantization $\underset{\sim}{Z}$, the spin component in that direction is:

$$\langle S^z \rangle = \int [s_1^z(1)\rho_1(1;\, 1')]_{1'=1}\, d\underset{\sim}{x}_1$$

$$= \frac{1}{2}\int [p_1(\overset{\alpha}{1};\, \overset{\alpha}{1}) - p_1(\overset{\beta}{1};\, \overset{\beta}{1})]d\underset{\sim}{r}_1$$

$$= \frac{1}{2}\int q_1(1;\, 1)\, d\underset{\sim}{r}_1 \qquad (11)$$

For states of definite spin the spinless and spin density matrices p_1 and q_1 are then:

$$p_1(1;\, 1') = \sum_{K\lambda} \rho_{K\lambda}\, [p_1(K\lambda|1;\, 1') + p_1(K\lambda|1;\, 1')]$$

$$q_1(1;\, 1') = \sum_{K} \rho_{K\lambda}\, [p_1(K\lambda|1;\, 1') - p_1(K\lambda|1;\, 1')] \qquad (12)$$

with the following physical significance of the diagonal elements:

$p_1(1;\, 1)\, d\underset{\sim}{r}_1$ = probability of finding any electron within the volume element $d\underset{\sim}{r}_1$ centered at $\underset{\sim}{r}_1$.

$q_1(1;\, 1)\, d\underset{\sim}{r}_1$ = probability of finding an unpaired electron with spin + 1/2 within the volume element $d\underset{\sim}{r}_1$ at $\underset{\sim}{r}_1$ minus that of finding it with spin - 1/2.

THE HYPERFINE INTERACTION HAMILTONIAN

The magnetic interaction between particles is a relativistic effect. Fermi[12] derived the expression for the energy of interaction between the electron and nuclear spin from Dirac's theory of relativity. A derivation consistent with these properties was developed by Casimir[13] and Ferrell[14] as follows. The hyperfine energy is obtained by considering the motion of an electron in the field,

$$\underset{\sim}{B}_n = \text{curl } \underset{\sim}{A}_n$$

induced by the nucleus of moment $\underset{\sim}{\mu}_n$, where the vector potential $\underset{\sim}{A}_n$ at a distance r from the nucleus n is defined by:

$$\text{div. } \underset{\sim}{A}_n = 0$$

$$A_n = \text{curl } \frac{\underset{\sim}{\mu}_n}{r} = \frac{\underset{\sim}{\mu}_n \times \underset{\sim}{r}}{r^3}$$

The energy of a particle in this magnetic field is given by the classical Hamiltonian of electrodynamics (see for instance (7) p. 108)[atomic units are used throughout this development - see Appendix ( )]:

$$\mathcal{H} = \sum_k \frac{1}{2} \left(\underset{\sim}{p} - \frac{1}{c} \underset{\sim}{A}_n\right)_k^2 + \text{potential Energy}$$

where the transition to quantum mechanics is achieved by replacing the momentum $\underset{\sim}{p}$ by the operator $- i \underset{\sim}{\nabla}$ if the particles do not possess spin. For an electron with spin $s = \frac{1}{2}$ and intrinsic magnetic moment $\underset{\sim}{\mu}_e = \beta \underset{\sim}{s} \cdot g$, an additional contribution to the energy arises from the scalar product $\underset{\sim}{\mu}_e \cdot \underset{\sim}{\beta}_n$. The electrostatic interaction between the nucleus and the electron charge clouds also contributes to the energy (quadrupole terms) but is non zero only

for nuclei of spin I = 1 and will not be considered here. Thus the hyperfine energy of the system, in the absence of quadrupole interactions is:

$$\begin{aligned}
\mathcal{H}_{hf}^{en} &= \left[\frac{1}{2}(\underset{\sim}{p} - \frac{1}{c}\underset{\sim}{A}_n)^2 - \frac{1}{2}\underset{\sim}{p}^2\right] - \underset{\sim}{\mu}_e \cdot \underset{\sim}{B}_n \\
&= -\left\{\beta\left[\left(\underset{\sim}{p} \cdot \frac{\underset{\sim}{\mu}_n \times \underset{\sim}{r}}{r^3} + \frac{\underset{\sim}{\mu}_n \times \underset{\sim}{r}}{r^3} \cdot \underset{\sim}{p}\right) - \frac{1}{c^2} A_n^2\right] + \underset{\sim}{\mu}_e \cdot \underset{\sim}{\nabla} \times \underset{\sim}{\nabla} \times \frac{\underset{\sim}{\mu}_n}{r}\right\} \\
&= -\left\{2\beta\, \mu_n \cdot \frac{\underset{\sim}{r} \times \underset{\sim}{p}}{r^3} + \underset{\sim}{\mu}_e \cdot \left[\underset{\sim}{\nabla}\left(\underset{\sim}{\nabla} \cdot \frac{\underset{\sim}{\mu}_n}{r}\right) - \underset{\sim}{\nabla}^2 \frac{\underset{\sim}{\mu}_n}{r}\right]\right\} \\
&= -\left\{2\beta \frac{\underset{\sim}{\mu}_n \underset{\sim}{\ell}}{r^3} + \underset{\sim}{\mu}_e \cdot \left[\underset{\sim}{\nabla}\,(\underset{\sim}{\mu}_n \cdot \underset{\sim}{\nabla}) - \frac{1}{3}\underset{\sim}{\mu}_n \underset{\sim}{\nabla}^2\right]\frac{1}{r}\right. \\
&\quad \left. - \frac{2}{3}\underset{\sim}{\mu}_e \cdot \underset{\sim}{\mu}_n \underset{\sim}{\nabla}^2 \frac{1}{r}\right\}
\end{aligned} \tag{13}$$

Use has been made of the definition of the orbital angular momentum $\underset{\sim}{\ell} = \underset{\sim}{r} \times \underset{\sim}{p}$ and of the vector identity curl curl = grad. div - $(\text{grad})^2$ keeping only the linear terms in $\underset{\sim}{A}_n$. The two terms arising from the electron spin magnetic moment have been separated according to their symmetry transformation property. The first is the anisotropic term

$$\underset{\sim}{\mu}_e \cdot \left[\underset{\sim}{\nabla}\,(\underset{\sim}{\mu}_n \cdot \underset{\sim}{\nabla}) - \frac{1}{3}\underset{\sim}{\mu}_n \underset{\sim}{\nabla}^2\right]\frac{1}{r} = \underset{\sim}{\mu}_n \cdot \left[\frac{3\underset{\sim}{r}\,\underset{\sim}{r}}{r^5} - \frac{1}{r^3}\right] \cdot \underset{\sim}{\mu}_e \tag{14}$$

It transforms under rotation as a spherical harmonic of order $\ell = 2$.

In magnetic fields of presently attainable magnitudes the electron and nuclear spin magnetic moments are

$$\underset{\sim}{\mu}_e = \beta\, \underset{\sim}{s} \cdot g$$

$$\underset{\sim}{\mu}_n = \beta_o\, g_n\, \underset{\sim}{I}_n$$

where β and β_o are respectively the Bohr and nuclear magnetons and where the g-factor for the electron with g_n isotropic, is a tensor

of second rank. The anisotropic energy may therefore be written as $\underset{\sim}{I}_n \cdot \underset{\sim}{a}_n \cdot \underset{\sim}{s}$ where $\underset{\sim}{a}_n$ is a tensor of second rank. When g is isotropic the term in $\underset{\sim}{I}_n^z$ is

$$(a_n \cdot \underset{\sim}{s})^z = \delta_n \left\{ \frac{3z(x\underset{\sim}{s}^x + y\underset{\sim}{s}^y + z\underset{\sim}{s}^z - r^2\underset{\sim}{s}^z}{r^5} \right\} ; \quad (\delta_n = g\, g_n |\beta| \beta_0)$$

$$= \frac{\delta_n}{r^3} \{(3\cos^2\theta - 1)\, \underset{\sim}{s}^z + \frac{3}{2} \sin\theta \cos\theta\, (e^{i\varphi}\underset{\sim}{s}^- + e^{-i\varphi}\underset{\sim}{s}^+)\}$$

$$= \frac{\delta_n}{r^3} \left(\frac{4\pi}{5}\right)^{1/2} \{2\, Y_{20}(\theta,\varphi)\, \underset{\sim}{s}^z + \sqrt{\frac{3}{2}}\, [Y_{21}(\theta,\varphi)\, \underset{\sim}{s}^- + Y_{2-1}(\theta,\varphi)\, \underset{\sim}{s}^+]\}. \tag{15a}$$

By rotating the axis, $x \rightarrow y \rightarrow z \rightarrow x$, the other two components are obtained and the general expression is Pake's[15] vector identity:

$$\underset{\sim}{I}_n \cdot \underset{\sim}{a}_n \cdot \underset{\sim}{s} = \frac{\delta_n}{r^3} [\underset{\sim}{A} + \underset{\sim}{B} + \underset{\sim}{C} + \underset{\sim}{D} + \underset{\sim}{E} + \underset{\sim}{F}] \tag{15b}$$

where

$$\underset{\sim}{A} = \underset{\sim}{I}_n^z\, \underset{\sim}{s}^z\, (3\cos^2\theta - 1)$$

$$\underset{\sim}{B} = \frac{1}{2}\, (3\cos^2\theta - 1)(\underset{\sim}{I}_n^z\, \underset{\sim}{s}^z - \underset{\sim}{I}_n \cdot \underset{\sim}{s})$$

$$\underset{\sim}{C} = \frac{3}{2} \sin\theta \cos\theta\, e^{-i\varphi}\, (\underset{\sim}{I}_n^z\, \underset{\sim}{s}^+ + \underset{\sim}{s}^z\, \underset{\sim}{I}_n^+)$$

$$\underset{\sim}{D} = C^* \text{ (complex conjugate of C)}$$

$$\underset{\sim}{E} = +\frac{3}{4} \sin^2\theta\, e^{-2i\varphi}\, \underset{\sim}{I}_n^+\, \underset{\sim}{s}^+$$

$$\underset{\sim}{F} = E^* \text{ (complex conjugate of E).}$$

Here (r,θ,φ) are the polar spherical coordinates of the electron with respect to the nucleus n and the Z axis is that of an applied external field. $\underset{\sim}{I}_n^+$, $\underset{\sim}{I}_n^-$, $\underset{\sim}{s}^+$ and $\underset{\sim}{s}^-$

are the spin raising and lowering operators ($\xi^{\pm} = \xi^{x} + i\,\xi^{y}$) which connect states with $\Delta m_I = \pm 1$ or $\Delta m_s = \pm 1$, and vanish for states of definite spin. When there exists an axis of quantization Z, the anisotropic term in a state of definite spin is then

$$\underline{I}_n^z (a_n \cdot \underline{s})^z = \frac{\delta_n}{r^3} (3 \cos^2\theta - 1)\, \underline{I}_n^z \underline{s}^z \,. \tag{15c}$$

Now from this expression the reason for the nomenclature is clear, since the term is angular dependent, with principal values:

$$a_n = \begin{pmatrix} -1/2\,\dfrac{\delta_n}{r^3} & & \\ & -1/2\,\dfrac{\delta_n}{r^3} & \\ & & \dfrac{\delta_n}{r^3} \end{pmatrix} .$$

That is, a_n is a tensor of zero trace which will vanish when averaged over all orientations as is the case for s-electrons ($\ell=0$). The angular dependence on $Y_{20}(\theta,\phi)$ in Eq. (15c) implies then that the term contribution will be non zero for the states $(\ell_1 m_1)$, $(\ell_2 m_2)$ of the electron (see Eq. (5)) when $(\ell_1 \ell_2 2)$ satisfy the properties of the sides of a triangle of even perimeter (triangular rule for the addition of angular momenta):

$$|\ell_1 + \ell_2| \geqq 2 \geqq |\ell_1 - \ell_2|$$
$$\ell_1 + \ell_2 + 2 = 2n, \; n = 2, 3, \cdots\cdots$$

and for

$$m_1 = m_2 \,.$$

The isotropic term is obtained from the classical theory of Coulomb fields [see for instance Panofsky and Phillips (14) page 3)],

$$\nabla^2 \frac{1}{|\underline{r} - \underline{r}_n|} = -4\pi\, \delta(\underline{r} - \underline{r}_n) \tag{16}$$

where the delta function is defined by:

$$\begin{cases} \delta(\underline{r} - \underline{r}_n) = 0, \quad \text{for } \underline{r} \neq \underline{r}_n \\ \int f(\underline{r})\, \delta(\underline{r} - \underline{r}_n) = f(\underline{r}_n), \quad \text{for } f(\underline{r}) \text{ continuous in the field region.} \end{cases}$$

This term is spherically symmetric and is therefore non-zero only for s-electrons.

§The hyperfine interaction Hamiltonian for the N-electron system of a complex molecular free radical can be expanded in terms of one electron operators:

$$\mathcal{H}_{hf}(\underline{x}) = \sum_i \mathcal{H}_{hf}(\underline{x}_i) \tag{17}$$

where

$$\mathcal{H}_{hf}(\underline{x}_i) = \sum_n \delta_n \underline{I}_n \cdot \left\{ \frac{\underline{\ell}_i - \underline{s}_i}{r_{in}^3} + \frac{3\, \underline{r}_{in} (\underline{r}_{in} \cdot \underline{s}_i)}{r_{in}^5} + \frac{8\pi}{3}\, \delta(\underline{r}_i - \underline{r}_n)\, \underline{s}_i \right\}$$

$$r_{in} = |\underline{r}_i - \underline{r}_n| \, .$$

In order to determine the expectation value of $\mathcal{H}_{hf}$ it must be noted that the operator contains the nuclear spin coordinates which must therefore be included in the wave function used in Eq. (2). If ψ, ψ_k are the ground and excited state eigenfunctions of the electronic Hamiltonian, then to first order, and as pointed out by Pryce (15)

$$\Phi = \left\{ \psi - \sum_k \frac{(\psi_k, \mathcal{H}_{hf} \psi)}{E_k - E} \psi_k \right\} \Theta \tag{18}$$

is an eigenfunction of the complete Hamiltonian, where E, E_k are the energies associated with the corresponding electronic states and Θ is the nuclear spin eigenfunction.

In polyatomic molecules the orbital degeneracy, when it exists in the ground state, is quenched as a consequence of the Jahn-Teller theorem (16, 17). This means that $\langle L^z \rangle \langle L^y \rangle$ and $\langle L^x \rangle$ are zero. The expectation value for the hyperfine interaction is then:

$$\mathcal{H}_{hf} = \sum_h \left\{ A_n \underset{\sim}{I}_n \cdot \underset{\sim}{S} + \underset{\sim}{I}_n \cdot A_n \cdot \underset{\sim}{S} \right\} \tag{19}$$

where, assuming that there exists an external axis of quantization, Z,

(a) $$A_n I_n^z S^z = \frac{8\pi}{3} \delta_n \int \left[I_n^z s_1^z \delta(\underset{\sim}{r}_1 - \underset{\sim}{r}_n) \rho_1(1;1') \right]_{1'=1} d\underset{\sim}{r}_1$$

$$= \frac{8\pi}{3} \delta_n I_n^z \frac{S^z}{S} \; 1/2 \, q_{1n}, \quad (q_{1n} = q_1(1;1)_{\underset{\sim}{r}_1 = \underset{\sim}{r}_n})$$

or

$$A_n = \frac{8\pi}{3} \delta_n q_{1n} \tag{19a}$$

(b) $$I_n^z (A_n \cdot \underset{\sim}{S})^z = \delta_n \int \left\{ I_n^z (a_{n\,1} \cdot s_1)^z \rho_1(1;1') \right\}_{1'=1} d\underset{\sim}{r}_1$$

$$= \delta_n I_n^z S^z \int \frac{(3 \cos^2 \theta_{1\,n} - 1)}{r_{1\,n}^3} \, q_1(1;1) \, d\underset{\sim}{r}_1 \tag{19b}$$

The molecular axis Z as well as the external axis of quantization z must be taken into account in the anisotropic term. The general case arises when the electron is in an atomic orbital not centered about n [see Fig. 1]. Then, the electronic and molecular coordinates are separated by making use of the addition theorem of spherical harmonics (see for instance (7) p. 370)

$$(3\cos^2\theta_{1n} - 1) = (3\cos^2\theta_{\nu n} - 1)\, P_2(\cos\bar{\theta}_1) + \frac{8\pi}{5} \sum_{\substack{m=-2,\\ -1,1,2}} Y_{2m}(\theta_{\nu n}, \varphi_{\nu n})\, Y_{2m}(\theta_1, \varphi_1) \tag{20}$$

and

$$\bar{r}_{1n} \cos\bar{\theta}_1 = R_{yn} - r_1 \cos\theta_1$$

$$r_1 \sin\theta_1 = r_{1n} \sin\bar{\theta}_1$$

if electron (1) is in an atomic orbital centered about ν. The significant contributions to (19b) will then arise from atomic orbitals centered about n and ν. If n is a hydrogen atom with an electron in a 1s orbit, then the significant non-zero contributions will arise from one-center integrals about ν and two-center integrals about ν and n. When Eq. (20) is substituted into (19b) the terms containing the molecular coordinates will come outside of the integral sign:

$$I_n^z (Q_n \cdot S)^z = \delta_n \left\{ (3\cos^2\theta_{\nu n} - 1) \int \frac{P_2(\cos\bar{\theta}_1)}{r_{1n}^3}\, Q_1(1;1)\, d\tau_1 + \frac{8\pi}{5} \sum_{m \neq 0} Y_{2m}(\theta_{\nu n}, \varphi_{\nu n}) \int \frac{Y_{2m}(\bar{\theta}_1, \varphi_1)}{r_{1n}^3}\, Q_1(1;1)\, d\tau_1 \right\} \tag{19b}$$

Thus, if the molecule undergoes rapid tumbling, as in solutions, the average value of the anisotropic coupling vanishes due to the properties of the spherical harmonic of order 2. The physical implication here is that in solutions the hyperfine structure of the ESR spectra will arise only from the isotropic contact term. This property was derived by Weissman (18).

APPLICATION TO THE HYPERFINE INTERACTION IN AROMATIC FREE RADICALS

The reactivity of the aromatic molecules lies in their ability to add or lose an electron from the π-electron system, thus forming a free radical. These are stabilized in a proper solvent in order to record their ESR spectra, where the observed hyperfine structure arises from the contact interaction term of the unpaired electron at the nuclei of the aromatic and α protons in aliphatic substituents, H^1 and the skeleton C^{13} or N^{14}. This means that the π-electrons of an aromatic free radical posses a certain degree of unpaired character, which is due to a $\sigma - \pi$ correlation interaction.

The best wave functions for an aromatic free radical are thus obtained by first assuming sigma-pi separability where the σ- and π-electrons are considered as individual groups in the electrostatic field of each other see for instance (6), p. 249 . The configurations which take into account the existence of the $\sigma - \pi$ valence bonds, indicated by the ESR experiments, are then introduced by means of a series perturbation. The procedure, which is based on the theorems developed by Lykos and Parr (19), is as follows:

A. The electronic system to a first approximation is described by:

$$\psi_0 = \hat{\mathcal{A}}_{\sigma\pi}\left[(\Sigma_0)(\Pi)\right] = \left\|\left[(^1\Sigma)\,(\Pi)\right]\right\| \tag{21}$$

where $(^1\Sigma)$ and (Π) are independent antisymmetric functions of the σ- and π-electrons respectively. They are given in terms of a complete orthonormal set of Slater determinants which describe the system:

$$(^1\Sigma_0) = A_1\,(^1\Sigma_1) + A_2\,(^1\Sigma_2) + \cdots$$

$$(\Pi) = B_1\,(\Pi_1) + B_2\,(\Pi_2) + \cdots \tag{22}$$

where

$$\int \Psi_0 \Psi_0^* \, d\underset{\sim}{x} = \int ({}^1\Sigma_0)({}^1\Sigma_0)^* \, d\underset{\sim}{x}_\sigma = \int (\Pi)(\Pi)^* \, d\underset{\sim}{x}_\pi = 1$$

$({}^1\Sigma_0)$ is a singlet and Ψ_0 and (Π) have the same spin multiplicity. Also, $({}^1\Sigma_0$ and (Π) are orthogonal since the σ- and π-electrons move in orbitals which are respectively symmetric and antisymmetric with respect to the plane of the aromatic ring.

B. The σ-π bonding property is introduced by the interaction of Ψ_0 with the configurations Ψ_K, where the σ-electron wave function is in an electronic triplet state or in a state of higher multiplicity, (Σ^K), leading to the ground state wave function:

$$\psi = C_0 \Psi_0 + \sum_{K=1}^{\infty} C_K \Psi_K + \cdots . \tag{23}$$

In the absence of an external magnetic field, the electronic energy of the system is obtained by expanding the spin-free Hamiltonian up to two particle operators:

$$\underset{\sim}{H} = \left[H_\sigma^{(1)} + \frac{1}{2!} \underset{\sim}{H}_{\sigma\sigma}^{(2)}\right] + \left[\underset{\sim}{H}_\pi^{(1)} + \frac{1}{2!} \underset{\sim}{H}_{\pi\pi}^{(2)}\right] + \frac{1}{2!} \underset{\sim}{H}_{\sigma\pi}^{(2)} + \cdots \tag{24}$$

where

$$\underset{\sim}{H}_\xi^{(1)} = \sum_{k=\xi\text{-electrons}} \left\{ \frac{\underset{\sim}{p}_k^{\,2}}{2} - \sum_n \frac{Z_n}{r_{kn}} \right\} .$$

The first term in $\underset{\sim}{H}_\xi^{(1)}$ represents the kinetic energy of the elecr trons and Z_n is the charge of the bare nuclei. The subindices indicate the system of electrons on which the operators act. By sigma-pi separability it is meant that $({}^1\Sigma_0)$ is an eigenfunction of the σ-electron operators alone, while (Π) is the eigenfunction of the effective Hamiltonian

$$\underset{\sim}{H}_\pi = \underset{\sim}{H}_{\text{core}}^{(1)} (\pi) + \frac{1}{2!} \underset{\sim}{H}_{\pi\pi}^{(2)} \tag{25}$$

where

$$\underset{\sim}{H}^{(1)}_{core}(\pi) = \underset{\sim}{H}^{(1)}_{\pi} + \underset{\sim}{G}^{0}_{\sigma}(\pi), \quad [\underset{\sim}{G}^{0}_{\sigma}(\pi) \equiv \underset{\sim}{J}^{0}_{\sigma}(\pi) - \underset{\sim}{K}^{0}_{\sigma}(\pi)] ,$$

$\underset{\sim}{G}^{0}_{\sigma}(\pi)$ arises from the last term in Eq. (24), which is the two-particle correltationfunction between the σ- and π-electrons. In the first approximation the π-electrons move in the electrostatic potential field set up by the nuclei and the σ-electrons, that is:

$$\underset{\sim}{J}^{0}_{\sigma}(\pi_1)\,\psi_{\pi}(1) = \frac{1}{2}\{\int \frac{1}{r_{1,1'}}\,\rho_1[(^1\Sigma_0)(^1\Sigma_0)|1';1')]d\underset{\sim}{x}_{1'}\}\,\psi_{\pi}(1)$$

$$\underset{\sim}{K}^{0}_{\sigma}(\pi_1)\,\psi_{\pi}(1) = \frac{1}{2}\int\{\frac{1}{r_{1,1'}}\,\underset{\sim}{P}_{1,1'}\,\rho_1[(^1\Sigma_0)(^1\Sigma_0)|1';1'']\psi_{\pi}(1)\}_{1''=1'}\,d\underset{\sim}{x}_{1'} \tag{26}$$

when $\psi_{\pi}(1)$ is a one-electron π-mo.

The σ-π correlation interaction:

$$\underset{\sim}{G}_{\sigma\pi} = \frac{1}{2!}\sum_{\sigma\pi}\frac{1}{r_{\sigma\pi}}$$

will now mix the excited configurations into the ground state

$$\Psi_K = {}^{2S+1}\underset{\sim}{\mathcal{O}}\,\underset{\sim}{\mathcal{A}}_{\sigma\pi}\,[(\Sigma^K)(\Pi)] \tag{27}$$

where ${}^{2S+1}\underset{\sim}{\mathcal{O}}$ is a projection operator defined by Löwdin which selects the states of (2S+1) spin multiplicity. For a single Slater determinant D_0 in Eq. (27), the eigenfunction of S^2 is then:

$${}^{2S+1}\underset{\sim}{\mathcal{O}}\,D_0 = \sum_{k=0}^{n} c_k\overline{D}_k \tag{28}$$

where $\overline{D}_k$ is the sum of the Slater determinants which result by applying all the possible k-spin permutations to D_0 and n is the total number of pairs of orbitals with opposite spin. The coefficients c_k are then determined from recurrence symmetry relationships [see Löwdin (4)]. For a doublet state these are given by:

$$\frac{c_k}{c_0} = (-1)^k \binom{n+1}{k}^{-1} \tag{29}$$

where c_0 is obtained by direct application of ${}^{2S+1}\underset{\sim}{\theta}$. Thus, to first order, the ground state wave function is:

$$\Psi = \Psi_0 - \sum_{K=1} \frac{\langle \underset{\sim}{H} \rangle_{0K}}{\langle \underset{\sim}{H} \rangle_{KK} \langle H \rangle_{00}} \Psi_K \,. \tag{30}$$

Here all the (Σ_i) and (Π_i) satisfy the sigma-pi separability theorems and therefore the expectation value of $\underset{\sim}{H}$ between the states Ψ_0 and Ψ_K will only contain the terms in $\underset{\sim}{G}_{\sigma\pi}$:

$$\langle \underset{\sim}{H} \rangle_{K0} = \langle \underset{\sim}{H} \rangle_{0K} = \langle \underset{\sim}{G}_{\sigma\pi} \rangle_{0K} = \langle \underset{\sim}{G}_{\sigma\pi} \rangle_{K0}$$

and

$$\langle \underset{\sim}{H} \rangle_{KK} - \langle \underset{\sim}{H} \rangle_{00} = \Delta\epsilon_K$$

where $\Delta\epsilon_K$ is the energy of excitation of the virtual processes which give rise to the hyperfine interaction.

The expectation value of the hyperfine interaction energy is now obtained from the wave function

$$\Psi = \psi\, \Theta \tag{31}$$

where Ψ is given by Eq. (30) and Θ is the nuclear spin eigenfunction. The excited spin states in Eq. (18) have been neglected here since they are of the order of $\delta_n/\Delta E$, where for protons $\delta_H/\Delta E \approx 8 \times 10^{-7}$. The hyperfine interaction for the aromatic free radicals in solution is then (see Eq. 19a):

$$\langle \mathcal{H}_{hf} \rangle = \frac{8\pi}{3} \sum_n \delta_n I_n^z \int \{ s_{\underset{\sim}{1}}^z \, \delta(\underset{\sim}{r}_1 - \underset{\sim}{r}_n) \rho_1(1;1') \}_{1'=1} \, d\underset{\sim}{x}_1$$

$$= \frac{8\pi}{3} \sum_n \delta_n I_n^z \frac{S^z}{S} \left(\tfrac{1}{2} q_{1n} \right), \tag{32}$$

where q_{1n} is the one electron spin density at the nucleus n. The one electron density matrix:

$$\rho_1(1;1') = C_0^2 \, \rho_1(00|1;1') - \sum_K [C_0 C_K^* \, \rho_1(K0|1;1') + C_K C_0^* \, \rho_1(0K|1;1')] + \cdots$$

can be derived to first order from Eq. (30).

$$C_0 = C_0^* = 1$$

$$C_K = C_K^* = \frac{\langle G_{\sigma\pi} \rangle_{0K}}{\Delta\epsilon_K} = \frac{\langle G_{\sigma\pi} \rangle_{K0}}{\Delta\epsilon_K}$$

$$\rho_{0K} = \rho_{K0} = C_0 C_K$$

That an unpaired π-electron does not contribute to the σ-electron densities in Ψ_0 is noted from:

$$\rho_1(00|1;1') = \rho_1[(^1\Sigma_0)(^1\Sigma_0)|1;1'] + \rho_1[(\Pi)(\Pi)|1;1']$$

since the one electron density matrices of the separate groups are additive. The effective one electron density matrix will therefore only contain the cross terms $\rho_1(K0|1;1')$.

The coupling constants for an aromatic free radical with total spin S = 1/2 can readily be calculated now from Eq. (32). The complete set of Slater determinants which describe the π-electron system are assumed to be eigenfunctions of S^2. This is true in general since the doublet state projection operator can

be applied successively to the π-electron antisymetrized products (Π) and to the $||(\Sigma)(\Pi)||$. The matrix elements between Ψ_0 and Ψ_K are to be evaluated between antisymmetrized products of the form:

$$||\sigma_o(1)\ \bar{\sigma}_o(2)\pi_i(3)\ ---||_0 ,$$

and

$$^2\underset{\sim}{\theta}||\sigma_o(1)\ \sigma_K^*(2)\bar{\pi}_j(3)\ ---||_K = \sqrt{\tfrac{2}{3}}\ ||\sigma_o(1)\ \sigma_K^*(2)\bar{\pi}_j(3)\ ---||_K$$

$$-\frac{1}{\sqrt{6}}\ ||\sigma_o(1)\ \sigma_K^*(2)\bar{\pi}_j(3)\ ---||_K - \frac{1}{\sqrt{6}}\ ||\sigma_o(1)\ \sigma_K^*(2)\bar{\pi}_j(3)\ ---||_K$$

Only three electrons need to be considered here since all the others are assumed to be paired. Although the excited state is doubly degenerate, only the $E_1(C_{3V})$ linear combination given above contributes to the hyperfine coupling.

Since $\underset{\sim}{G}_{\sigma\pi}$ is a single particle operator in both the σ- and π-electrons non zero terms will arise only from antisymmetrized products which differ by not more than one set in each system, for instance (σ_o, σ_K^*) and (π_i, π_j). Thus, in terms of the complete set of Slater determinants which describe the system, see Eq. (22):

$$\langle G_{\sigma\pi}\rangle_{OK} = \sum_{ij} B_i(c_j B_j^K) \int \{\frac{1}{2}\frac{1}{r_{12}}(1-\underset{\sim}{P}_{12})\rho_2(OK|1,2;1',2')\}_{\substack{1'=1\\2'=2}} dx_1 dx_2$$

where in order to separate the space and spin coordinates the Derac identity [see for instance, Dirac (22) p. 221]

$$\underset{\sim}{P}_{12} = \bar{\underset{\sim}{P}}_{12}\ \frac{1}{2}(1+4\underset{\sim}{s}_1\cdot\underset{\sim}{s}_2)\ ,\quad \begin{cases} s^x = \frac{1}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \\ s^y = \frac{1}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} \\ s^z = \frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\end{cases}$$

is used. Here the $\underset{\sim}{s}$ operate on the electron spin functions

$\alpha = \binom{1}{0}$ and $\beta = \binom{0}{1}$, while $\bar{\underset{\sim}{P}}_{12}$ interchanges the space coordinates of electrons 1 and 2. Thus if Z is the external axis of quantization:

$$\langle G_{\sigma\pi}\rangle_{OK} = -\frac{1}{2}\sum_{ij} B_i(c_j B_j^K)\int \{4\,\bar{\underset{\sim}{P}}_{12}\, \underset{\sim}{s}_1^z\, \underset{\sim}{s}_2^z \frac{1}{r_{12}}\rho_2(OK|1,2;1',2')\}_{\substack{1=1'\\2=2'}} d\underset{\sim}{x}_1\, d\underset{\sim}{x}_2$$

$$= -\frac{1}{2}\sum_{ij} B_i(c_j B_J^K)\int \frac{1}{r_{12}}\, q_1^{\pi}(\pi_i\pi_j|1,2)\; q_1(\sigma_o\sigma_K^*|1,2)\; d\underset{\sim}{r}_1\, d\underset{\sim}{r}_2$$

$$= -\frac{1}{2}\sum_{ij} B_i(c_j B_j^K)\; K_{ij}^{OK}$$

and

$$\rho_1(KO|1,1') = \rho_1(OK|1,1') = \sum_k (c_k B_k^K)\, B_k\, \rho_1(\sigma_o\sigma_K^*\,|\,1;1) \qquad (33)$$

Here it is assumed that (Σ_o) and (Σ^K) can be expressed in terms of a single Slater determinant while (Π) must be approximated by a series expansion where B_i and B_i^K are the coefficients of (Π_i) in the states Ψ_O and Ψ_K and c_i is the coefficient of the spin permutation (see Eq. 28) which makes the components of Ψ_O and Ψ_K identical except for one set of orbitals in ρ_1 and two for ρ_2.

The σ_o, σ_K^*, and π_i and π_j are molecular orbitals given by Eq. (4):

$$\left.\begin{aligned}\sigma_O &= T_O^+(\underset{\sim}{b}) = \sum_\ell T_{Oi}(b)_\ell\\ \sigma_K^* &= T_K^+(\underset{\sim}{a}) = \sum_\ell T_{K\ell}(a)_\ell,\end{aligned}\right\}\begin{pmatrix}(b)_\ell\\(a)_\ell\end{pmatrix} \equiv \frac{1}{\sqrt{2}}\begin{pmatrix}\frac{1}{1+S_{12}} & \frac{1}{1+S_{12}}\\ \frac{-1}{1-S_{12}} & \frac{-1}{1-S_{12}}\end{pmatrix}\begin{pmatrix}\phi_{\ell 1}\\ \phi_{\ell 2}\end{pmatrix}$$

$$\pi_i = T_i^+(\underset{\sim}{C}:(2p_z)] = \sum_n T_{in}\, C_n:(2p_z)$$

$$\pi_j = T_j^+[\underset{\sim}{C}:(2p_z)] = \sum_n T_{jn}\, C_n:(2p_z), \qquad (T_i^+,\, S\, T_j) = \delta_{ij} \qquad (34)$$

where the linear transformations $\underset{\sim}{T}_0$ and $\underset{\sim}{T}_K$ and $\underset{\sim}{T}_i$ and $\underset{\sim}{T}_j$ are column vectors operating respectively on the space of the σ- and π-orbitals, in such a manner that the energy of the two systems is independently minimized:

$$\delta\langle(^1\Sigma_0)|\mathcal{H}_\sigma|(^1\Sigma_0')\rangle = 0$$

$$\delta\langle(\Pi)|\mathcal{H}_\pi|(\Pi)\rangle = 0$$

ϕ_{i1} and ϕ_{i2} are directed orbitals† centered at neighboring atoms 1 and 2, see Fig. 3, used in forming the sigma bonding and anti-bonding orbitals, $(b)_i$ and $(a)_i$. S is the overlap matrix for the $C:(2p_z)$ orbitals. Thus in Eq. (32) the effective one electron density matrix is:

$$\overline{\rho}_1(1;1') = \sum_{Kijk} \frac{\rho_1(\sigma_0\sigma_K^*|1;1')\ K_{ij}^{OK}}{\Delta\epsilon_K} B_i(c_jB_j^K)\ B_K(c_KB_K^K) \qquad (36)$$

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†The directed hybrid atomic orbitals (see for instance Van Vleck (23) are: a) for the carbon atoms in a planar aromatic ring:

$$\begin{pmatrix}\phi_1\\ \phi_2\\ \phi_3\\ C:(2p_z)\end{pmatrix} = \begin{pmatrix}\sin\chi & -\cos\chi & & 0\\ \frac{1}{\sqrt{2}}\cos\chi & \frac{1}{\sqrt{2}}\sin\chi & \frac{1}{\sqrt{2}} & 0\\ \frac{1}{\sqrt{2}}\cos\chi & \frac{1}{\sqrt{2}}\sin\chi & -\frac{1}{\sqrt{2}} & 0\\ 0 & 0 & 0 & 1\end{pmatrix}\begin{pmatrix}C:(2s)\\ C:(2p_x)\\ C:(2p_y)\\ C:(2p_z)\end{pmatrix}, \quad \cos\chi = \sqrt{\frac{2\cos\beta}{\cos\beta-1}} \qquad (35a)$$

where β is the bond angle $\widehat{\phi_2\phi_3}$ (= 120° for sp^2 hybrids as in benzene, and b) for the tetrahedral orbitals in the CH_3 group:

$$\begin{pmatrix}2p\sigma\\ 2h_1\\ 2h_2\\ 2h_3\end{pmatrix} = \begin{pmatrix}\sin\alpha & -\cos\alpha & 0 & 0\\ \frac{1}{\sqrt{3}}\cos\alpha & \frac{1}{\sqrt{3}}\sin\alpha & 0 & \sqrt{2/3}\\ \frac{1}{\sqrt{3}}\cos\alpha & \frac{1}{\sqrt{3}}\sin\alpha & \frac{1}{\sqrt{2}} & \frac{-1}{\sqrt{6}}\\ \frac{1}{\sqrt{3}}\cos\alpha & \frac{1}{\sqrt{3}}\sin\alpha & -\frac{1}{\sqrt{2}} & \frac{-1}{\sqrt{6}}\end{pmatrix}\begin{pmatrix}C:(2S)\\ C:(2p_x)\\ C:(2p_y)\\ C:(2p_z)\end{pmatrix}, \quad \sin\alpha = \sqrt{2\cot\theta} \qquad (35b)$$

where θ is the bond angle $\widehat{(2p\sigma)(2h_i)}$, i = 1,2,3 ($\theta = 2 \arcsin\sqrt{2/3} > \pi/2$, for true tetrahedral hybrids as in CH_4).

If an average energy $\Delta\epsilon = \Delta\epsilon_K$ may be assumed for a single type of σ-orbital excitation ($\sigma \rightarrow \sigma^*$) the sum over the complete set K above yields:

$$\overline{\rho}_1^{\sigma}(1;1') = \frac{\rho_1(\sigma\ \sigma^*|1;1')}{\Delta\epsilon} \sum_{ij} \rho_{ij}^{\pi}\ K_{ij}^{\sigma\sigma^*}, \quad [\rho_{ij}^{\pi} = B_i B_j] \tag{36}$$

Now, since the σ-orbitals are localized, the significant contributions to $K_{ij}^{\sigma\sigma^*}$ are the one and two center integrals between bonded atoms. Consequently the contact term will be non zero only for σ-orbitals centered about the particular nucleus. This means that for aromatic protons H^1, the C-H bond orbitals need only be considered in Eq. 36 while for the ring skeleton nuclei C^{13} and N^{14} all the directed σ-orbitals and the 1S orbital about the center must be taken into account. Thus, for an aromatic proton bonded to the nth carbon atom:

$$\overline{\rho}_1(1;1')_H = \frac{K_{\pi\pi}^{11}\ \rho_{on}^{\pi}}{2\Delta\epsilon(1-s^2)^{\frac{1}{2}}} [-\rho_1(H{:}1S\ H{:}1S|1;1') + \rho_1(C_n{:}\phi_1\ C_n{:}\phi_1|1;1')] \tag{37}$$

and for C^{13} on (N^{14}) in the ring skeleton at $\underset{\sim}{r}_n$:

$$\overline{\rho}_1(1;1') = \rho_{on}^{\pi}\left\{\sum_{\ell=1,2,3} \frac{(K_{\pi\pi}^{ii})_n}{2\ \epsilon_i(1-s_j^2)^{\frac{1}{2}}} [\rho_1(\phi_{ni}\ \phi_{ni}|1;1') - \rho_1(\phi_{n'i}\ \phi_{n'i}|1;1')]\right.$$

$$\left. + \frac{K_{\pi\pi}^{SS}}{2\Delta\epsilon'(1-s^2)^{\frac{1}{2}}} \rho_1(C_n{:}1S\ C_n{:}2S|1;1')\right\}$$

$$- \sum_{i=1,2,3} \rho_{on_i}^{\pi} \frac{(K_{\pi\pi}^{ii})_{n_i}}{2\Delta\epsilon_i(1-s_i^2)^{\frac{1}{2}}} [\rho_1(\phi_{ni}\ \phi_{ni}|1;1') - \rho_1(\phi_{n'i}\ \phi_{n'i}|1;1')]$$

where

$$\rho^{\pi}_{on} = \sum_{m} \sum_{\ell k} \rho^{\pi}_{k\ell} (T_{\ell n})_k (T_{km})_\ell S_{mn}$$

is the probability of finding an unpaired π-electron in the neighborhood of the nth atom in the ring, and the states (Π_ℓ) and (Π_k) differ at most by one mo. $(\pi_{\ell k}, \pi_{k\ell})$. The directed orbitals ϕ_{n_i} and $\phi_{n'_i}$ are respectively centered about the neighboring atoms C_n and $C_{n'}$, see Fig. 3. Also, the contribution from the exchange integrals correspond to the virtual excitation of the three σ-bonds at C_n, see Fig. 2. Thus,

$$K^{11}_{\pi\pi} = (\sin^2\chi\, K^{ss}_{zz} + \cos^2\chi\, K^{xx}_{zz} - K^{1'1'}_{zz})(1-s^2)^{-1/2} = K_1 \cdot (1-s^2)^{-1/2}$$

$$K^{22}_{\pi\pi} = (\frac{\cos^2\chi}{2} K^{ss}_{zz} + \frac{(1+\sin^2\chi)}{2} K^{xx}_{zz} - K^{2'2'}_{zz})(1-s^2)^{-1/2} = K_2 \cdot (1-s^2)^{-1/2}$$

$$K^{33}_{\pi\pi} = (\frac{\cos^2\chi}{2} K^{ss}_{zz} + \frac{(1+\sin^2\chi)}{2} K^{xx}_{zz} - K^{3'3'}_{zz})(1-s^2)^{-1/2} = K_3 \cdot (1-s^2)^{-1/2}$$

$$K^{SS}_{\pi\pi} = K^{ss}_{zz} = K_S \tag{38}$$

where the parameter χ varies with the σ-bond angle, see Eq. (35) (for sp^2 hybrids $\sin^2\chi = 1/3$, $\cos^2\chi = 2/3$). The carbon non-zero one center integrals are $K^{ss}_{zz} = K^{yy}_{zz}$ where the atomic orbitals indicated by (S,s,x,y,z) are the C (1S, 2S, $2p_x$, $2p_y$, $2p_z$). If the two center integrals are neglected then for sp^2 hybrids:

$$K_1 = K_2 = K_3 = K$$

where (39)

$$K = \frac{1}{3} K^{ss}_{zz} + \frac{2}{3} K^{xx}_{zz}$$

In this approximation, the hyferfine splitting constants, are given in the form derived by McConnell and Chesnut (2) and MacLachlan, Dearman and Lefebvre (24), and Karplus and Fraenkel (25):

$$A_{H^1} = Q_H \, \rho^{\pi}_{on}$$

$$A_{C^{13}} = (S_1 + Q_{1C}) \, \rho^{\pi}_{on} + Q_{2C} \, (\rho^{\pi}_{on-1} + \rho^{\pi}_{on+1}) \qquad (40)$$

where

$$Q_H = -\frac{4\Pi}{3} \delta_{H^1} \frac{q_{1H} K_1}{\Delta\epsilon(1-s^2)}, \quad [q_{1H} \approx \langle |\phi_{H:1s}(0)|^2 \rangle]$$

$$S = \frac{4\pi}{3} \frac{q_{sc} \, K_S}{\Delta\epsilon'(1-s^2)}, \quad [q_{sc} = \langle |\phi^{(0)}_{C:2s} \, \phi^{(0)}_{C:1s}| \rangle]$$

$$Q_{1C} = \frac{4\pi}{3} \delta_{C^{13}} \frac{q_{11C} \langle K \rangle}{\Delta\epsilon(1-s^2)}, \quad [q_{11C} \approx \langle |\phi_{C:2s}(0)|^2 \rangle], \quad [\langle K \rangle = \tfrac{1}{3}(K_1 + 2K_2)]$$

$$Q_{2C} = \frac{4\pi}{3} \delta_{C^{13}} \frac{q_{12C} \, K_2}{\Delta\epsilon(1-s^2)}, \quad [q_{12C} \approx \tfrac{1}{2} \cos^2\chi \, \langle |\phi_{C:2s}(0)|^2 \rangle]$$

where the parameter $\cos^2\chi = 2/3$ for exact sp^2 hybrids as in benzene. Thus, it may be said that for sp^2 hybrids the Q's are universal constants.

The experimental evidence is that the π-electron coupling to an aliphatic side chain proceeds significantly only to the α-protons. This can be explained on the basis of hyperconjugation as Bersohn (26) and MacLachlan (27) have done successfully for the tolu- and xylosemiquinones and for Würster's blue ions. The $-CH_3$ (or $-NH_2$) fragment is attached to the aromatic system through the C-C σ-bond but the excited triplet states which contribute

to the H^1 splitting are those of the three C-H σ-bonds. This means that there exists a correlation interaction, leading to a valence bond, between the π- and the $-CH_3$ σ-electrons.

Since the three protons in $-CH_3$, see Fig. 3, are exactly equivalent, due to the rapid rotations about the C-C axis which occur in solution, the three directed C-H bonds may be reduced according to C_{3v} symmetry:

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix} = T_3^\dagger \begin{pmatrix} (b_1) \\ (b_2) \\ (b_3) \end{pmatrix}$$

$$\begin{pmatrix} \sigma_1^* \\ \sigma_2^* \\ \sigma_3^* \end{pmatrix} = T_3^\dagger \begin{pmatrix} (a_1) \\ (a_2) \\ (a_3) \end{pmatrix} \quad T_3^\dagger = \begin{pmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ \sqrt{2/3} & -1/\sqrt{6} & -1/\sqrt{6} \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} \tag{41}$$

where the (b_i) and (a_i) $(i = 1,2,3)$ refer to the CH_i bonds, see Eq. (34).

The effective density matrix for H_3 is then,

$$\overline{\rho}_1(1;1')_{H_3} = \sum_{i=1,2,3} \frac{K_{\pi\pi}^{ii}\, \rho_{on}^{\pi}}{\epsilon}\, \rho_1(\sigma_i \sigma_i^*\, 1;1') \tag{42}$$

The highest contribution, however, arises from the virtual excitations $\sigma_2 \rightarrow \sigma_2^*$ since the exchange integral is between orbitals with maximum overlap:

$$K_{\pi\pi}^{22} = K_{zz}^{z'z'} - (K_{zz}^{H_1H_1} - K_{zz}^{H_1H_2}) = \overline{K} \tag{43}$$

where z, z' are respectively carbon $2p_z$ orbitals at C_n and $C_{n'}$ (see Fig. 3) and (H_1, H_2, H_3) are the H:1S orbitals for the CH_3 protons.

The C^{13} splitting in $-CH_3$ arises from the virtual processes ($\sigma_{CC'} \rightarrow \sigma^*_{CC'}$), ($\sigma_1 \rightarrow \sigma^*_1$) and ($C{:}1S \rightarrow \sigma^*_i$); (i=0,1,2,3 in the C-$CH_3$ group).

$$\overline{\rho}_1(1;1')_{C'} = \rho^{\pi}_{on}\left[\frac{K_{C'}}{\Delta\epsilon}\,\rho_1(\sigma\ \sigma^*|1;1') + \frac{K_{S'}}{\Delta\epsilon'}\,\rho_1(1S\ \sigma^*|1;1')\right] \qquad (44)$$

where

$$K_{C'} = K^{CC}_{\pi\pi} - K^{C'C'}_{\pi\pi}$$

C and C' are respectively the hybrid orbitals centered at C_n and $C_{n'}$ in Fig. 3. The highest contributions are, however, from the one center integrals $K^{CC}_{\pi\pi}$, which is the same process as for aromatic protons, and K'_S. The hyperfine coupling constants for the $-CH_3$ group are then

$$A_{(H_3)_{n'}} = Q_{H_3}\,\rho^{\pi}_{on}$$

$$A_{C^{13}_{n'}} = (S_1 + Q_{C'})\,\rho^{\pi}_{on} \qquad (45)$$

where

$$Q_{H_3} = -\frac{4\pi}{3}\,\delta_{H'}\,\frac{q_{1H_3}\,\overline{K}}{\Delta\epsilon(1-s^2)}, \quad \left\{q_{1(H_3)} = \frac{1}{3}\left[\langle|\phi_{H:1s}(0)|^2\rangle - \langle|\phi_{H:1s}(0)\,\phi_{H:1s}(\underset{\sim}{r}_{12})|\rangle\right]\right\}$$

$$Q_{C'} = -\frac{4\pi}{3}\,\delta_{C^{13}}\,\frac{q_{1C'}\,K_{C'}}{\Delta\epsilon(1-s^2)}, \quad \left\{q_{1C'} = \sin^2\alpha\,\langle|\phi_{C:2s}(0)|^2\rangle\right\}$$

$$S_{1'} \cong S_1$$

$\sin^2\alpha = 1/4$ for tetrahedral hybrids, see Eq. 35 and r_{12} is the distance between two H atoms in the CH_3 groups.

This approximation, where the spin density q_{1n} in the σ-electron plane is proportional to the probability of finding an unpaired π-electron in that neighborhood ρ_{on}, is verified by evaluating the Q's by two different methods.

A) The excitation energy of the virtual processes $\Delta\epsilon(\sigma \rightarrow \sigma^*)$ and the exchange integrals $K_{\pi\pi}^{\sigma\sigma^*}$ are obtained semiempirically. The first is evaluated in the Heitler-London (28) approximation, where for a diatomic molecule A-B the bond energies are:

$$E_\sigma = E_o + \frac{J_{AB} + K_{AB}}{1 + S_{AB}^2} \qquad E_{\sigma^*} = E_o + \frac{J_{AB} - K_{AB}}{1 - S_{AB}^2}$$

and therefore

$$\Delta\epsilon(\sigma \rightarrow \sigma^*) = 2\,\frac{K_{AB} - S_{AB}^2 J_{AB}}{1 - S_{AB}^4} \tag{46}$$

E_o is the kinetic energy of the electrons and J_{AB} and K_{AB} are the coulomb and exchange energies respectively. For Slater type orbitals it can be shown that the contributions to the total bond energy are 10 to 15% from J_{AB} and the rest from K_{AB}, and since $S_{AB} < 1$,

$$\Delta\epsilon(\sigma \rightarrow \sigma^*) \cong 2K_{AB} \approx .85D \tag{47}$$

where D is the dissociation energy of the bond. The experimental values of interest are then (see for instance Cottrell (28), chapter 9)

$$D(C_6H_5 - H) = .162 , \qquad (\Delta\epsilon_H \approx .138)$$

$$D(C_6H_5CH_2\text{-}H) = .133 , \qquad (\Delta\epsilon_{H_3} \approx .113) \tag{48}$$

$$D(H_3C\text{-}CH_3) = .133 , \qquad (\Delta\epsilon_{(C-C)} \approx .113)$$

The carbon atomic exchange integrals have been evaluated by Ufford (30) from the spectroscopic term values [see for instance Condon and Shortley (31) p. 178], thus:

$$K_{zz}^{ss} = \langle G_1 \rangle = \frac{1}{3} \langle G^1(2p,2S) \rangle_C = 0.1062$$

$$K_{zz}^{xx} = \frac{1}{2} K_{zz}^{+1+1} = \frac{3}{2} \langle F_2 \rangle = \frac{3}{50} \langle F^2(2p,2p) \rangle_C = 0.0130 \tag{49}$$

where $\langle G^1 \rangle$ and $\langle F^2 \rangle$ are the term value averages for the ground and excited states of C evaluated by Ufford. For sp^2 hybrids:

$$K = [\frac{1}{3} \langle G_1 \rangle_C + \langle F_2 \rangle_C] = 0.04406$$

The two center integrals have been evaluated for sp^2 hybrids by Altman (31) with Stater atomic orbitals. For interelectronic distances found in aromatic compounds, [see for instance (32) M234] these are

$$K_{zz}^{z'z'}(R_o = 2.53) = -0.1003 \qquad K_{zz}^{2'2'}(2.53) = 0.03557$$

$$K_{zz}^{z'z'}(2.91) = -0.04557 \qquad K_{zz}^{1s'1s'}(2.02) = 0.02737$$

$$K_{zz}^{z'z'}(3.49) \approx -0.015 \tag{49}$$

Altman also evaluated the carbon one center integrals which were higher in magnitude than those given by Ufford, however, this discrepancy is unlikely to occur for the two center integrals

since the Slater orbitals are known to be a better approximation far from the nucleus than close to it. The exchange integrals in Eq. (40) and (45) are then:

$$K_1 = 0.01669$$

$$K_2 = K_3 = 0.0085$$

$$\overline{K} \cong -0.030$$

$$K_{C'} \cong K_1 \qquad (50)$$

The values of K_s and $\Delta\epsilon'$ have been estimated by Karplus and Fraenkel:

$$K_s = .023$$

$$\Delta e' \cong 10$$

The proportionality constants thus obtained Q°, are given in Table I.

B) If the probability of finding an unpaired π-electron in the neighborhood of the nth ring atom, ρ_{on} is known then the Q's may be evaluated directly from the ESR spectra. The two conventional methods of approach to the problem, the VB and MO have been used successfully, and the comparison with the constants obtained above is given in Table I.

Hence, the agreement between theory and experiment is evident from Table I. It is also important to note that, as Das et al (50) have pointed out in the theory of the hyperfine interaction of the N^{14} atom, the contribution to the contact term from all the electrons in the system must be taken into account. Indeed, for molecular free radicals Karplus and Fraenkel (25) and

TABLE 1: SEMIEMPIRICAL VALUE OF Q

Particle	Spin	g-factor[a]	$\delta_n \times 10^9$ $(2Ra^3)$	$\frac{8\pi}{3}\delta_n\, a_{in}$[b] (oe)	calculated from the Q_1^0	Q_2^0	Q_2^0[c]
e^-	1/2	2.0023					
H^1	1/2	5.5854	80.79	506.2 (1S)			
H^2	1	0.8574	12.40	77.74 (1S)			
C^{13}	1/2	1.4043	20.31	31.82 $R(0)^2$ 5460 (1S)(2S) 1223 $(2S)^2$	48	-14	
N^{14}	1	0.4036	5.871	9.15 $R(0)^2$ (1S)(2S) 569 $(2S)^2$	23	-6	
O^{17}	5/2	0.7572	10.95	17.15 $R(0)^2$ 1390 $(2S)^2$			
F^{19}	1/2	5.2546	76.00	119.0 $R(0)^2$ 14,086 $(2S)^2$			
Na^{23}	3/2	1.4774	21.37	33.93 $R(0)^2$ $(3S)^2$			
S^{33}	3/2	0.4285	6.198	9.70 $R(0)^2$			

Semi empirical value of Q (oe.)

Correlation Interaction			calculated from the unpaired electron density and ESR spectra					
	Q_H^0 or $Q_{C'}$	$Q_{H_3}^0$	Q_1	Q_2	$Q_{2'}$ (c)	S_1	Q_H	Q_{H_3}
	-30 (d)	21 (e)					-21+17 (f) ±(22 to 23) (h)	10 (g) ±(20 to 32) (i)
	-4	3					±4.7 (j)	
-12.7 (c)	-18		±50 (k) 56.5 (n)	∓14 (k)	±15.6 (l)	∓9.8 (k) -12.7 (n)	±22 (m)	
-15.4 (o)	-8		± 25 (p)		±14 (q)			
							±39.3 (s)	

(a) The g-factors ($g_n = \frac{\mu_n}{I_n}$) are taken from the table of experimental values given by Ramsey, N.F., "Nuclear Moments", John Wiley and Sons, Inc. N.Y. (1953).

(b) Except for the H:IS atomic orbital the value of $R(o)^2$ has been evaluated from Hartree-Fock wave functions, see Hartree, D.R. "The Calculation of Atomic Structures", John Wiley and Sons, Inc., N.Y. (1957)(Appendix 2), Roothaan, C.C.J., L.M. Sachs and A.W. Weiss, Rev. Mod. Phys. 32, 186 (1960); Allen, L.C., J. Chem. Phys 34, 1156 (1961).

(c) Q_2' is the contribution from neighborning atoms in the π-electron system other than C.

(d) From the work in references (2), (24), (26), and (34).

(e) From the work in reference (27).

(f) From the ESR spectrum of $CH(COOH)_2$ (42)(43).

(g) From the NMR shifts of $V(C_5H_7O_2)_3$ (49).

(h) From the work of references (2), (26), and (45).

(i) From the work of references (26)(27) and (52).

(j) From the work in reference (36).

(k) From the work in references (25) and (47).

(l) Contribution from the virtual process ($\sigma_{CO} \longrightarrow \sigma_{CO}^*$) determined from the C^{13} splitting of the dihydroxysemiquinone ion (52).

(m) From the work in reference (52) for the methyl derivatives of the p-benzosemiquinone ion.

(n) From the work of references (25), (37) and (41) for the C^{13} splitting in the CH_3 radical.

(o) From the work in reference (50) for atomic N^{14}.

(p) From the work in reference (40).

(q) From the work in reference (39) for the tetracyanoethylene negative ion.

(r) From the work in reference ( ) for the Wurster's flue ions.

(s) From the work in reference (46) for the tetrafluono p-benzosemi quinone ion.

Ben Jémia and Lefebvre (51) estimate that for each C-H bond excitation the virtual processes ($c{:}1s \rightarrow \sigma^*$) account for 15% (-4.12 oe) of the total contributions, to the C^{13} splitting in the CH_3 and CH radicals.

The a priori knowledge of ρ_{on} is therefore of utmost importance since it enables the proper assignment of a chemical structure to a free radical from its ESR structure.

Applications

The importance of the two particle correlation in a chemical bond is the most significant contribution to be derived from this type of calculation. In general, it is found that the hyperfine coupling constants at the end of a bond are of opposite sign, and therefore arise from antiparallel spin polarization. This is a consequence of the combined effects of the Pauli exclusion principle and the correlation interaction, which demand that the probability of finding two electrons of unlike as well as like spin in the same neighborhood be zero.

Using the VB method to interpret the hyperfine splitting in triphenyl methyl, Brovetto and Ferroni (53) found that the π-electron densities alternate in sign for neighboring aromatic carbon atoms, whereas the single determinant Hückel MO approximation without overlap would predict no change in sign (26). This however is a consequence of the mathematical approximations. Since in the VB method the dominating terms are the bond exchange energies, the electrons remain far apart, in the resulting wave function, slightly more than the actual repulsion energy would demand (5). Conversely in the MO approximation, only the electrons

of like spin remain apart due to the antisymmetry condition (Fermi correlation) but if the correlation property is introduced by means of a series expansion where the perturbation is the two electron interaction, the two methods converge to the same answer.

An example of academic interest, in which both approximations have been used, is the allyl radical discussed by McConnell and Chesnut, The VB wave function is discribed in terms of four particles, three electrons and one hole, with $\frac{4!}{2!3!} = 2$ cannonical structures in the Pauling-Rummer diagram, (see for instance (7) chapter 13):

$$(\Pi) = \frac{1}{\sqrt{2}}\left[(\Pi_1) + (\Pi_2)\right] = \frac{1}{\sqrt{2}}\left[1 + \underset{\sim}{P}_{C_1C_3}\right](\Pi_1) \tag{52}$$

where

$$(\Pi_1) = \frac{1}{\sqrt{2}} \begin{matrix} C_1 & - & C_2 \\ O & - & C_3 \end{matrix} - \begin{matrix} C_1 & - & C_2 \\ O & - & C_3 \end{matrix}$$

$$(\Pi_2) = \frac{1}{\sqrt{2}} \begin{matrix} C_1 & C_2 \\ O & C_3 \end{matrix} - \begin{matrix} C_1 & C_2 \\ O & C_3 \end{matrix}$$

Here the Slater determinant wave functions are expressed symbolically. The atomic orbitals which are bonded together are connected by an arrow pointing towards the spin function α. and the unpaired orbital is bonded to the hole.

The probability of finding an unpaired electron in the neighborhood of Cn is then obtained directly from the superposition diagram:

$$\rho_{no} = \sum_{ij} \frac{(-1)^{n_{ij}+1}}{2^{b-c_{ij}}} \rho_{ij}, \quad \{(\Pi) = \sum_i B_i(\Pi_i)\}$$

where b is the number of π-electron bonds, c_{ij} the number of closed contours in the superposition diagram of (Π_i) and (Π_j) and n_{ij} the number of bonds which separate n from the hole in a closed contour. The terms are zero if the hole and C_n are in different closed contours. Thus, for the allyl radical the VB approximation yields:

$$\rho_{10} = \rho_{30} = \frac{2}{3}$$

$$\rho_{20} = -\frac{1}{3}$$

In the MO approximation the transformation which minimizes the one π-electron energy has been obtained by Chalvet and Daudel (54)

$$\underset{\sim}{T} = \begin{pmatrix} 0.4357 & 0.7217 & 0.6022 \\ 0.5836 & 0 & -0.8994 \\ 0.4537 & -0.7217 & 0.6022 \end{pmatrix}$$

with energies

$$\epsilon_1 = 1.4934\ \beta$$
$$\epsilon_2 = -1.540\ \beta$$
$$\epsilon_3 = -1.339\ \beta$$

β is the benzene resonance integral and the corresponding ℓcao mo's are used to generate the Slater determinants which form the basis set for the expansion of the π-electron system, see Eq. (22):

$$^2(\Pi) \cong \underset{\sim}{B}^{+\,2}(\underset{\sim}{\Pi}) \qquad (53)$$

where

$$\underset{\sim}{B} = \begin{pmatrix} 0.9249 \\ -.2049 \\ -.3133 \\ -.0660 \end{pmatrix}, \qquad (\underset{\sim}{\Pi}) = \begin{pmatrix} (\Pi_1) \\ (\Pi_2) \\ (\Pi_3)_1 \\ (\Pi_3)_2 \end{pmatrix}$$

and

$$^2(\Pi_1) = ||\pi_1\bar{\pi}_1\pi_3||$$

$$^2(\Pi_2) = ||\pi_2\bar{\pi}_3\pi_3||$$

$$^2(\Pi_3)_1 = {}^2\underset{\sim}{\mathcal{O}}||\pi_1\bar{\pi}_2\pi_3||$$

$$= \sqrt{\frac{2}{3}}\,\{||\pi_1\bar{\pi}_2\pi_3|| - \frac{1}{2}||\pi_1\pi_2\bar{\pi}_3|| - \frac{1}{2}||\bar{\pi}_1\pi_2\pi_3||\}$$

$$^2(\Pi_3)_2 = \frac{1}{\sqrt{2}}\,\{||\bar{\pi}_1\pi_2\pi_3|| - ||\pi_1\pi_2\bar{\pi}_3||\}$$

and (2)

$$\rho^{\pi}_{01} = \rho^{\pi}_{03} = 0.57$$

$$\rho^{\pi}_{02} = -0.11$$

Here the sign of the coupling constant is also found to alternate along the bonds. This is a general characteristic of the type of compound defined as an "Alternant Hydrocarbon."

The problems of actual interest are more complicated than the allyl radical, and as the number of electrons increase the MO approximation with the two electron correlation taken into account is found to be most suitable. For some aromatic free radicals the method of "alternant molecular orbitals" developed by Löwdin (4) can be applied with some degree of success. An

alternant hydrocarbon is a compound where the aromatic system can be divided into two subsets of atoms, I and II, in such a manner, that no two atoms of a subset are bonded together. It is then a characteristic of the alternant hydrocarbons that the single electron MO's occur in pairs, with equidistant energy separation from a zero level, in the same manner as electrons and holes are situated with respect to the conduction band:

$$\psi_i = \sum_{\nu \text{ in } I} T_{\nu i} \bar{\phi}_\nu + \sum_{\mu \text{ in } II} T_{\mu i} \bar{\phi}_\mu, \text{ with energy } E_o - \epsilon_i$$

$$\psi_{i'} = \sum_{\nu \text{ in } I} T_{\nu i} \bar{\phi}_\nu - \sum_{\mu \text{ in } II} T_{\mu i} \bar{\phi}_\mu, \text{ with energy } E_o + \epsilon_i \qquad (54)$$

For convenience the $\bar{\phi}$ are orthonormal atomic orbitals which are obtained from the real atomic orbitals ϕ by means of the following transformation:

$$\bar{\underset{\sim}{\phi}} = \underset{\sim}{S}^{-\frac{1}{2}} \underset{\sim}{\phi} = (\underset{\sim}{I} + \underset{\sim}{s})^{-\frac{1}{2}} \underset{\sim}{\phi}, \quad [s_{ij} = \int \phi_i^{(1)} \phi_j^{(1)} d\underset{\sim}{x}_1 - \delta_{ij}]$$

or

$$\bar{\phi}_\nu = \phi_\nu - \frac{1}{2} \sum_\xi{}' \phi_\xi S_{\xi\nu} + \frac{3}{8} \sum_{\xi\eta}{}' \phi_\xi S_{\xi\eta} S_{\xi\nu} + \cdots \qquad (55)$$

The electronic system may then be described in terms of the lcao mo's:

$$\begin{pmatrix} \psi_{iI} \\ \psi_{iII} \end{pmatrix} = \begin{pmatrix} \cos\theta_i & \sin\theta_i \\ \cos\theta_i & -\sin\theta_i \end{pmatrix} \begin{pmatrix} \psi_i \\ \psi_{i'} \end{pmatrix}$$

which are used to construct the single Slater determinant D used to generate the doublet state:

$$(\Pi) = {}^2\underset{\sim}{\mathcal{O}}\, D \qquad (56)$$

where

$$D = ||\psi_{1I}\,\bar{\psi}_{1II} \cdots \psi_{nI}\,\bar{\psi}_{nII}\,\psi_o||$$

$$= \sum_{j=1}^{n} \sum_{k}^{k+j} (\cos\theta)^{2n-j} (\sin\theta)^{j} \Big\{ ||\cdots\psi_k,\bar{\psi}_k \cdots \psi_{(k+j)},\bar{\psi}_{(k+j)} \cdots \psi_o|| - ||\cdots\psi_k\bar{\psi}_{k'} \cdots \psi_{(k+j)'}\bar{\psi}_{(k+j)} \cdots \psi_o|| \Big\}$$

when the parameter θ is independent of k, and the unpaired electron orbital is denoted by ψ_o. Here the significance of the angle θ is as follows:

$\theta = 0°$, $\psi_{iI} = \psi_{iII} = \psi_i \equiv$ lower half, bonding MO's

$\theta = 45°$, $\begin{pmatrix}\psi_{iI}\\ \psi_{iII}\end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix}\begin{pmatrix}\psi_i\\ \psi_{i'}\end{pmatrix} \equiv$ purely alternant MO's

$\theta = 90°$, $\psi_{iI} = -\psi_{iII} = \psi_{i'} \equiv$ upper half, antibonding MO's

The ground state wave function will correspond to a value of $\tan\theta < 1$ since for $\theta = 45°$ the exchange integrals tend to zero. This means that in Eq. (56) $\tan\theta$ is a perturbation which introduces configuration interaction into the π-electron system.

For an odd alternant hydrocarbon with (2n+1) aromatic carbon atoms and (2n+1) electrons the wave function is then (55)

$$^2(\Pi) = \frac{1}{\sqrt{N}} \prod_{i=1,\cdots n} \cos^2\theta_i \Big\{ ||\psi_1\bar{\psi}_1 \cdots \psi_n\bar{\psi}_n\,\psi_o|| + c_o(3) \sum_i \tan\theta_i \,[\,||\cdots\psi_i\psi_{i'}\bar{\psi}_o\cdots|| - \tfrac{1}{2}||\cdots\bar{\psi}_i\psi_{i'}\psi_o\cdots|| - \tfrac{1}{2}||\cdots\psi_i\bar{\psi}_{i'}\psi_o\cdots||\,] + \cdots \Big\} \qquad (55)$$

where the coefficient for the doublet operator for three electrons is $c_o(3) = 2/3$ [see for instance, Löwdin (4)] and N is the normalization constant.

$$N = \prod_{i=1,\cdots n} \cos^4\theta_i \left[1 + \frac{2}{3} \sum_{i=1}^{n} \tan^2\theta_i + \cdots\right]$$

The π-electron density matrix correct to second order is then:

$$\rho_o = \frac{1}{1+\frac{2}{3}\sum_{i=1}^{n}\tan^2\theta_i+\cdots}\left\{\rho_{oo}\left(1-\frac{2}{9}\sum_{i=1}^{n}\tan^2\theta_i\right)+\frac{4}{3}\sum_{i=1}^{n}\tan\theta_i\left[\rho_{ii'}+\frac{1}{3}\tan\theta_i(\rho_{ii}+\rho_{i'i'})\right]+\cdots\right\} \tag{56}$$

where ρ_o is the density matrix for the orthonormal set $\underset{\sim}{\Phi}$ and for the sake of simplicity the superscript π has been eliminated. Thus, in the neighborhood of C_ν:

$$\rho_{o\nu} = \frac{1}{1+\frac{2}{3}\sum_i \tan^2\theta_i+\cdots}\left\{T_{\nu o}^2\left(1-\frac{2}{9}\sum_{i=1}^{n}\tan^2\theta_i\right)\right.$$

$$\left. + \frac{4}{3}\sum_i T_{\nu i}\tan\theta_i\left[T_{\nu i'}+\frac{2}{3}T_{\nu i}\tan\theta_i\right]+\cdots\right\} \tag{57}$$

Now since the symmetry requires that for an odd alternant hydrocarbon $T_{o\mu}$ (μ in II) $\equiv 0$ the π-electron density in the neighborhood of C_μ will be negative. The general result is thus applicable to the allyl radical which is the smallest odd alternant free radical.

The even alternant hydrocarbons, with 2n aromatic atoms form two types of free radicals according to whether an electron is added or abstracted from the system. The π-electron wave function for the positive ion with (2n-1) electrons is then:

$$
\begin{aligned}
{}^2(\Pi)^{(+)} = \frac{\prod\limits_{i=1,\ldots n-1}}{\sqrt{N_+}} \Bigg\{ & \cos^2\theta_i \ \cos\theta_n \,||\psi_1\bar{\psi}_1 \cdots \psi_{n-1}\bar{\psi}_{n-1}\psi_n|| \\
& + \sin\theta_n \,||\psi_1\bar{\psi}_1 \cdots \psi_{n-1}\bar{\psi}_{n-1}\psi_n|| \\
& + \frac{2}{3}\sum_i \tan\theta_i \Big[\cos\theta_n \Big(||\cdots\psi_i\psi_{i'}\bar{\psi}_n\cdots|| - \frac{1}{2}||\cdots\bar{\psi}_i\psi_{i'}\psi_n\cdots|| \\
& + \frac{1}{2}||\cdots\psi_i\psi_{i'}\psi_n\cdots|| \Big) \\
& + \sin\theta_n \Big(||\cdots\psi_i\psi_{i'}\bar{\psi}_{n'}\cdots|| - \frac{1}{2}||\cdots\bar{\psi}_i\psi_{i'}\psi_{n'}\cdots|| - \frac{1}{2}||\cdots\psi_i\bar{\psi}_{i'}\psi_{n'}\cdots|| \Big) \Big] \\
& + \cdots \Bigg\}
\end{aligned}
\tag{58a}
$$

where

$$
N_+ = \prod_{i=1,\cdots n-1} \cos^4\theta_i \left[1 + \frac{2}{3}\sum_{i=1}^{n-1} \tan^2\theta_i + \cdots\right]
$$

For the negative ion the extra electron is to be placed in an orbital orthonormal to ψ_{nI} in Eq. (54):

$$
\psi_{n,III} = -\sin\theta_n\psi_n + \cos\theta_n\psi_{n'}.
$$

Thus,

$$
\begin{aligned}
{}^2(\Pi)^- = \prod_{\substack{i=1,\cdots n \\ \sqrt{N_-}}} & \cos\theta_i(1+\tan^2\theta_n)\Big\{\cos\theta_n \|\psi_1\bar{\psi}_1\cdots\psi_n\bar{\psi}_n\psi_{n'}\| \\
& + \sin\theta \,\|\psi_1\bar{\psi}_1\cdots\psi_{n'}\bar{\psi}_{n'}\psi_{n'}\| + \frac{2}{3}\sum_{i=1}^{n-1}\tan\theta_i\Big[\cos\theta_n\Big\{\|\cdots\psi_i\psi_{i'}\bar{\psi}_{n'}\cdots\| \\
& - \frac{1}{2}\|\cdots\bar{\psi}_i\psi_{i'}\psi_{n'}\cdots\| - \frac{1}{2}\|\cdots\psi_i\bar{\psi}_{i'}\psi_{n'}\cdots\|\Big\} \\
& + \sin\theta_n\Big\{\|\cdots\psi_i\psi_{i'}\bar{\psi}_{n}\cdots\| - \frac{1}{2}\|\cdots\bar{\psi}_i\psi_{i'}\psi_{n'}\cdots\| \\
& - \frac{1}{2}\|\cdots\bar{\psi}_i\psi_{i'}\psi_{n'}\cdots\|\Big\}\Big]\cdots\Big\}
\end{aligned}
\tag{58b}
$$

where

$$
N^- = \prod_{i=1,\cdots n}\cos^4\theta_i(1+\tan^2\theta_n)^2[1+\frac{2}{3}\sum_{i=1}^{n-1}\tan^2\theta_i]
$$

The π-electron density matrices for the two free radicals will have similar functional dependence on θ_i:

$$
\begin{aligned}
\rho_o(+\text{ ion}) \; & \frac{1}{1+\frac{2}{3}\sum_{i=1}^{n-1}\tan^2\theta_i}\Big\{[1-\frac{2}{9}\sum_{i=1}^{n-1}\tan^2\theta_i][\rho_{nn}\cos^2\theta_n + \rho_{n'n'}\sin^2\theta_n] \\
& + \frac{4}{3}\Sigma\tan\theta_i\,[\rho_{ii'} + \frac{1}{3}\tan\theta_i(\rho_{ii}+\rho_{i'i'})] \\
& + \rho_{nn'}\sin^2\theta_n\,[1+\tan^2\theta_n - \frac{2}{9}\sum_{i=1}^{n-1}\tan^2\theta_i] + \cdots
\end{aligned}
$$

$$
\rho_o(-\text{ ion}) = \underset{\sim}{P}_{nn'}\,\rho_o(+\text{ ion}) \tag{59}
$$

Now, since Coulson and Rushbrooke (56), Pople (57) and McLacklan (58) have shown that $\rho_{n'n'} = \rho_{nn}$ the physical significance of Eq. (59) is that for a constant σ-π parameter Q_H the correct

electron densities for the even alternant hydrocarbons with C_{2v}, or higher, symmetry may be approximated from the Hückel MO approximation:

$$\frac{\rho_{o\nu}(\exp)}{\rho_{o\nu}(\text{Hückel})} \cong 1 + \frac{8}{9}\sum_{i=1}^{n-1} \tan^2\theta_i \left(\frac{T_{\nu i}^2 + T_{\nu i'}^2}{2T_{\nu n}^2} - 1\right) + \cdots \qquad (60)$$

Thus if the electron density at the 2n carbon atoms could be measured, the $\tan^2\theta_i$ correlation parameters would be obtained by inverting the matrix in Eq. (60). This in general is not possible since some of the substituent in the aromatic system do not have a magnetic moment or the abundance of the paramagnetic nuclei is beneath the detection limit. The validity of the Hückel approximation is indeed evident from the ESR spectra of the ions of anthracene, tetracene, perylene and naphthacene observed by Weissman de Boer and Conradi (59) and Carrington, Dravnicks and Symons (60). Here the splitting for the unipositive and negative ions is different indicating that there exists a different correlation interaction for two different ions where:

$$\frac{\rho_{o\nu}(\exp \text{ for the + ion})}{\rho_{o\nu}(\exp \text{ for the - ion})} \cong 1 + \frac{8}{9}\sum_{i=1}^{n-1} (\tan^2\theta_{i+} - \tan^2\theta_{i-})\left(\frac{T_{\nu i+}^2 + T_{\nu i'}^2}{2T_{\nu n}^2} - 1\right) + \cdots \qquad (61)$$

Thus The complexity of the problem increases further as heteroatoms are introduced into the aromatic system. However, if the Coulomb and resonance integrals for the heteroatom can be estimated with some degree of accuracy (61), then the single determinant Hückel MO's predict electron densities in fair agreement with the experimental values (26)(45). Hence, these compounds are only

pseudoalternant hydrocarbons since the bonding and antibonding symmetry orbitals are not equidistant from a zero level. However, the two particle correlation can still be evaluated from Eq. (60). Also, great caution should be practiced in using the universal value of the σ-π parameter since Q_H is a function of the σ-bond angle and the σ-bond distances.

SUMMARY

In conclusion, it is important to note that

(a) For every type of σ-bond in an aromatic free radical, there exists a semiempirical constant, known as the σ-π parameter, which, together with the probability of finding an unpaired π-electron in that neighborhood, may be used to predict the hyperfine splitting constant at the nucleus of an atom forming the bond.

(b) The sign of the hyperfine coupling constant is found to alternate along a chain of atoms as a consequence of strong, two electron correlation interaction which demands opposite spin polarization at the ends of a chemical bond.

(c) The success of the Hückel MO approximation, with a single Slater determinant, in predicting the correct π-electron densities in alternant as well as pseudoalternant free radicals is due to the fact that the correction for two particle correlation interactions can be introduced by pairing the orbitals which lie symmetrically above and below a zero level. The correct electron density is then given by the Hückel approximation with a small correction which is a function of a π-electron correlation parameter θ_i.

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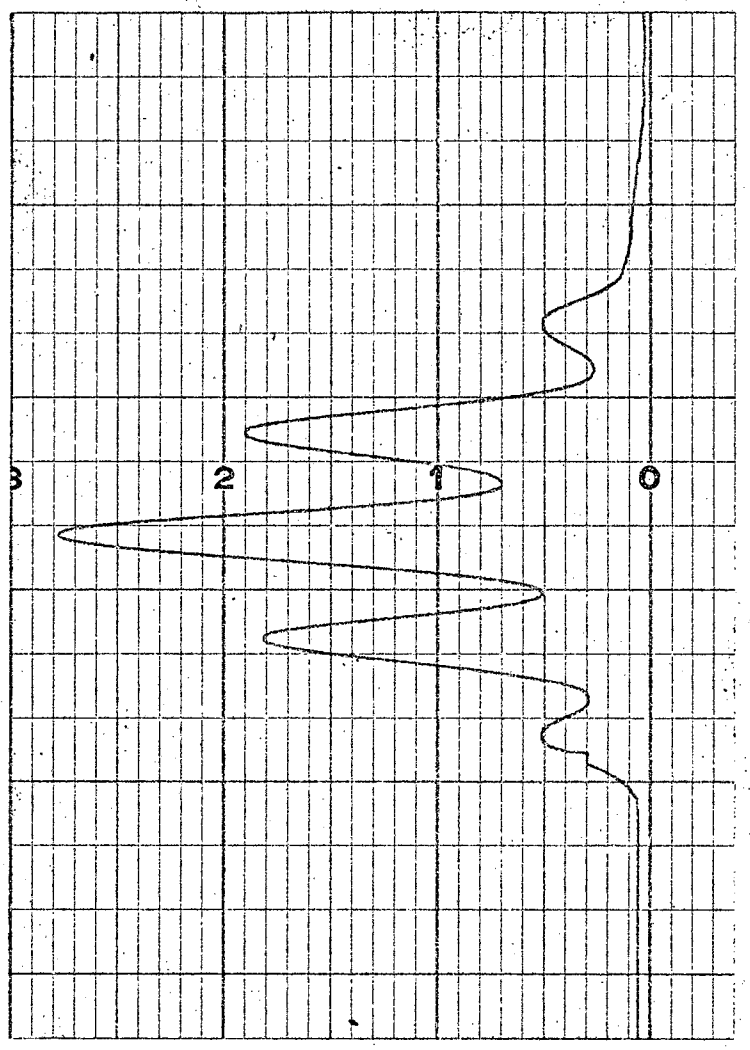

Fig 1 ESR Spectrum of p-benzosemiquinone.

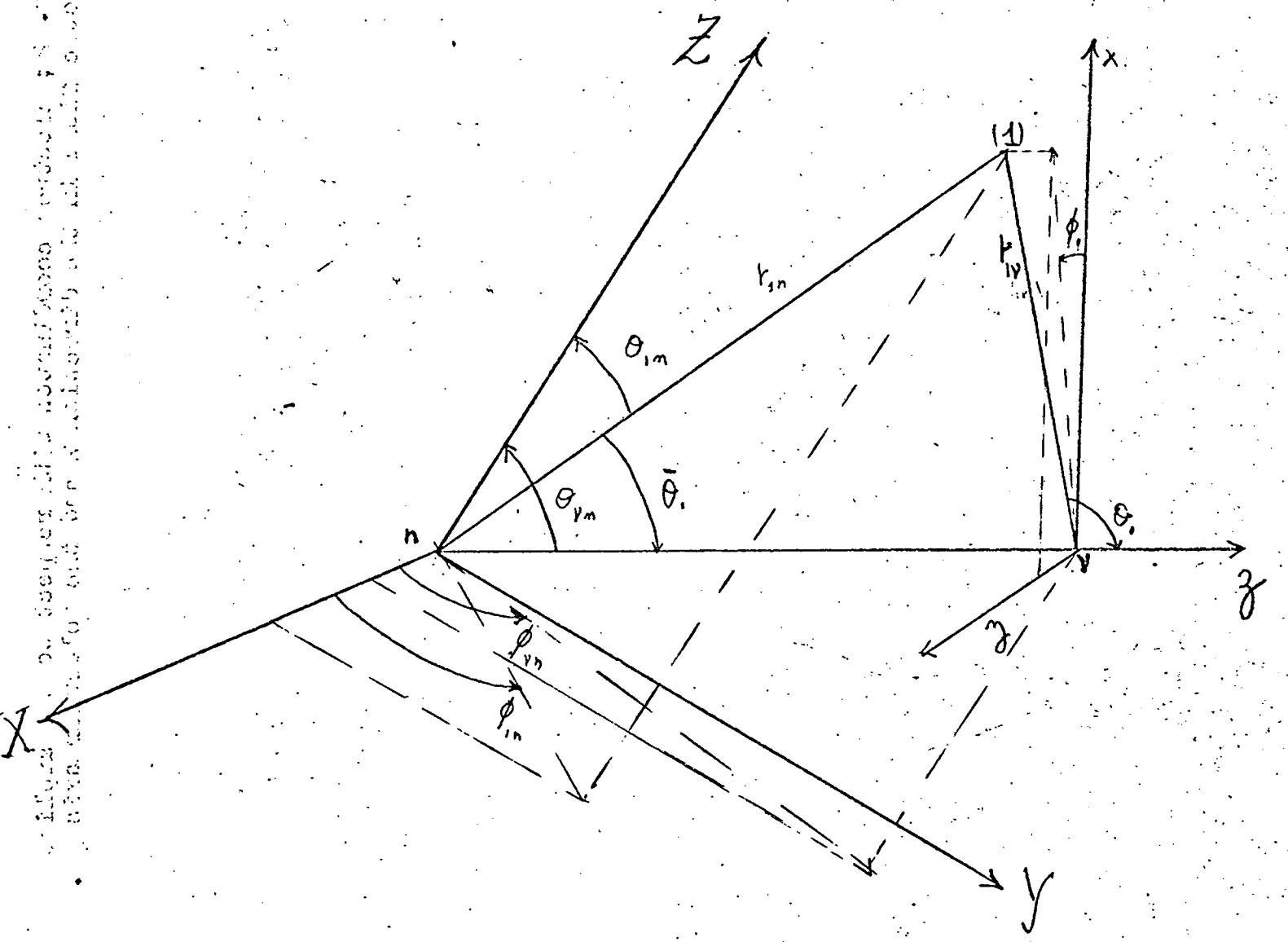

Fig 2: ELECTRON COORDINATES WITH RESPECT TO THE AXIS OF QUANTIZATION Z AND THE MOLECULAR ζ .

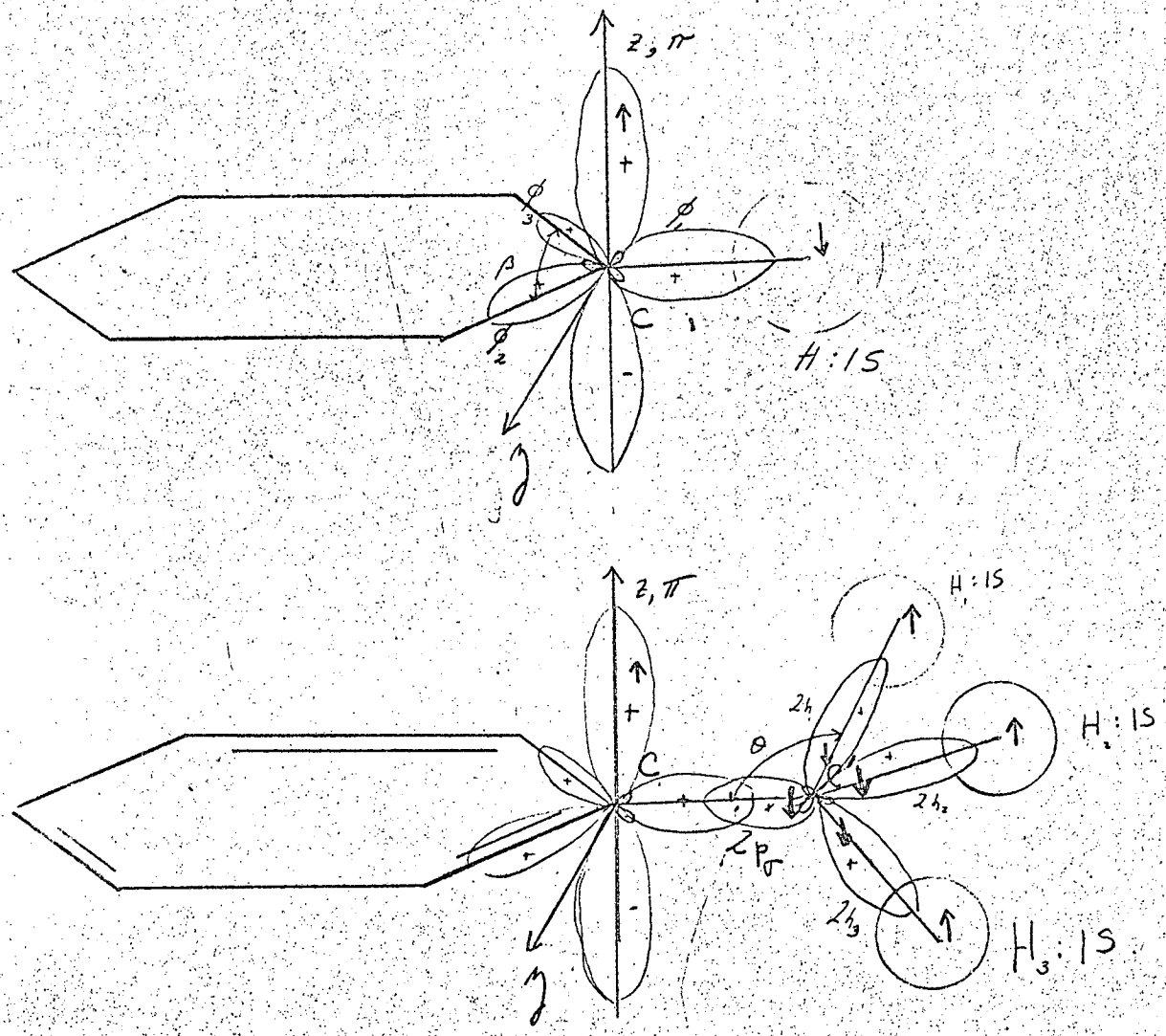

Fig. 3: Directed hybrid orbitals in an aromatic hydrocarbon and $-CH_3$ group. (The spin polarization at the corresponding nuclei has been indicated by an arrow in the orbital).

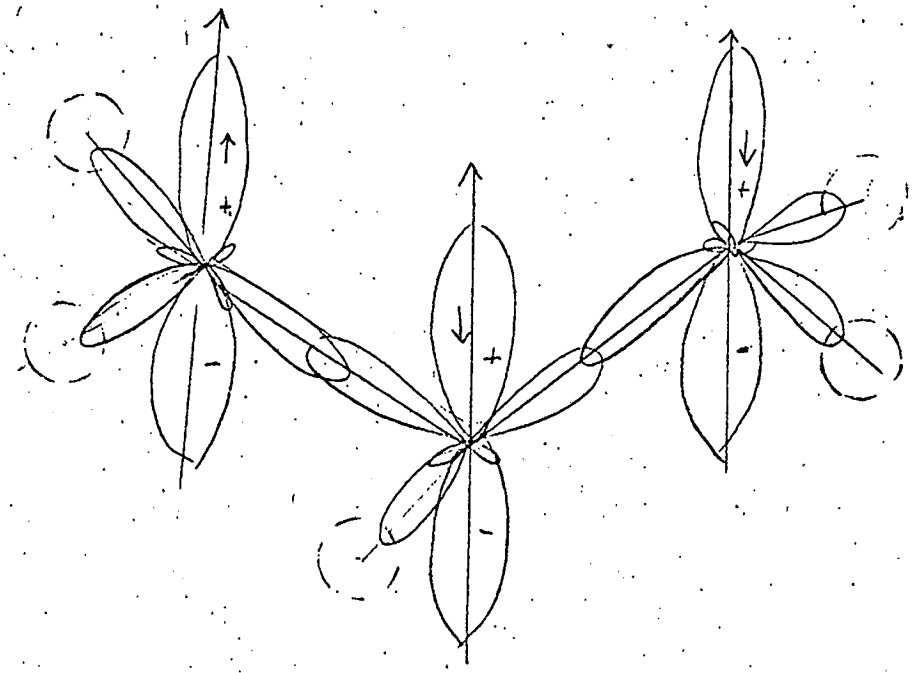

Fig. 4: Directed hybrid orbitals in the allyl radical. (The spin polarization at the nucleus has been indicated by an arrow in the corresponding orbitals):

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