I

STUDIES OF THE SPIN DISTRIBUTIONS IN AROMATIC RADICALS

II

ELECTRON RESONANCE STUDIES OF SOME SANDWICH COMPOUNDS

Thesis by

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ABSTRACT

I. Studies of the Spin Distributions in Aromatic Radicals

It is shown that if conventional molecular orbital theory is extended in such a way as to include electron correlation, according to the proposal of Löwdin, negative spin density is predicted at unstarred positions of odd alternant hydrocarbon radicals. However, it is found that Löwdin's suggested method of alternant orbitals is not a sufficiently good approximation to the ground state of an even alternant hydrocarbon ion for the effects of electron correlation on the π electron spin density to be estimated. As a check of the validity of this approximate wave function for the radicals, the method of alternant orbitals function for the allyl radical is developed and compared numerically with the results of a π-π configuration calculation.

Calculation of spin densities by simple valence bond theory is described for several odd alternant radicals. For the perinaphthenyl and trivinylmethyl radicals, the secular equation is solved and the ground state eigenvector is derived. Normalization gives the coefficients of the various structures for the benzyl, α-methylnaphthanyl and β-methylnaphthanyl radicals from the coefficient ratios given by Pauling and Wheland.

Equations are derived which relate the π electron spin density at an atom in the π molecular framework to that hyperfine coupling constant due to the atom itself. Previously, McConnell and Chesnut have shown that there is a linear relation between the proton coupling constant and the π electron spin density at the adjacent carbon atom in π molecular radicals. In the case of the coupling constant of the carbon atom itself, for instance, it is shown that the relation is also a linear one, but the spin density at any neighbor atom must be included. It is concluded that negative spin density at a neighbor results in "donation" of spin density to the atom in question and to the observation of an abnormally large coupling constant. Estimation of the necessary constants for C^{13} is carried out semi-empirically in a simple way.

II. Electron Resonance Studies of Some Sandwich Compounds

ESR signals from pure polycrystalline nickelocene and cobaltocene are observed at liquid helium temperature. Although little information of a quantitative nature can be obtained from a powder spectrum, comparison with the predictions of Robertson is made whenever possible. The ESR spectrum of vanadocene as a substitutional impurity in a single crystal of ferrocene at room temperature is measured. The angular dependence of the absorption peaks is interpreted using the spin Hamiltonian given by Schulz-Du Bois for the isoelectronic ion, Cr^{+3}. This analysis allows the evaluation of the splitting of the ground quartet which is present in zero magnetic field, $|2D| = 50$ Kmc.

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Section 1

STUDIES OF THE SPIN DISTRIBUTIONS IN AROMATIC RADICALS

Introduction

One of the most interesting applications of electron spin resonance has been to the study of the electronic structure of the neutral radicals and singly charged ions of aromatic hydrocarbons by means of the hyperfine interaction (1, 2, 3). The unpaired spin (s) can move over the entire conjugated network of the carbon atoms, and the magnetic nuclei serve as probes to measure the density of electron spin at various positions within the molecule. It has been shown (3) that the Fermi contact hyperfine interaction a_H between the proton and electron spins of the radical in solution is directly proportional to the "unpaired electron spin density," ρ, at the carbon atom of the C-H bond.

Dirac's relativistic theory shows that the spinning electron is magnetically equivalent to an electric current (4)

$$j = \frac{e\hbar}{2mc} \text{ curl} \langle \Psi^{*} \underset{\sim}{\sigma} \Psi \rangle . \qquad \text{(I-1)}$$

Besides the dipole-dipole coupling of the nuclear and electron spins which averages to zero in a rapidly tumbling molecule in solution, there will remain the Fermi contact interaction (5)

$$\mathcal{H} = \frac{8\pi}{3} \, g \left(\frac{e\hbar}{2mc}\right) \frac{\mu_I}{I} \sum_{k} \delta \left(r_k - r_N\right) S_k \cdot I_N \qquad \text{(I-2)}$$

which is proportional to the unpaired electron spin density (3)

$$\rho(r_N) = \frac{1}{S_z} \langle \Psi^* | \sum_k \delta(r_k - r_N) S_{\mu z} | \Psi \rangle \qquad \text{(I-3)}$$

at the nucleus itself.

The discovery of hyperfine interaction from aromatic ring protons (6) was unexpected because the odd electron of the radical moves in a π molecular orbital with a node in the molecular plane of the C-H bond. Experiments with deuterated compounds (7) showed that the observed splitting was not caused by the vibrational bending of the C-H bond out of the molecular plane, and Bersohn (8) and McConnell (9) showed that σ - π electron exchange is responsible.

Figure I-1 represents the side view of an isolated C-H fragment with the C atom occurring in sp^2 hybridization. McConnell and Bersohn both used valence bond theory to explain the presence of unpaired spin on the hydrogen atom. The exchange integral $J(c\pi)$ mixes the normal structure I with the excited one II, and polarises the C-H bond, giving spin densities of

$$\pm \rho' = \frac{J(\pi h) - J(c\pi)}{2J(ch)} \qquad \text{(I-4)}$$

in h and c respectively. Reasonable values of the exchange integrals lead to

$$\rho' = -0.05 \qquad \text{(I-5)}$$

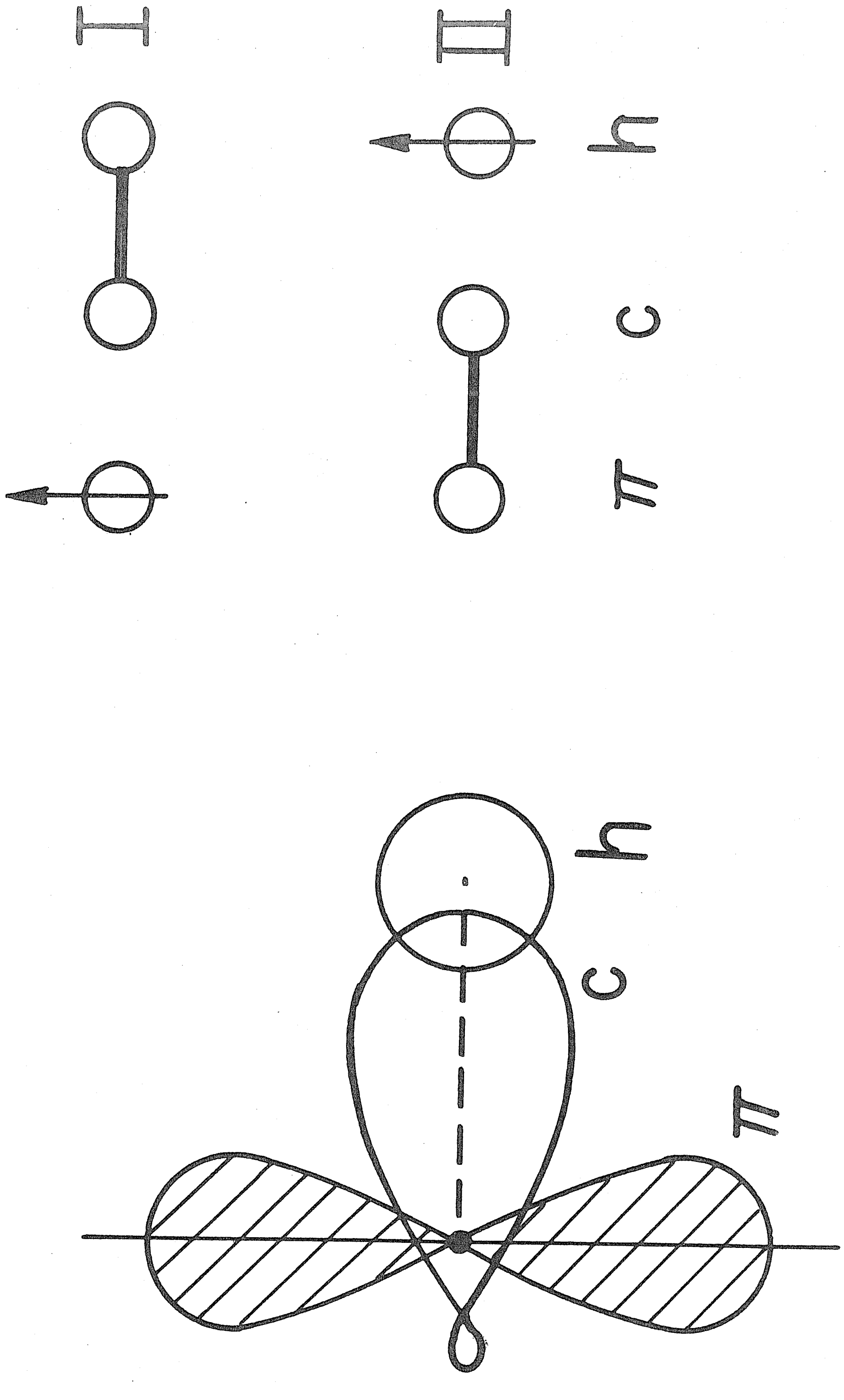


Fig. 1-1. Polarization of C-H bond by σ-π exchange interaction.

in agreement with experiment. Weissman (10) has treated the same problem with molecular orbital theory. In his theory the two electrons in the C-H bond occupy the orbital $\sigma = \frac{1}{\sqrt{2}}(c + h)$, while the anti-bonding orbital $\sigma^* = \frac{1}{\sqrt{2}}(c - h)$ is empty. The $\sigma - \pi$ exchange integral then mixes the normal state ψ_o with the excited doublet configuration ψ_1, again

$$\begin{aligned} \psi_o &= |\sigma\bar{\sigma}\pi| \\ \psi_1 &= \frac{1}{\sqrt{6}}\left|2\,\sigma\sigma^*\bar{\pi} - \sigma\bar{\sigma}^*\pi - \bar{\sigma}\sigma^*\pi\right| \end{aligned} \qquad (I-6)$$

polarising the spins ($\sigma\bar{\sigma} \equiv \sigma(1)\alpha(1)\sigma(2)\beta(2)$). McConnell (9) showed that simple molecular orbital theory predicts a linear relation between the π electron spin density on the carbon atom and the proton hyperfine interaction due to the bonded hydrogen atom

$$a_H = Q\rho\ . \qquad (I-7)$$

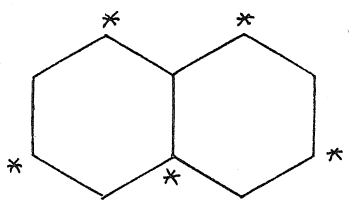
Since simple valence bond and molecular orbital theories give very similar values for ρ', it seems clear that I-7 holds independent of any approximation in the theoretical treatment of the π electrons; this point was studied using the Dirac vector model (3,11, 12). $\sigma - \pi$ exchange interaction was treated as a small perturbation and I-7 was proved without any restrictive assumptions about the π electron wave function.

A hydrocarbon radical is considered to be an ensemble of interacting C-H fragments, and it is with the electronic structure of these radicals that we shall be concerned in this section. In the pages which follow, predictions of the functions $\rho(r_N)$ from various approximations to the ground state wave functions, ψ, are investigated. In particular the method of alternant orbital molecular orbital theory (MAO) and the simple valence bond theory (SVB) approximations are studied. We shall find that both MAO and SVB (3) correctly predict the presence of negative spin density (electron density whose spin polarization is opposite to the total molecular spin polarization) in neutral aromatic radicals. Also equations similar to I-7 are developed which relate the spin density at a particular atom within the π framework to the contact hyperfine interaction due to the atom itself (e.g. C^{13}, N^{14}, S^{35}, etc.).

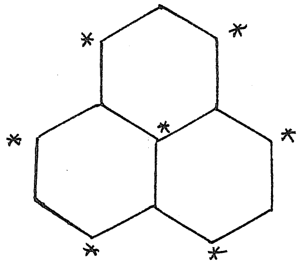
A. Method of Alternant Orbitals

Introduction

An alternant hydrocarbon (13,14) is a conjugated molecule whose spatial configuration is such that its member carbon atoms may be separated into two sets, starred atoms and unstarred atoms, such that no starred atom is bonded to any other starred atom. An example of an even alternant hydrocarbon is naphthalene, whose atoms may be separated in the manner,



and perinaphthenyl is an example of an odd alternant radical. If one adopts the convention that the starring will be carried out such that there are more starred atoms than unstarred, perinaphthenyl must be represented as



If the π electrons of these molecules are described by LCAO (linear combination of atomic orbital) molecular orbital theory, the set of conditions which leads to a minimum π-electron energy gives rise to a secular equation for the coefficients of the $2p_z$ atomic orbitals of the n bonded carbon atoms (15)

$$(\mathscr{H}_{rr} - E)\, c_r + \sum_{s \neq r} (\mathscr{H}_{rs} - S_{rs} E)\, c_s = 0; \quad r = 1, 2, \ldots, n; \qquad \text{(IA-1)}$$

where c_r -- coefficient of the $2p_z$ atomic orbital, χ_r, centered on carbon atom r.

$\mathscr{H}_{rs}$ -- $\langle \chi_r | \mathscr{H} | \chi_s \rangle$

$\mathscr{H}$ -- sum of one electron energy operators

S_{rs} -- $\langle \chi_r | \chi_s \rangle$.

We shall neglect overlap between atomic orbitals and suppose that each atomic orbital is normalized

$$S_{rs} = \delta_{rs}. \qquad \text{(IA-2)}$$

Further the energy of a molecular orbital, an eigenvalue of the determinant of the coefficients of IA-1, will be measured in terms of its difference from the coulomb integral for a carbon atom which is in the sp^2 hybridization, $\mathscr{H}_{rr}$. For hydrocarbons all these integrals $\mathscr{H}_{rr}$ are equal in value, and we can write the secular equation

$$-\epsilon c_r + \sum_s{}' \beta_{rs} c_s = 0; \quad r = 1, 2, \ldots, n \qquad \text{(IA-3)}$$

in which $\epsilon = E - \mathscr{H}_{rr}$ and $\beta_{rs} \equiv \mathscr{H}_{rs}$. If we now divide the atoms into those belonging to the two sets, the secular determinant of IA-3 takes the form (16)

$$\begin{vmatrix}
-\epsilon & 0 & \cdots\ 0 & \beta_{h+1,1} & \beta_{h+2,1} & \cdots\ \beta_{n,1} \\
0 & -\epsilon & \cdots\ 0 & \beta_{h+1,2} & \beta_{h+2,2} & \cdots\ \beta_{n,2} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & \cdots\ -\epsilon & \beta_{h+1,n} & \beta_{h+2,n} & \cdots\ \beta_{n,n} \\
\beta_{1,h+1} & \beta_{2,h+1} & \cdots\ \beta_{n,h+1} & -\epsilon & 0 & \cdots\ 0 \\
\beta_{1,h+2} & \beta_{2,h+2} & \cdots\ \beta_{n,h+2} & 0 & -\epsilon & \cdots\ 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\beta_{1,n} & \beta_{2,n} & \cdots\ \beta_{n,n} & 0 & 0 & \cdots\ -\epsilon
\end{vmatrix} = 0 \qquad \text{(IA-4)}$$

in which the atoms of one set are numbered from 1 to h and the atoms of the other set are numbered from h+1 to n. This is equivalent to writing down two secular equations, one for each set:

$$-\epsilon c_r + \sum_{s=h+1}^{n} \beta_{rs} c_s = 0 ; \ r = 1, 2, \ldots, h \qquad \text{(IA-5)}$$

and

$$-\epsilon c_r + \sum_{s=1}^{h} \beta_{rs} c_s = 0 ; \ r = h+1, h+2, \ldots, n. \qquad \text{(IA-6)}$$

Longuet-Higgins shows that the roots of IA-4 are related in the manner (16)

$$\underline{\text{n even}} \quad \epsilon_1 < \epsilon_2 < \ldots < \epsilon_{\frac{n}{2}} < 0 < \epsilon_{\frac{n}{2}+1} < \ldots < \epsilon_n \tag{IA-7}$$

with $\epsilon_{n-j+1} = -\epsilon_j$

$$\underline{\text{n odd}} \quad \epsilon_1 < \epsilon_2 < \ldots < \epsilon_{\frac{(n-1)}{2}} < \epsilon_{\frac{(n+1)}{2}} = 0 < \ldots < \epsilon_n \tag{IA-8}$$

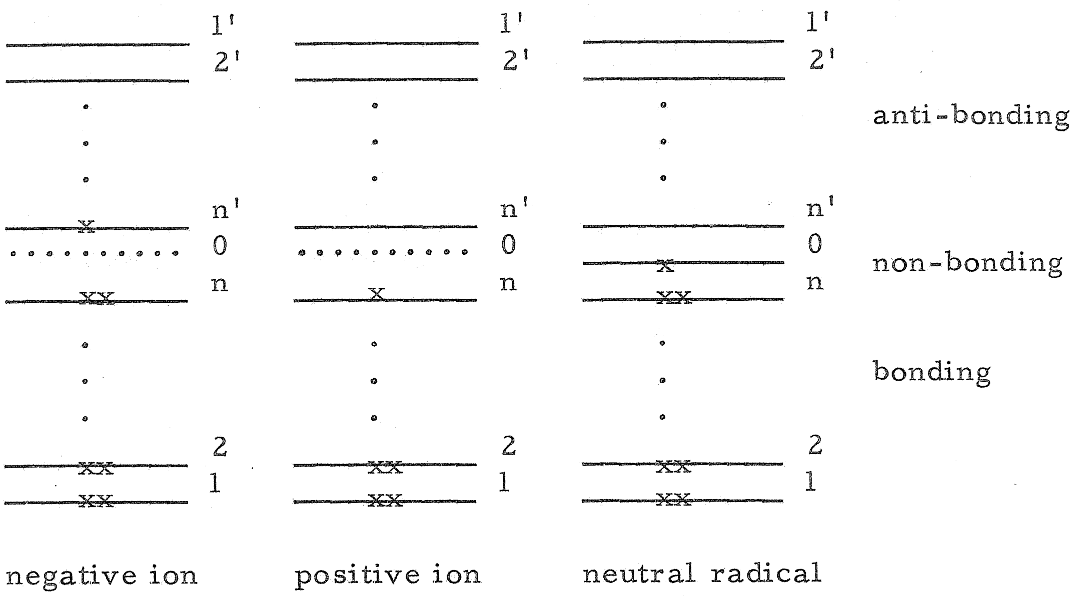
with $\epsilon_{n-j+1} = -\epsilon_j$.

The coefficient of the atomic orbital r which is a part of the molecular orbital n-j+1 is

$$\begin{aligned} \underline{\text{n even}} \quad & c_{r,n-j+1} = -c_{rj} \;;\; r = 1, 2, \ldots, h \\ & c_{r,n-j+1} = +c_{rj} \;;\; r = h+1, h+2, \ldots, n \end{aligned} \tag{IA-9}$$

$$\begin{aligned} \underline{\text{n odd}} \quad & c_{r,n-j+1} = -c_{rj} \;;\; r = 1, 2, \ldots, h \\ & c_{r,n-j+1} = +c_{rj} \;;\; r = h+1, h+2, \ldots, n \\ & c_{r,\frac{(n+1)}{2}} = 0 \;;\; r = 1, 2, \ldots, h . \end{aligned} \tag{IA-10}$$

Equations IA-7 - IA-10 show that there is a pairing property both of the energy and the coefficients of the molecular orbitals in alternant hydrocarbon molecules. The energy levels can be diagramed in the following way



For both the even and odd alternant hydrocarbons, there is symmetry about the zero of energy such that for each bonding molecular orbital there is a corresponding "conjugate" anti-bonding orbital whose energy is the negative of that of the bonding orbital. In the case of the odd alternant radical there is a non-bonding orbital with zero energy. The anti-bonding orbitals themselves can be derived from the bonding by replacing the coefficient of a starred atom by itself and by replacing the coefficient of the unstarred atom by its negative. Since the non-bonding orbital of the odd alternant case has no "conjugate" orbital, its coefficients on unstarred atoms is zero.

The Hamiltonian of IA-1 is a sum of one electron Hamiltonians, and electron correlation $(\frac{e^2}{r_{ij}})$ is not taken explicitly into account. When this effect is calculated explicitly, excited configurations in which electrons are permuted among all the levels in the energy diagram are mixed in with the ground molecular orbital configuration ψ_o. For example ψ_o is written for the odd alternant case

$$\psi_o = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 \ \ldots \ \phi_o| \qquad \text{(IA-11)}$$

and the monoexcited functions ψ_i are of the form

$$\psi_j = |\phi_1 \bar{\phi}_1 \ldots \phi_j \ldots \phi_o \bar{\phi}_o| \qquad \text{(IA-12)}$$

and

$$\psi_i = |\phi_1 \bar{\phi}_1 \ldots \bar{\phi}_i \ldots \phi_{K'} \ldots \phi_o| \qquad \text{(IA-13)}$$

etc.

Löwdin (17) has recently proposed another way in which electron correlation may be introduced into the ground state wave function. Electrons with the same spin are automatically correlated by the Pauli principle, but electrons with unlike spins have no similar mechanism to avoid proximity and a resulting large Coulomb repulsion. Löwdin's proposal is essentially to place electrons with different spins into different spatial orbitals such that the probability of close approach is reduced automatically. Thus, for alternant molecules, the wave function has the form

$$T_o = |(a\phi_1 + b\phi_{1'})(a\phi_2 + b\phi_{2'})\ldots(a\phi_n + b\phi_{n'})(a\bar{\phi}_1 - b\bar{\phi}_{1'})\ldots(a\bar{\phi}_n - b\bar{\phi}_{n'})| \qquad \text{(IA-14)}$$

where again the bonding molecular orbital of IA-14 is ϕ_j

$$\phi_j = \sum_{r=1}^{h} c_{jr}\chi_r + \sum_{r=h+1}^{n} c_{jr}\chi_r \quad \text{with energy } \epsilon_j$$

and $\phi_{j'}$ is the conjugate anti-bonding orbital

$$\phi_{j'} = -\sum_{r=1}^{h} c_{jr}\chi_r + \sum_{r=h+1}^{n} c_{jr}\chi_r \quad \text{with energy} \; -\epsilon_j \, .$$

a and b are parameters which are determined by minimization of the energy and, since the MO's are normalized, are related by the equation

$$a^2 + b^2 = 1 \tag{IA-15}$$

from which the single parameter ϑ can be defined by

$$\begin{aligned} \cos\vartheta &= a \\ \sin\vartheta &= b \, . \end{aligned} \tag{IA-16}$$

It must be recognized that the one-electron orbitals combined in this way are no longer normalized.

$$\int (a\phi_i + b\phi_{i'})(a\phi_j - b\phi_{j'})\, d\tau = \cos 2\vartheta\, \delta_{ij} \, . \tag{IA-17}$$

In the development which will follow we shall be interested in the paramagnetic neutral odd alternant radicals and the singly charged ions of the even alternant hydrocarbons. The MAO description of the first case is written

$$T_o = \left| (a\phi_1 + b\phi_{1'}) \ldots (a\phi_n + b\phi_{n'})\, \phi_o (a\bar{\phi}_1 - a\bar{\phi}_{1'}) \ldots (a\bar{\phi}_n - b\bar{\phi}_{n'}) \right| \tag{IA-18}$$

The wave functions necessary for the even alternant ions will be discussed later. T_o is not an eigenfunction of S^2, and in following paragraphs we shall develop a projection operator which when operating on T_o produces the proper multiplicity.

The qualitative aspects of Löwdin's proposal now become clear. When $\vartheta = 0^{\circ}$, electrons with α spins tend to accumulate on the starred set of atoms and electrons with β spins on the unstarred atoms. When $\vartheta = 45°$ $(a=b=1)$, this spin separation is complete, and the picture is similar to valence bond theory. In molecular orbital theory language, ϑ has the effect of mixing the excited configuration with the ground configuration, which can be seen if T_o is expanded in powers of a and b or ϑ.

Simple Hückel molecular orbital theory has been successfully applied to the interpretation of the proton hyperfine splittings of the ESR spectra of single charged ions of even alternant hydrocarbons (18,19,20). Within this simple approximation previously diagramed, the theoretical π electron spin density at carbon atom C is merely the square of the coefficient of the atomic orbital centered on C in the singly occupied LCAO MO. In this section we will be concerned primarily with the estimation of π electron spin densities in neutral odd alternant hydrocarbon radicals. It was seen that simple Hückel theory predicts that the odd electron moves in an orbital which has zero density at the unstarred atoms. This prediction cannot be correlated with experiment either qualitatively or quantitatively. The failure of the simple approximation implies that the calculation must be carried out with an approximate ground state wave function in which cognizance of electron correlation has been taken explicitly.

McConnell and Chesnut (3) have pointed out that elementary valence bond theory or molecular orbital theory with $\pi - \pi$ configuration interaction predicts negative signs for the spin density at unstarred positions. McConnell (21) has carried out the calculation of the spin densities for the allyl radical using these two types of functions and has shown that this is indeed the case. Since the total spread of the ESR spectra of these radicals is a measure of the sum of the absolute values of the spin densities at the various positions in the molecule to which a proton is bound, introduction of negative spin density has the effect of increasing the spread. This result has been borne out by experiment for the cases of triphenylmethyl (22), dimesitylmethyl (22) and perinaphthenyl (23). Hoijtink (59) reports the results of the calculation of spin densities in the ions and neutral radicals of alternant hydrocarbons using a wave function obtained by first order $\pi - \pi$ configuration interaction and finds negative spin densities in the radicals.

We shall carry out this calculation using the function proposed by Löwdin, and we shall find that negative spin densities occur within this approximation also.

Projection Operator

T_o is degenerate with respect to S^2 and can be written as a sum of component functions which are proper eigenfunctions of this operator

$$T_o = \sum_k [k(k+1)]^{\frac{1}{2}} \Omega_k . \qquad \text{(IA-19)}$$

If IA-19 is multiplied by the operator $[S^2 - k(k+1)]$ (24), the term $S=k$ is annihilated from the expansion; so that an operator of the form

$$^{2S+1}O = \prod_{k}^{k \neq S} [S^2 - k(k+1)] \Big/ [S(S+1) - k(k+1)] \qquad \text{(IA-20)}$$

removes from IA-19 all terms save the one for which $k = S$ and is the desired projection operator.

Following the notation of Lowdin (25, 26), we write the following functions T_k obtained by k interchanges of the spins of the electrons among the sets $(a\phi_1 + b\phi_{1'}) \ldots (a\phi_n + b\phi_{n'})\, \phi_o$, abbreviated $(\alpha \ldots \alpha\alpha/$, and $(a\bar{\phi}_1 - b\bar{\phi}_{1'}) \ldots (a\bar{\phi}_n - b\bar{\phi}_{n'})$, abbreviated $/\beta \ldots \beta)$. The functions T_k, composed of "half" determinants, make up in all possible ways of permuting the α's and the β's. For example we write

$$\begin{aligned}
T_o &= \{\alpha \ldots \alpha\alpha \,/\, \beta \ldots \beta\} \\
T_1 &= \{(\beta \ldots \alpha\alpha) + \ldots + (\alpha \ldots \beta\,\alpha) + (\alpha \ldots \alpha\beta) \,/ \\
&\qquad (\alpha \ldots \beta) + \ldots + (\beta \ldots \alpha)\} \\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(IA-21)} \\
&\;\;\vdots \\
T_{n-1} &= \{\beta \ldots \beta \,/\, (\alpha \ldots \beta) + \ldots + (\beta \ldots \alpha)\}
\end{aligned}$$

The total number of electrons, 2n-1, is made up of n α's and n-1 β's.

The projected function can be expanded in terms of the functions T_k

$$^{2S+1}{}_0T_o = \sum_{k=0}^{n-1} C_k T_k \, , \qquad \text{(IA-22)}$$

and our problem becomes the determination of the expansion coefficients, C_k. We begin by writing S^2 in the manner of the Dirac vector model (27)

$$S^2 = -\frac{1}{4} N(N-4) + \sum_{i>j} P_{ij} \qquad \text{(IA-23)}$$

in which P_{ij} is the pairwise permutation of the N electrons. The quantity $S^2 T_k$ must now be evaluated, and a counting procedure can be employed for this task. $S^2 T_k$ is composed of

$$\left[-\frac{1}{4} N(N-4) + \sum_{i>j} P_{ij}\right]\binom{n-1}{k}\binom{n}{k} = \left[-(n^2 - 3n + \frac{5}{4}) + (2n-1)(n-1)\right] \cdot \binom{n-1}{k}\binom{n}{k}$$

determinants. Since IA-23 contains only pairwise permutations, all the components of $S^2 T_k$ must belong to T_{k-1}, T_k and T_{k+1}. The manner in which the "half" determinants are partitioned among T_{k-1}, T_k and T_{k+1} is arrived at by noting that there are (n-1-k)(n-k) ways of interchanging one more pair of α and β to form a member of T_{k+1} but only k·k ways of reducing the number of interchanges by one to yield a member of T_{k-1}. The number of T_k components must arise from the terms in IA-23 which produce no interchange. Normalization by the total number of determinants in each group produces the desired partition:

$$T_{k-1}: \quad k^2 \frac{\binom{n-1}{k}\binom{n}{k}}{\binom{n-1}{k-1}\binom{n}{k-1}} = (n-k)(n-k+1)$$

$$T_k: \quad -(n^2 - 3n + \frac{5}{4}) + (2n-1)(n-1) - k^2 - (n-k)(n-k-1) = (n-k)(2k+1) - \frac{1}{4}$$

$$T_{k+1}: \quad (n-k)(n-k-1) \frac{\binom{n-1}{k}\binom{n}{k}}{\binom{n-1}{k+1}\binom{n}{k+1}} = (k+1)^2 \quad .$$

This results in

$$S^2\, T_k = (n-k)(n-k+1)\, T_{k-1} + [(n-k)(2k+1) - \frac{1}{4}]\, T_k + (k+1)^2\, T_{k+1} \quad . \tag{IA-24}$$

The equality

$$S^2\, ({}^{2S+1}{}_0\, T_o) = S(S+1)\; {}^{2S+1}{}_0\, T_o \tag{IA-25}$$

is true by hypothesis, and it follows from IA-22 that

$$S^2 \, (\sum_k C_k\, T_k) = S(S+1) \sum_k C_k\, T_k \quad . \tag{IA-26}$$

Combination of equations IA-24 and IA-26 produces the recurrence relation

$$(n-k)(n-k-1)\,C_{k+1} + \left[(n-k)(2k+1) - \frac{1}{4} - S(S+1)\right] C_k + k^2\, C_{k-1} = 0 \quad \text{(IA-27)}$$

We are interested in the doublet projection operator and the first few terms of IA-27 for this case are

$$\frac{C_1}{C_o} = -\frac{1}{n}$$

$$\frac{C_2}{C_o} = \frac{2}{n(n-1)}$$

$$\frac{C_3}{C_o} = -\frac{6}{n(n-1)(n-2)}$$

which can be generalized

$$\frac{C_k}{C_o} = (-1)^k \binom{n}{k}^{-1} . \qquad \text{(IA-28)}$$

The desired result then has the form

$$^2 0\, T_o = \frac{1}{C_o} \sum_{k=0}^{n-1} (-1)^k \binom{n}{k}^{-1} T_k . \qquad \text{(IA-29)}$$

C_o is obtained by the direct application of the doublet projection operator. The procedure which will be described here will make use of this general result only for a small number of electrons, namely the cases of three and five electrons. For three electrons C_o has the value $\frac{2}{3}$ and for five electrons the value $\frac{1}{2}$.

Wave Functions

Before the development of the necessary wave functions, we must become cognizant of the inherent differences between the odd alternant radicals and the even alternant ions. One can carry out the division of atoms into the two sets uniquely for the odd alternant radicals, but a similar procedure is impossible for the even alternant ions. Because of this lack of uniqueness for the selection of the members of the starred and unstarred sets, we shall proceed here with the discussion of the neutral radicals and reserve the development of equations for the ions until the end of this subsection.

The assumption is made that b is a small quantity, and T_o is expanded in a power series in b. The justification for this assumption will be discussed later. If terms in b^2 are retained in the development of T_o one obtains

$$
\begin{aligned}
T_o \doteq\; & a^{2n} \left| \phi_1\ \phi_2 \ldots \phi_n\ \phi_o\ \bar{\phi}_1\ \bar{\phi}_2 \ldots \bar{\phi}_n \right| \\
& a^{2n-1} b \sum_{i=1}^{n} \Big\{ \left| \phi_1\ \phi_2 \ldots \phi_{i'} \ldots \phi_n\ \phi_o\ \bar{\phi}_1\ \bar{\phi}_2 \ldots \bar{\phi}_i \ldots \bar{\phi}_n \right| \\
& - \left| \phi_1\ \phi_2 \ldots \phi_i \ldots \phi_n\ \phi_o\ \bar{\phi}_1\ \bar{\phi}_2 \ldots \bar{\phi}_{i'} \ldots \bar{\phi}_n \right| \Big\} \\
& + a^{2n-2} b^2 \sum_{i>j=1}^{n} \Big\{ \left| \phi_1\ \phi_2 \ldots \phi_{i'} \ldots \phi_{j'} \ldots \phi_n\ \phi_o\ \bar{\phi}_1\ \bar{\phi}_2 \ldots \right. \\
& \left. \bar{\phi}_i \ldots \bar{\phi}_j \ldots \bar{\phi}_n \right| - \left| \phi_1\ \phi_2 \ldots \phi_{i'} \ldots \phi_j \ldots \phi_o\ \bar{\phi}_1 \right.
\end{aligned}
\qquad \text{(IA-30)}
$$

$$\bar{\phi}_2 \ldots \bar{\phi}_i \ldots \bar{\phi}_{j'} \ldots \bar{\phi}_n| - |\phi_1 \phi_2 \ldots \phi_i \ldots \phi_j \ldots \phi_n$$

$$\phi_o \bar{\phi}_1 \bar{\phi}_2 \ldots \bar{\phi}_{i'} \ldots \bar{\phi}_{j'} \ldots \bar{\phi}_n| + |\phi_1 \phi_2 \ldots \phi_i \ldots \phi_j \ldots$$

$$\phi_n \phi_o \bar{\phi}_1 \bar{\phi}_2 \ldots \bar{\phi}_{i'} \ldots \bar{\phi}_{j'} \ldots \bar{\phi}_n|\} - a^{2n-2} b^2 \sum_{i=1}^{n} |\phi_1 \tag{IA-30}$$

$$\phi_2 \ldots \phi_{i'} \ldots \phi_j \ldots \phi_n \phi_o \bar{\phi}_1 \bar{\phi}_2 \ldots \bar{\phi}_{i'} \ldots \bar{\phi}_j \ldots \bar{\phi}_n| \quad .$$

The function IA-30 now contains only Slater determinants made up of orthogonal molecular orbitals. Retention of terms of order b^2 in the wave function leads to a result for the spin density which includes terms in b up to fourth order. This is equivalent to the assertion, in configuration language, that only configurations up to those corresponding to two-electron excitations contribute significantly to the ground state wave function.

We now apply the doublet projection operator IA-20 to IA-30 and note that the determinantal functions $|\phi_1 \phi_2 \ldots \phi_n \phi_o \bar{\phi}_1 \bar{\phi}_2 \ldots \bar{\phi}_n|$ and $\sum_i |\phi_{i'} \phi_j \phi_o \bar{\phi}_{i'} \bar{\phi}_j|$ are already eigenfunctions of S^2. We must extract the doublet component from the functions in $\sum_{i=1}^{n} \{|\phi_{i'} \phi_o \bar{\phi}_i| - |\phi_i \phi_o \bar{\phi}_{i'}|\}$ which contain three singly filled orbitals and from the functions in $\sum_{i>j=1}^{n} \{|\phi_{i'} \phi_{j'} \phi_o \bar{\phi}_i \bar{\phi}_j| - |\phi_{i'} \phi_j \phi_o \bar{\phi}_i \bar{\phi}_{j'}| - |\phi_i \phi_{j'} \phi_o \bar{\phi}_{i'} \bar{\phi}_j| + |\phi_i \phi_j \phi_o \bar{\phi}_{i'} \bar{\phi}_{j'}|\}$ which contain five such orbitals. The result of the application of the doublet projection operator to IA-30 is

$$
{}^{2}0\,T_o = a^{2n}\,|\phi_1 \cdots \phi_o \cdots \bar{\phi}_n| + \sqrt{\frac{2}{3}}\; a^{2n-1}\, b \sum_{i=1}^{n} \frac{1}{\sqrt{6}} \cdot
$$

$$
\{|\phi_{i'}\phi_o\bar{\phi}_i| - |\phi_i\phi_o\bar{\phi}_{i'}| + 2\,|\phi_{i'}\bar{\phi}_o\phi_i|\}
$$

$$
- a^{2n-2}\, b^2\, \frac{\sqrt{12}}{3} \sum_{i>j=1}^{n} \frac{1}{\sqrt{12}} \{ 2\,|\phi_i\phi_{i'}\phi_o\bar{\phi}_{j'}\bar{\phi}_j|
$$

$$
+ 2\,|\phi_{j'}\phi_j\phi_o\bar{\phi}_i\bar{\phi}_{i'}| - |\phi_{i'}\phi_{j'}\phi_o\bar{\phi}_i\bar{\phi}_j|
$$

$$
+ |\phi_i\phi_{j'}\phi_o\bar{\phi}_{i'}\bar{\phi}_j| + |\phi_{i'}\phi_j\phi_o\bar{\phi}_i\bar{\phi}_{j'}| - |\phi_i\phi_j\phi_o\bar{\phi}_{i'}\bar{\phi}_{j'}| \}
$$

$$
- a^{2n-2} b^2 \sum_{i=1}^{n} |\phi_{i'}\phi_j\phi_o\bar{\phi}_{i'}\bar{\phi}_j| \quad . \qquad \text{(IA-31)}
$$

However, equation IA-31 is no longer normalized and must be divided by $\sqrt{N}$ where

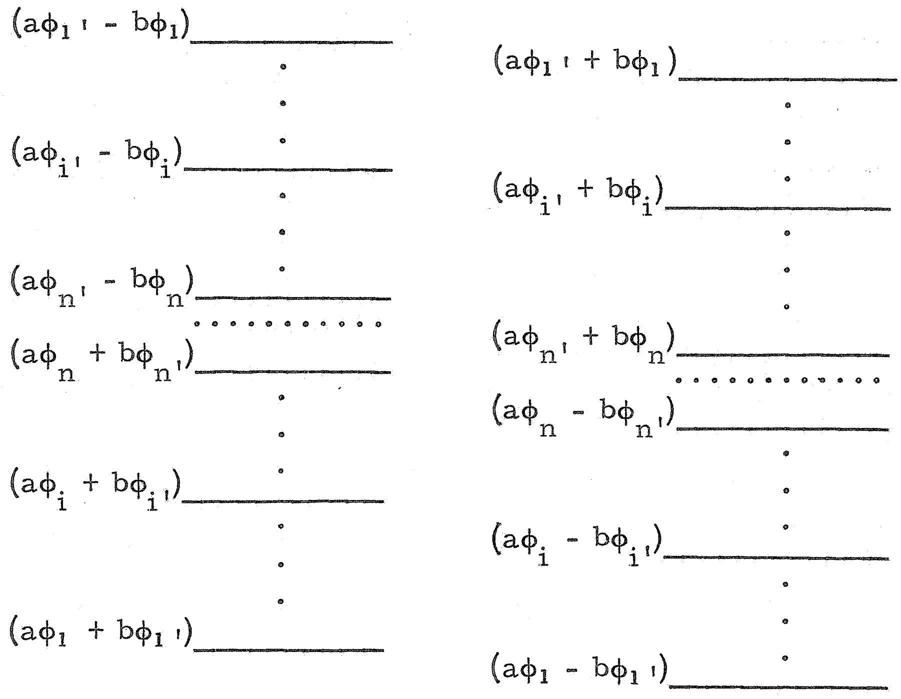
$$
N = a^{4n} + \frac{2n}{3}\, a^{4n-2} b^2 + a^{4n-4} b^4 \left(\frac{2n^2 + n}{3}\right) \quad . \qquad \text{(IA-32)}
$$

We now turn to the similar problem for the even alternant ions. As was mentioned in the introduction to this section, MAO allows α spin to accumulate on the starred atoms and β spin on the unstarred atoms. However, for even alternant molecules the two sets of atoms are physically indistinguishable. Mathematically, this means that the description of the ground state of the π electrons with one determinant, similar to IA-18, is no longer possible. Let us illustrate this point for the case of neutral benzene: The proper function before projection is the symmetrical combination of the two possible ways of arranging the α and β electrons,

$$\frac{1}{\sqrt{2}} \left[\,|(a\phi_1 + b\phi_{1'}) \ldots (a\bar{\phi}_3 - b\bar{\phi}_{3'})| + |(a\phi_1 - b\phi_{1'}) \ldots (a\bar{\phi}_3 + b\bar{\phi}_{3'})|\, \right] .$$

In this function starred and unstarred atoms are treated on the same basis which is certainly physical reality. The consequence of this combination is that all terms linear in the parameter b vanish by cancellation. This same type of result is evidence in self-consistent field theory in which there is no connection between the ground configuration and singly excited configurations if the basis molecular orbitals are self-consistent (28).

The array of alternant orbitals which is to be filled singly by the π electrons for even alternant ions is diagramed as follows.



α electrons β electrons

There are then four possible ways of assigning the 2n+1 (2n-1) electrons of the negative ion (positive ion) to these orbitals which produce configurations for which $S_z = \frac{1}{2}$. Thus, we can write for the negative ion

$$A = |\ldots(a\phi_i + b\phi_{i'})\ldots(a\phi_{n'} - b\phi_n)\ldots(a\bar{\phi}_i - b\bar{\phi}_{i'})\ldots|$$

$$B = |\ldots(a\phi_i - b\phi_{i'})\ldots(a\phi_{n'} - b\phi_n)\ldots(a\bar{\phi}_i + b\bar{\phi}_{i'})\ldots| \quad ,$$

$$C = |\ldots(a\phi_i + b\phi_{i'})\ldots(a\phi_{n'} + b\phi_n)\ldots(a\bar{\phi}_i - b\bar{\phi}_{i'})\ldots|$$

$$D = |\ldots(a\phi_i - b\phi_{i'})\ldots(a\phi_{n'} + b\phi_n)\ldots(a\bar{\phi}_i + b\bar{\phi}_{i'})\ldots|$$

as the configurations which have the lowest energy.

Then, to be general we must take as the approximation to the ground state function for the negative ion a linear combination of the various possibilities

$$T_o(-) = c_a A + c_b B + c_c C + c_d D \, . \qquad \text{(IA-33)}$$

Consider the energies of the various component determinants which make up IA-33. If the expectation value of the sum of one electron Hamiltonians is calculated, A, B, C, and D are exactly degenerate. If $\frac{e^2}{r_{ij}}$ is explicitly contained in the Hamiltonian and A, B, C, D are expanded in powers of b, the energy of these determinants is the same up to terms of order b^3. Thus any error made in assuming that these determinants are exactly degenerate will be small, and we shall proceed here by making that assumption.

$$c_a = c_b = c_c = d \qquad \text{(IA-34)}$$

After performing some simple algebra IA-33 becomes

$$T_o(-) = (M')^{-\frac{1}{2}}\Big\{\big|(a\phi_1 + b\phi_{1'})\ldots\phi_{n'}(a\bar{\phi}_1 - b\bar{\phi}_{1'})\ldots\big|$$

$$+ \big|(a\phi_1 - b\phi_{1'})\ldots\phi_{n'}(a\bar{\phi}_1 + b\bar{\phi}_{1'})\ldots\big|\Big\}. \qquad \text{(IA-35)}$$

Expansion and projection of IA-35 gives the proper doublet ground state

$${}^2O\,T_o(-) = (M)^{-\frac{1}{2}}\Big\{a^{2n+1}\,|\phi_1\ldots\phi_n\phi_{n'}\bar{\phi}_1\ldots\bar{\phi}_n| - \frac{\sqrt{12}}{3}\,a^{2n-2}\,b^2\,\cdot$$

$$\sum_{i>j=1}^{n}\frac{1}{\sqrt{12}}\Big[2\,|\phi_i\phi_{i'}\phi_{n'}\bar{\phi}_{j'}\bar{\phi}_j| + 2\,|\phi_{j'}\phi_j\phi_{n'}\bar{\phi}_i\bar{\phi}_{i'}|$$

$$+ |\phi_{i'}\phi_j\phi_{n'}\bar{\phi}_i\bar{\phi}_{j'}| - |\phi_{i'}\phi_{j'}\phi_{n'}\bar{\phi}_i\bar{\phi}_j| + |\phi_i\phi_{j'}\phi_{n'}\bar{\phi}_{i'}\bar{\phi}_j| - |\phi_i\phi_j\phi_{n'}\bar{\phi}_{i'}\bar{\phi}_{j'}|\Big]$$

$$- a^{2n-2}\,b^2\sum_{i=1}^{n-1}|\phi_{i'}\phi_n\phi_{n'}\bar{\phi}_{i'}\bar{\phi}_n|\,. \qquad \text{(IA-36)}$$

Here the normalization factor M is given by the relation

$$M = \tfrac{1}{4}\left[a^{4n+2} + a^{4n-2}\,b^2\cdot(n-1)\left(\frac{11}{2}\,n-8\right)\right]. \qquad \text{(IA-37)}$$

McLachlan has shown recently (29) that for alternant hydrocarbon ions one can regard the motion of the 2n+1 electrons of a negative ion to be the motion of 2n-1 positive holes. This requires that any observation of the ESR or electronic spectrum of a positive ion be the same as that of the corresponding negative ion. This prediction has indeed been borne out by experiment.(20, 63, 31, 32) For the present calculation this means that it is unnecessary for the wave function for the positive ion to be derived explicitly since the prediction of spin densities from IA-36 will suffice for both cases.

We now proceed with evaluation of matrix elements of IA-31 and IA-36 of the spin density operator I-3 .

Matrix Elements of Spin Density Operator

The spin density operator is defined in the introduction

$$\rho(r) = \frac{1}{S_z} \sum_{\mu} \delta(r - r_{\mu}) \, S_{\mu z} \tag{I-3}$$

To avoid unnecessary labor of enumeration, the various components of the wave functions IA-31 are abbreviated

I ≡ ground molecular orbital configuration

II ≡ monoexcited functions

III ≡ diexcited functions with electrons in two different antibonding orbitals

IV ≡ diexcited with two electrons in same antibonding orbital.

Similarly for the ions, we define the functions I(-), III(-), and IV(-).

As an example of the procedure for calculation of matrix elements of I-3 , the quantity $\langle \mathrm{II} | \rho | \mathrm{III} \rangle$ for the odd alternant radical will be evaluated.

$$\langle \mathrm{II} | \rho | \mathrm{III} \rangle = \frac{1}{\sqrt{72}} \sum_{i=1}^{n} \sum_{j \neq i}^{n} (-\phi_j\phi_{j'} - \phi_j\phi_{j'} - \phi_j\phi_{j'} - \phi_j\phi_{j'})$$

$$= - \frac{4}{\sqrt{72}} (n-1) \sum_{j=1}^{n} \phi_j\phi_{j'} \; . \tag{IA-38}$$

There arises a non-zero term only from those determinants in III which contain two electrons in different antibonding orbitals with opposite spins. The part of the element coming from any term for which i=k in the double summation vanishes because more than two orthogonal orbitals are different.

All the matrix elements of I-3 are now listed in matrix form:

$$\begin{pmatrix} |\phi_o|^2 & \sqrt{\frac{2}{3}}\sum_{i=1}^{n}|\phi_i\phi_{i'}| & 0 & 0 \\ \sqrt{\frac{2}{3}}\sum_{l=1}^{n}|\phi_i\,\phi_{i'}| & \frac{1}{6}\sum_{i}^{n}\left(4|\phi_i|^2+4|\phi_{i'}|^2-2|\phi_o|^2\right) & -\sqrt{\frac{2}{9}}(n-1)\sum_{i}^{n}|\phi_i\phi_{i'}| & \frac{2}{\sqrt{6}}\sum_{i}^{n}|\phi_i\phi_{i'}| \\ 0 & -\sqrt{\frac{2}{9}}(n-1)\sum_{i}^{n}|\phi_i\phi_{i'}| & \frac{n(n-1)}{2}|\phi_o|^2 & 0 \\ 0 & \frac{2}{\sqrt{6}}\sum_{i}^{n}|\phi_i\phi_{i'}| & 0 & n|\phi_o|^2 \end{pmatrix}$$

Matrix elements for the ions are so similar that they need not be listed here.

Spin Density Relations

Now that matrix elements of the spin density operator are available, the spin density function $\rho(r)$ can be evaluated either in terms of the molecular orbitals ϕ_i or the atomic orbitals χ_r. For the odd alternant radicals the molecular orbital spin density is found to be

$$\rho\,(r) = (N)^{-1}\Big[\, a^{4n}\phi_o\phi_o + \frac{4}{3}\, a^{4n-1}\, b \sum_{i=1}^{n} \phi_i\phi_{i'}$$

$$+ \frac{1}{9}\, a^{4n-2}\, b^2 \sum_{i=1}^{n} (4\phi_{i'}\phi_{i'} + 4\,\phi_i\phi_i - 2\phi_o\phi_o)$$

$$+ (\frac{8}{9}\, n + \frac{4}{9})\, a^{4n-3}\, b^3 \sum_{i=1}^{n} \phi_i\phi_{i'}$$

$$+ (\frac{2n^2 + n}{3})\, a^{4n-4}\, b^4\, \phi_o\phi_o \Big] . \qquad \text{(IA-39)}$$

In IA-39 the molecular orbitals ϕ_i are functions of the vector r.

In the calculation of the atomic orbital spin density function, differential overlap is neglected, which means that only diagonal terms of the spin density matrix (21) are retained. However, this procedure is likely to lead, in the present case, to spin densities which would be calculated using the "atomic orbital delta function" (33), rather than to the diagonal element of the atomic orbital spin density matrix. This is because of the nature of the "atomic orbitals" involved. Pairing of the molecular orbitals arises either in the Hückel method or in a semi-empirical scheme similar to that proposed by Pariser and Parr (34). It is likely that the orthogonal orbitals used in these schemes are really some sort of localized linear combination of non-orthogonal atomic orbitals similar to that proposed by Lowdin (35). The atomic charge density can be calculated either by using the non-orthogonal atomic orbitals with a definition of the charge density including overlap (36) or by first expressing the atomic orbitals in terms of the Löwdin orbitals and then calculating the charge density from the formula suitable for orthogonal AO's. These two procedures lead to the same value in the case of conjugated hydrocarbons (35). The same result should hold here. Therefore, the diagonal elements of the spin density matrix calculated from orthogonalized atomic orbitals represent in fact the unpaired spin density calculated with the inclusion of overlap.

Expressing the density on the starred atoms, ρ_A, and the density on the unstarred atoms, ρ_B, as a function now of the parameter ϑ we arrive at the relations

$$\rho_A = (N')^{-1} \left[c_{oA}^2 \cdot Y + \frac{2}{3} \tan \vartheta + \frac{4}{9} \tan^2 \vartheta + \frac{4n+2}{9} \tan^3 \vartheta \right] \cdot \chi_A^2(r) \tag{IA-40}$$

$$\rho_B = (N')^{-1} \left[-\frac{2}{3} \tan \vartheta + \frac{4}{9} \tan^2 \vartheta - \frac{4n+2}{9} \tan^3 \vartheta \right] \cdot \chi_B^2(r) \tag{IA-41}$$

in which

$$N' = 1 + \frac{2n}{3} \tan^2 \vartheta + \frac{2n^2+n}{3} \tan^4 \vartheta$$

and

$$Y = 1 - \frac{2}{3} \tan \vartheta - \frac{2n+4}{9} \tan^2 \vartheta - \frac{4n+2}{9} \tan^3 \vartheta + \frac{2n^2+n}{3} \tan^4 \vartheta ,$$

and $\chi_A(r)$ and $\chi_B(r)$ are atomic orbitals centered on atoms A and B respectively. In going from the molecular orbital spin density to the atomic orbital spin density, advantage has been taken of the fact that the coefficients of the molecular orbitals obey the relation (13)

$$2 \sum_{i=1}^{n} c_{iA}^{2} + c_{oA}^{2} = 1.$$

When this same procedure is applied to the even alternant ions, the unfortunate consequence results for the molecular orbital density

$$\rho(r) = (M')^{-1} \phi_n \phi_n (M') = \phi_n \phi_n \qquad \text{(IA-42)}$$

which is the same prediction as that given by simple Hückel theory. Thus MAO is unsuccessful in introducing the effects of electron correlation on the spin densities of even alternant ions.

Discussion of the causes for the success of this approximation for the odd alternant radicals but its failure for the ions will be continued at the conclusion of this section. In the remainder of this section we shall concern ourselves with the spin densities in the radicals only.

Sign of Tan ϑ

Inspection of IA-41 shows that the sign of the spin density at an unstarred atom is governed by the sign of tan ϑ. In order to confirm the presence of a negative sign of spin density at an unstarred atom, tan ϑ must be shown to have a positive sign. To carry this out we will calculate the value of the quantity $\frac{b}{a}$ which is obtained by first order configuration interaction.

If the function IA-31 is restricted to terms linear in b, it can be considered as having arisen from a configuration interaction of the basic molecular orbital determinant, $|\phi_1 \ldots \phi_n \, \phi_o \, \bar{\phi}_1 \ldots \bar{\phi}_n| = \psi_o$, with the normalized combinations of excited configurations,

$$\frac{1}{\sqrt{n}} \sum_{i=1}^{n} \frac{1}{\sqrt{6}} \left(|\phi_{i'} \, \phi_o \, \bar{\phi}_i| - |\phi_i \, \phi_o \, \bar{\phi}_{i'}| + 2\,|\phi_i \, \bar{\phi}_o \, \phi_{i'}| \right) = \psi_1 .$$

By first order perturbation theory, we have

$$\Psi_{\text{groundstate}} = \psi_o + \lambda \psi_1 \qquad \text{(IA-43)}$$

in which

$$\lambda = - \frac{\mathscr{H}_{o1}}{E_1 - E_o} \qquad \text{(IA-44)}$$

and

$$\mathscr{H}_{o1} = \int \psi_o \, \mathscr{H} \, \psi_1 \, d\tau \qquad \text{(IA-45)}$$

where $\mathscr{H}$ is the total Hamiltonian for the system and E_o and E_1 are the zeroth order energies corresponding to ψ_o and ψ_1. It is readily shown that

$$\mathscr{H}_{o1} = - \frac{1}{\sqrt{n}} \sqrt{\frac{3}{2}} \sum_{i=1}^{n} \zeta^{io}_{i'o} \qquad \text{(IA-46)}$$

where

$$\zeta^{io}_{i'o} = \iint \phi_i(1) \, \phi_o(1) \, \frac{e^2}{r_{ij}} \, \phi_{i'}(2) \, \phi_o(2) \, d\tau_1 \, d\tau_2 . \qquad \text{(IA-47)}$$

It has further been shown (60) that

$$\zeta^{io}_{i'o} = \zeta^{io}_{io'} = \zeta^{io}_{io}$$

since $\phi_{o'} = \phi_o$.

ζ^{io}_{io} is the familiar exchange integral K_{io}, and we can now apply the general theorem of Roothaan (37) by which all such molecular exchange integrals arising from orthogonal molecular orbitals are necessarily positive. Therefore $\mathcal{H}_{o1}$ is a negative quantity and by equation IA-44 λ has a positive value. λ in turn can be identified with $(\sqrt{n} \cdot \sqrt{\frac{3}{2}})\frac{b}{a}$ which completes the demonstration of the fact that tan ϑ calculated in this manner is a positive quantity. Furthermore, E_1 represents an average monoexcitation energy. A similar first order perturbation calculation of the quantity $(\frac{b}{a})^2$ would show that it is inversely proportional to an average two-electron excitation energy.

Limiting Case: a=b.

Now that spin density relations for the odd alternant radicals have been developed, the question must be posed: What happens to these formulae when as much correlation as possible is allowed, namely when a=b? Recalling the equations for ϕ_i and $\phi_{i'}$, the equation for an α electron is

$$\psi_k(\alpha) = a\,\phi_k + b\,\phi_{k'} = (a+b)\sum_{r=h+1}^{n} c_{kr}\,\chi_r + (a-b)\sum_{r=1}^{h} c_{kr}\,\chi_r$$

which when a=b becomes

$$\psi_k(\alpha)_{a=b} = 2 \sum_{r=h+1}^{n} c_{kr} \chi_r \tag{IA-48}$$

and similarly for the β spin

$$\psi_k(\beta)_{a=b} = 2 \sum_{r=1}^{h} c_{kr} \chi_r \; . \tag{IA-49}$$

Thus π electrons with α spin are totally localized in molecular orbitals with amplitude only at the starred set and those with β spin are in MO's which vanish everywhere except on the unstarred set. Therefore it is clear that $\langle \psi | \mathcal{P} | \psi \rangle$ will be negative at unstarred and positive at the starred atoms. However, the question really is whether the projector operator introduces any mathematical funny business because only certain doublets are retained.

To answer this question we shall proceed in a slightly different way from the arguments which have proceeded. Consider a set of molecular orbitals $g_1 \ldots g_n$ which have density only at the starred atoms and $f_1 \ldots f_{n-1}$ which have amplitude only at the unstarred atoms ($2n-1$ is here the total number of electrons). Further require that the g's and f's are orthonormal. The starting function (not an eigenfunction of S^2) is

$$T_o = \mathcal{A}\,[\,\bar{f}_1(1) \ldots \bar{f}_{n-1}(n-1) g_1(n) \ldots g_n(2n-1)\,] \, . \tag{IA-50}$$

$\mathcal{A}$ is the operator for antisymmetrization and renormalization. We will require a good deal of the notation of the section on the projection operator and begin by abbreviating the molecular orbitals g and f by α and β and in serial order

$$T_o = \mathcal{A}\,(\beta\beta_{(n-1)}\ldots\beta\alpha\alpha_{(n)}\alpha\alpha)\ .$$

By equation IA-29 the proper normalized doublet function is given by

$$^2O\,T_o = \left[\frac{2}{n+1}\right]^{\frac{1}{2}} \sum_{k=0}^{n-1} (-1)^k \binom{n}{k}^{-1} T_k\ .$$

The spin density function is

$$\rho(r) = \langle {}^2O\,T_o \,|\, \rho \,|\, {}^2O\,T_o \rangle$$

$$= \frac{2}{n+1} \sum_{i,j=0}^{n-1} (-1)^{i+j} \binom{n}{i}^{-1} \binom{n}{j}^{-1} \langle T_i \,|\, \rho \,|\, T_j \rangle \qquad \text{(IA-51)}$$

Since the T_k's are constructed from orthogonal orbitals and ρ is a one-electron operator, any two electron permutation causes the matrix element to vanish, so that only the unity operation of $\mathcal{A}$ gives a non-zero result. Recalling now that T_i is constructed from T_j by a product of two electron permutations from the α (g) set to the β (f) set, the same argument requires that i=j. Equation IA-51 becomes

$$\rho(r) = \frac{2}{n+1} \sum_{i=0}^{n-1} \binom{n}{i}^{-2} \langle T_{i'} \,|\, \rho \,|\, T_{i'} \rangle \qquad \text{(IA-52)}$$

where $T_{i'}$ is a simple product of the starting sets of MO's.

The problem of evaluating the matrix elements in IA-52 is another counting problem similar to the problem of determining the projection operator, and the reader should be relieved that only the result is reported:

$$\langle T_{i'} \mid \rho \mid T_{i'} \rangle_{\alpha \text{ set}} = \binom{n-1}{k}^{2} \left[\frac{n-2k}{n-k} \right] \cdot |g_r|^2 \; ; \quad r = \text{starred}$$

and

$$\langle T_{i'} \mid \rho \mid T_{i'} \rangle_{\beta \text{ set}} = \binom{n-1}{k}\binom{n}{k} \frac{2k-n+1}{n-1} \cdot |f_s|^{2} \; ; \quad s = \text{unstarred} \qquad \text{(IA-53)}$$

for each r and s.

Then the molecular orbital spin density for the set of MO's made up from starred atoms is

$$\bar{\rho}_r = \left(\frac{2}{n+1}\right) \sum_{k=0}^{n-1} \binom{n}{k}^{-2} \binom{n-1}{k}^{2} \left[\frac{n-2k}{n-k} \right]$$

$$= \frac{2}{n+1} \sum_{k=0}^{n-1} \left[\frac{(n-k)(n-2k)}{n} \right] .$$

This sum is easily evaluated and is found to be equal to $\frac{(n+1)(n+2)}{6n}$, so that

$$\bar{\rho}_r = \frac{n+2}{3n} \qquad \text{(IA-54)}$$

By a similar development for the molecular orbitals over the unstarred atoms, the relation is

$$\bar{\rho}_s = \left(\frac{2}{n+1}\right) \sum_{k=0}^{n-1} \left(\frac{n-k}{n}\right)\left(\frac{2k-n+1}{n-1}\right) = -\frac{1}{3} . \tag{IA-55}$$

There is encouragement that no algebraic mistakes were made since

$$\sum_{s=1}^{n-1} \bar{\rho}_s + \sum_{r=1}^{n} \bar{\rho}_r = 1 .$$

The explicit form of the various molecular orbitals has been left unspecified since all that was sought was the molecular orbital spin density. This completes the demonstration that the important equation IA-39 will tend to a reasonable limit (if the expansion is complete) when the value of b reaches its maximum.

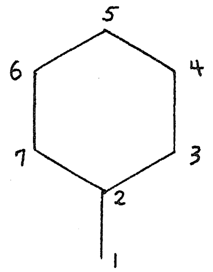
Illustrative Calculations

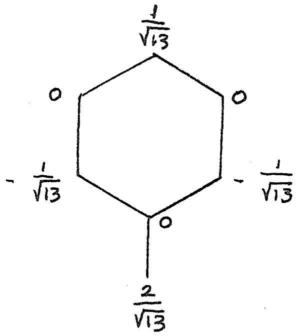
At least two examples of the experimental determination of the electron-proton coupling constants in odd alternant hydrocarbon radicals are available. The ESR spectra of triphenylmethyl (22) and perinaphthenyl radicals (23, 38) have been interpreted in terms of negative spin density at the unstarred carbon atoms. We shall take the values of the spin density at the unstarred carbons of these radicals and calculate a value of the parameter ϑ. With this quantity the value of the spin density at the starred atoms will be computed and compared with those deduced from experiment.

For ease of numerical computation we assume that b is such a small quantity that terms of order b^2 in equations IA-40 and IA-41 can be neglected. Neglecting all but terms linear in b, we have

$$\begin{aligned} \rho_A &= \left(1 - \frac{2}{3}\tan\vartheta\right) c_{oA}^2 + \frac{2}{3}\tan\vartheta \\ \rho_B &= -\frac{2}{3}\tan\vartheta \end{aligned} \qquad \text{(IA-56)}$$

For the case of triphenylmethyl experiment shows (39) that $|\rho_3| = |\rho_5| = 2|\rho_4|$ with the numbering shown below.





Also the values of the AO coefficients of the Hückel non-bonding orbital are included.

The sum of all the absolute values of the spin density at carbon atoms linked to a proton has been shown to be 1.57 (40). From a comparison of these two results one finds that

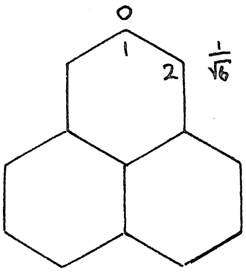
$$3\left(2|\rho_3| + 2|\rho_4| + |\rho_5|\right) = 24|\rho_4| = 1.57$$

$$|\rho_4| = 0.065$$

$$\rho_4 = -0.065$$

The value of ρ_4 is also the value of the quantity $-\frac{2}{3}\frac{b}{a}$ which enters in the calculation of the positive spin density. Using the coefficients listed we obtain in this way $\rho_3 = \rho_5 = 0.137$, which is indeed very nearly twice the value of ρ_4. The spin density at the methyl carbon is calculated to be 0.360.

For the perinaphthenyl radical $|\rho_1|$ is measured as 0.098. Thus $\rho_1 = -0.098$ from which ρ_2 is calculated to be 0.247 which compares to the experimental value of 0.327.



Considering that for triphenylmethyl $\frac{b}{a} = 0.097$ and for perinaphthenyl $\frac{b}{a} = 0.147$, it can be seen that neglect of higher powers of $\frac{b}{a}$ in the spin density relations is justified.

Conclusions

It has been shown that if conventional MO theory is extended in such a way as to include electron correlation, according to the proposal of Löwdin, then negative spin density is predicted at the unstarred positions of odd alternant hydrocarbon radicals. However, MAO is unsuccessful in accounting for the effects of electron correlation in the even alternant hydrocarbon ions.

MAO has very special pairing properties, bonding to conjugate antibonding, from which the approximate ground state wave function is constructed. It has been shown that the first order mixing of MAO configurations depends on the integrals $\zeta_{oi'}^{oi}$ for the radicals, and the similar mixing for the ions depends on the integrals $\zeta_{ii}^{ii'}$. From symmetry considerations alone this latter integral can be shown to vanish (if i is a symmetric function, then i' must be antisymmetric and vice versa). It seems to be the fact that for the radicals mixing is allowed for this particular pairing scheme, but for the ions $i \rightarrow i'$ pairing is much smaller than, for instance, $i \rightarrow j'$ where j' is any other antibonding orbital other than the one conjugate to i. Thus it must be concluded that the function IA-36 represents poorly the ground state wave function of the alternant hydrocarbon ions.

For the radicals the spin densities found are expressible in terms of the parameter ϑ and the coefficients of the non-bonding molecular orbital. Actual calculation of the spin densities can be carried out in a semi-empirical way from a procedure firmly based on the molecular orbital concept. Previously it had been possible to estimate these quantities from simple valence bond theory.

It is shown in the appendix that it is possible to relax the hidden assumption of a single correlation parameter $\frac{b}{a}$ and to introduce a different parameter $\frac{b_j}{a_j}$ for each pair of conjugate orbitals. The conclusion of negative spin density at unstarred positions is still preserved in this more general treatment, but the formulae developed appear to be less useful for the calculation of spin densities for practical application.

In the next section the MAO wave function for the allyl radical is calculated from first principles in as general a way as possible. Comparison of this function to that predicted from a complete π - π configuration interaction treatment is given. The excellence of the agreement of these two methods is a good indication that the representation of the ground state of an odd alternant hydrocarbon radical by equation IA-31 is indeed a good one.

B. Comparison of the Methods of $\pi - \pi$ Configuration Interaction and Alternant Orbitals for Allyl.

The $\pi - \pi$ configuration interaction (CI) problem in the allyl radical has been treated by several authors (41, 42, 43, 44). McConnell (21) has employed the CI wave function given by Chalvet and Daudel (42) to evaluate the spin density matrix for this compound. We shall perform the CI calculation again from scratch here because none of the previous people explicitly enumerated the values of the necessary molecular integrals. In order that a meaningful comparison of CI and MAO be obtained, the integrals used must be the same for both cases. Thus, it is very little additional labor to carry out the CI calculation simultaneously.

The following set of starting functions is chosen for the electron wave function of allyl:

$$\begin{aligned}
\Phi_1 &= |\phi_1\ \bar{\phi}_1\ \phi_2| \\
\Phi_2 &= \frac{1}{\sqrt{2}}\ [|\phi_2\ \bar{\phi}_1\ \phi_3| - |\phi_1\ \bar{\phi}_3\ \phi_2|] \\
\Phi_3 &= \frac{1}{\sqrt{6}}\ [\,2\,|\phi_1\ \bar{\phi}_2\ \phi_3| - |\phi_1\ \bar{\phi}_3\ \phi_2| + |\phi_2\ \bar{\phi}_1\ \phi_3|] \\
\Phi_4 &= |\phi_2\ \phi_3\ \bar{\phi}_3|
\end{aligned} \qquad \text{(IB-1)}$$

in which

$$\begin{aligned}
\phi_1 &= 0.424544\ \chi_1 + 0.600395\ \chi_2 + 0.424544\ \chi_3 \\
\phi_2 &= 0.721262\ (\chi_1 - \chi_3) \\
\phi_3 &= 0.610762\ (\chi_1 + \chi_3) - 0.888297\ \chi_2\ ,
\end{aligned} \qquad \text{(IB-2)}$$

where again χ_r is the $2p_z$ atomic orbital centered on carbon atom r. The ϕ_i's are orthogonal and normalized with the inclusion of overlap.

The proper Hamiltonian for the π electrons of allyl is

$$\mathcal{H} = \sum_{i=1}^{3} \mathcal{H}^{(i)}_{\text{core}} + \sum_{i>j=1}^{3} \frac{e^2}{r_{ij}} \tag{IB-3}$$

The core Hamiltonian is given by (45)

$$\mathcal{H}_{\text{core}}(i) = T(i) + U_{\text{core}}(i)$$

in which T(i) is the kinetic energy of π electron i and $U_{\text{core}}(i)$ is the potential energy operator of the electron i in the field of the core. It is through this core potential that electrons other than π electrons are made manifest. The atomic coulomb integral for atom p is given by

$$\alpha_p \equiv \mathcal{H}^{\text{core}}_{pp} = \int \chi_p(1)\, \mathcal{H}_{\text{core}}(1)\, \chi_p(1)\, d\tau_1 \tag{IB-4}$$

and the atomic exchange integral between p and q by

$$\beta_{pq} \equiv \mathcal{H}^{\text{core}}_{pq} = \int \chi_p(1)\, \mathcal{H}^{(1)}_{\text{core}}\, \chi_q(1)\, d\tau_1\,. \tag{IB-5}$$

The core potential for the particular π electron 1 can be written (34)

$$\mathcal{U}_{\text{core}}(1) = U_p(1) + \sum_{q\neq p} U_q(1) + \sum_r U^*_r(1) \tag{IB-6}$$

where the atoms q are charged in the core (e.g. the carbon atoms of benzene) and the atoms r are uncharged in the core (e.g. the hydrogen atoms of benzene); * denotes a potential due to an uncharged atom. $U_q(1)$ can be further expressed in terms of the potential of the uncharged atom q less an averaged potential due to the electron 2

$$U_q(1) = U_q^*(1) - \int \chi_p(2) \quad \chi_q(2) \quad \frac{e^2}{r_{12}} \quad d\tau_2 \tag{IB-7}$$

If the atomic orbitals χ_p are eigenfunctions in the sense

$$[\, T(1) + U_p(1) \,] \quad \chi_p(1) = W_p \; \chi_p(1)$$

then the atomic coulomb integral, a_p, can be expressed as

$$a_p = W_p - \sum_{q \neq p} [\, (pp \mid qq) + (q{:}pp) \,] - \sum_r (r{:}pp) \tag{IB-8}$$

in which the atomic coulomb repulsion integral $(pp \mid qq)$ is

$$(pp \mid qq) = \iint \chi_p(2) \quad \chi_p(1) \quad \frac{e^2}{r_{12}} \quad \chi_q(1) \quad \chi_q(2) \; d\tau_1 \; d\tau_2 \tag{IB-9}$$

and the coulomb penetration integral between χ_p and neutral atoms q and r is

$$(q{:}pp) = - \int \chi_p(1) \; U_q(1) \quad \chi_p(1) \; d\tau_1 \tag{IB-10}$$

Considering now the molecular orbital energy, we can write this quantity in terms of the atomic integrals which have been developed. The energy of a particular molecular orbital configuration $| \ldots \phi_i(i) \ldots \phi_j(j) \ldots |$ is

$$
\begin{aligned}
E &= \langle |\ldots\phi_i(i)\ldots\phi_j(j)\ldots| \; | \; \mathcal{H} \; | \; |\ldots\phi_i(i)\ldots\phi_j(j)\ldots| \rangle \\
&= 2 \sum_i \langle \phi_i(i) \; | \mathcal{H}_{core}(i) \; | \; \phi_i(i) \rangle \\
&\quad + 2 \sum_{i>j} \langle \phi_i(i) \;\; \phi_j(j) \; | \; \frac{e^2}{r_{ij}} \; | \; \phi_i(i) \;\; \phi_j(j) \rangle \\
&\quad - \sum_{i>j} \langle \phi_i(i) \;\; \phi_j(j) \; | \; \frac{e^2}{r_{ij}} \; | \; \phi_j(i) \;\; \phi_i(j) \rangle \quad ,
\end{aligned}
\tag{IB-11}
$$

or $E = 2 \sum_i \mathcal{E}_i + 2 \sum_{ij} J_{ij} - \sum_{ij} K_{ij}$. In terms of the atomic integrals these molecular integrals take the form

$$
\begin{aligned}
\mathcal{E}_i = \sum_j c_{ij}^2 \Big\{ W_{pj} &- \sum_{q \neq j} \left[(jj\,/\,qq) + (q\!:\!jj) \right] - \sum_r (r\!:\!jj) \Big\} \\
&+ \sum_{k \neq j} c_{ik}\, c_{ij} \Big\{ S_{jk}\, W_{pj} - \sum_{q \neq k} \left[(kj\,/\,qq) + (q\!:\!jk) \right] \\
&- \sum_r (r\!:\!kj) \Big\}
\end{aligned}
\tag{IB-12}
$$

$$
J_{ij} = \zeta^{ii}_{jj} = \sum_{p,q,r,s,} c_{ip}\, c_{iq}\, c_{jr}\, c_{js}\, (pq\,/\,rs) \tag{IB-13}
$$

$$
K_{ij} = \zeta^{ij}_{ij} = \sum_{p,q,r,s} c_{ip}\, c_{jq}\, c_{ir}\, c_{js}\, (pq\,|\,rs) \tag{IB-14}
$$

The off-diagonal elements are very similar, and we shall list them for the case at hand.

$$\mathscr{H}_{11} = 2\varepsilon_1 + \varepsilon_2 + J_{11} + 2J_{12} - K_{12}$$

$$\mathscr{H}_{12} = -\sqrt{2}\,(\varepsilon_{13} + \zeta^{13}_{11} + \zeta^{13}_{22} - \frac{1}{2}\zeta^{12}_{23})$$

$$\mathscr{H}_{13} = \sqrt{\frac{3}{2}}\;\zeta^{12}_{23}$$

$$\mathscr{H}_{14} = K_{13}$$

$$\mathscr{H}_{22} = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + J_{12} + J_{13} + J_{23} - \frac{1}{2}K_{23} - \frac{1}{2}K_{12} + K_{13}$$

$$\mathscr{H}_{23} = \frac{\sqrt{3}}{2}\,(K_{12} - K_{22})$$

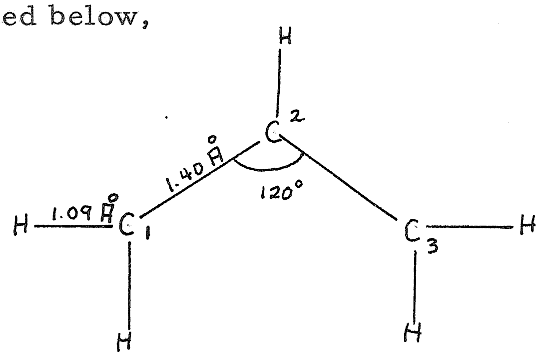
$$\mathscr{H}_{24} = -\sqrt{2}\,(\varepsilon_{13} + \zeta^{13}_{22} + \zeta^{13}_{33} - \frac{1}{2}\zeta^{12}_{23})$$

$$\mathscr{H}_{33} = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + J_{12} + J_{13} + J_{23} - K_{13} + \frac{1}{2}K_{12} + \frac{1}{2}K_{23}$$

$$\mathscr{H}_{34} = -\sqrt{\frac{3}{2}}\;\zeta^{12}_{23}$$

$$\mathscr{H}_{44} = \varepsilon_2 + 2\varepsilon_3 + 2J_{23} + J_{33} - K_{23}\,.$$

To evaluate these matrix elements numerically with the integrals which are tabulated in the literature, a table of the integrals ζ^{kl}_{ij} must be constructed from the tabulated atomic integrals $(mn|pq)$ and $(mn{:}p)$ and the atomic orbital coefficients of IB-2. The model for allyl which is taken is depicted below,



and the atomic integrals $(mn|pq)$ are taken from the benzene CI calculation of Parr, Craig and Ross (46) and the penetration integrals involving the hydrogen atoms are computed from the tables of Roothaan (47). These are listed in table IB-1 and the results of the computation of the integrals ζ_{ij}^{kl} are given in table IB-2. The numerical values in ev of the matrix elements are

$$\mathcal{H}_{11} = 3\,W_{2p} \quad -29.9746$$

$$\mathcal{H}_{12} = -0.0404$$

$$\mathcal{H}_{13} = 3.5346$$

$$\mathcal{H}_{14} = 2.7929$$

$$\mathcal{H}_{22} = 3\,W_{2p} \quad -19.2279$$

$$\mathcal{H}_{23} = 0.0223$$

$$\mathcal{H}_{24} = 0.02030$$

$$\mathcal{H}_{33} = 3\,W_{2p} \quad -18.9004$$

$$\mathcal{H}_{34} = -3.5346$$

$$\mathcal{H}_{44} = 3\,W_{2p} \quad -13.6341$$

Solution of the secular determinant for its lowest root is carried out by an iterative process, and the ground state function is found to be

$$\Psi_{CI} = 0.9284\ \Phi_1 + 0.0069\ \Phi_2 - 0.3106\ \Phi_3 - 0.2038\ \Phi_4 \qquad \text{(IB-15)}$$

with correlation energy of 1.7975 ev. This compares very well with the result of Chalvet and Daudel which is (in our language)

$$\Psi_{CI} = 0.9249\ \Phi_1 + 0.0660\ \Phi_2 - 0.3133\ \Phi_3 - 0.2049\ \Phi_4 \,.$$

The method of alternant orbitals predicts for allyl a function of the form

Table IB-1

Atomic Coulomb and Penetration Integrals

$(11|11) = 16.930$ ev
$(11|22) = 9.027$
$(11|33) = 5.668$
$(11|12) = 3.313$
$(11|23) = 1.870$
$(11|13) = 0.376$
$(12|12) = 0.923$
$(13|13) = 0.017$
$(12|13) = 0.136$
$(13|22) = 0.524$

$(1:22) = 0.856$
$(1:33) = 0.013$
$(1:12) = 1.887$
$(1:13) = 0.109$
$(1:23) = 0.039$

$(h_1|11) = 0.566$
$(h_1|12) = 0.074$
$(h_1|13) = 0.077$

Table IB-2

Two-Electron Molecular Integrals ζ^{ij}_{kl} in ev.

ij → kl ↓	11	12	13	22	23	33
11	11.521994	0.000000	-1.471344	10.025212	0.000000	11.590981
12	0.000000	2.969544	0.000000	0.000000	2.886110	0.000000
13	- 1.471345	0.000000	2.792910	1.315789	0.000000	- 1.643441
22	10.025212	0.000000	1.315789	11.435649	0.000000	0.000000
23	0.000000	2.886110	0.000000	0.000000	2.943822	0.000000
33	11.590980	0.000000	- 1.643441	10.193919	0.000000	12.092824

$$\Psi_{\mathrm{MAO}} = \frac{\Phi_1 - \sqrt{\frac{2}{3}} \tan\vartheta \; \Phi_3 - \tan^2\vartheta \; \Phi_4}{\left(1 + \sqrt{\frac{2}{3}} \tan^2\vartheta + \tan^4\vartheta\right)^{\frac{1}{2}}} \qquad \text{(IB-16)}$$

in which ϑ is determined by minimization of the energy. The equation for the energy as a function of ϑ is given by

$$E(\vartheta) = \frac{\mathcal{H}_{11} - 2\sqrt{\frac{2}{3}} \tan\vartheta \; \mathcal{H}_{13} + \tan^2\vartheta \left(\frac{2}{3}\mathcal{H}_{33} - 2\,\mathcal{H}_{14}\right) + 2\sqrt{\frac{2}{3}} \tan^3\vartheta \; \mathcal{H}_{34} + \tan^4\vartheta \; \mathcal{H}_{44}}{1 + \frac{2}{3} \tan^2\vartheta + \tan^4\vartheta} \, . \qquad \text{(IB-17)}$$

Figure IB-1 shows this function, and the minimum in energy occurs at $\tan\vartheta = 0.4500$. This value of the parameter gives

$$\Psi_{\mathrm{MAO}} = 0.9221\;\Phi_1 - 0.3388\;\Phi_3 - 0.1867\;\Phi_4 \qquad \text{(IB-18)}$$

and a correlation energy of 1.7797 ev. The spin density matrix (27) from IB-18 is

$$\rho = \begin{pmatrix} 0.6388 & -0.1028 & -0.2424 \\ -0.1028 & -0.2645 & -0.1028 \\ -0.2424 & -.1028 & 0.6388 \end{pmatrix} . \qquad \text{(IB-19)}$$

The agreement of IB-15 and IB-18 is quite good and shows that for allyl the pairing scheme of MAO is the dominant one since the coefficient of the one configuration Φ_2 which is neglected by MAO is quite small in the CI function. However, as the size of the hydrocarbon radical increases, MAO will neglect more and more configurations

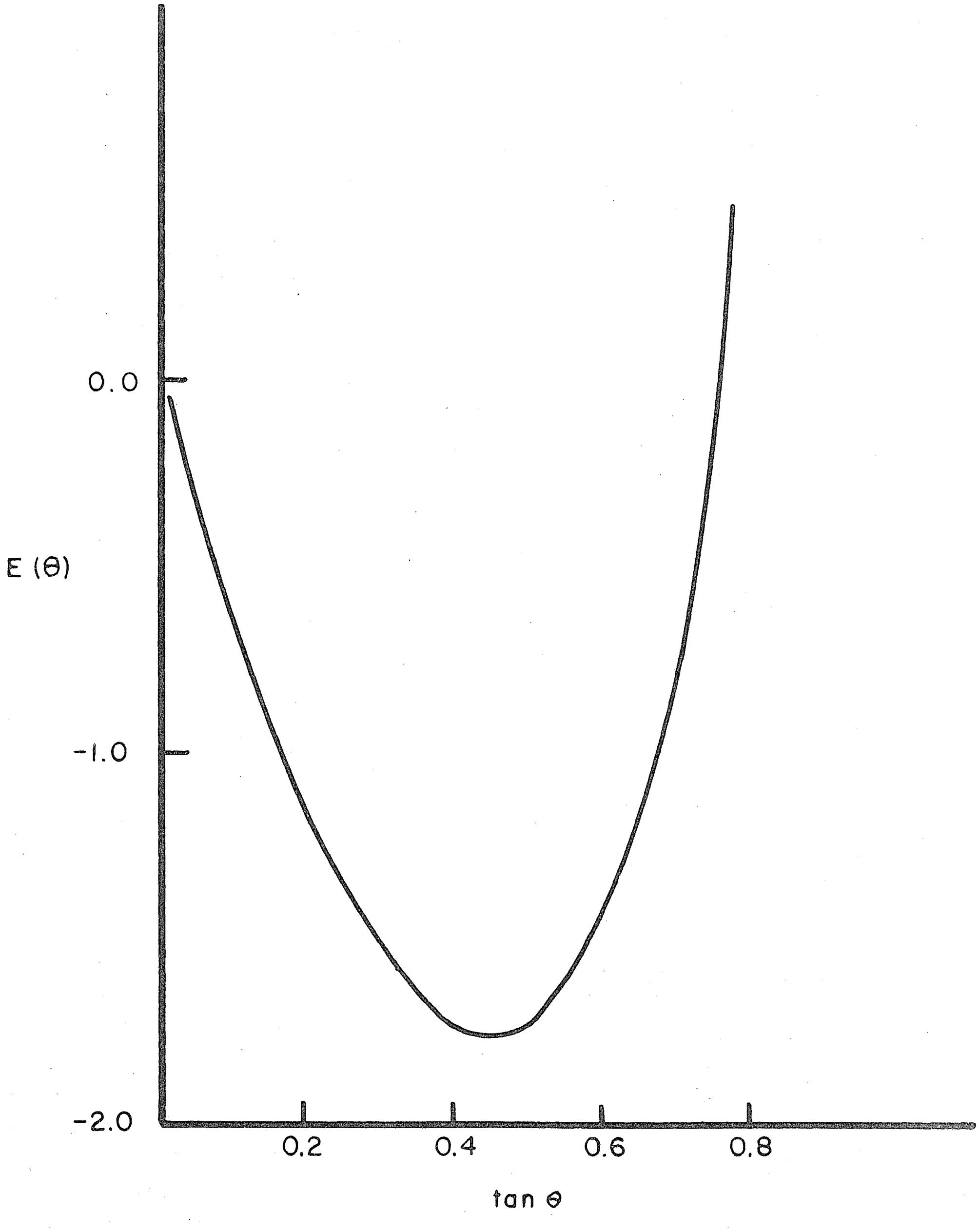


Fig. IB-1. Equation (IB-17) as a function of the correlation parameter tan ϑ.

which have non-zero coefficients in the CI treatment. It is interesting to compare the results of MAO for benzene (48) with the CI treatment (46). Here MAO accounts for 85% of the correlation energy, and again the configurations neglected by MAO are of very small consequence in the CI function. That work and the result here for allyl give support to the validity of a wave function similar to IA-14 or IA-31 being a good approximation to the ground state of an odd alternant hydrocarbon radical.

C. SIMPLE VALENCE BOND CALCULATIONS OF SPIN DENSITIES

Theory

Brovetto and Ferroni (49) were the first to apply simple valence bond theory to the calculation of the ESR spectra of odd-alternant free radicals, taking for their example triphenylmethyl radical. Their calculation made possible the interpretation of the complex spectrum which was observed; however, although it may have been tacitly assumed, no mention was made of a linear relation between the hyperfine interaction of a particular proton and the spin density at the carbon atom to which that proton is bonded. McConnell (9) and McConnell and Chesnut (3) have shown the validity of valence bond theory for the derivation of the linear relation for the case of the C-H fragment.

To derive the spin density function in terms of the spin densities at the individual carbon atoms we must evaluate the quantity

$$\rho(r) = \langle \Psi | \rho | \Psi \rangle \quad . \qquad \text{(I-3)}$$

Ψ is the ground state electronic wave function and in the language of simple valence bond theory is given by the superposition of the canonical structures, ϕ_i, not including long bond (bonds to a non-nearest neighbor) or ionic structures.

$$\Psi = \sum_i C_i \phi_i \quad . \qquad \text{(IC-1)}$$

McLachlan (30) has proved recently that all the coefficients c_i in IC-1 are necessarily positive within the following set of conditions:

1. Neglect of all ionic structures.
2. Exchange integrals between atoms of the same set (starred or unstarred) are set equal to zero.
3. All the other exchange integrals involved in the calculation of the ground state wave function are negative.

Thus we can write

$$\rho(r) = \sum_{ij} C_i C_j \langle \phi_i | \rho | \phi_j \rangle \qquad \text{(IC-2)}$$

and note that any sign dependence must arise from the matrix element $\langle \phi_i | \rho | \phi_j \rangle$.

We shall now prove that for an odd-alternant radical the matrix element in question is given by the equation

$$\langle \phi_i | \rho | \phi_j \rangle = 0, \pm \frac{1}{2^{n-m}} \qquad \text{(IC-3)}$$

for which the zero results for all atoms in a "closed" island of the $\phi_i - \phi_j$ superposition diagram, and the $+\frac{1}{2^{n-m}}$ $(-\frac{1}{2^{n-m}})$ results for the starred (unstarred) atoms in the "open" island of the $\phi_i - \phi_j$ superposition diagram. In IC-3 n is the number of bonds in any principal resonance structure and m is the number of "closed" islands in the superposition diagram. A typical canonical structure which represents bonds between atoms a^* and b, c^* and d, ..., p^* and q, in which $a^*, c^*, \ldots, p^*$ are starred atoms and b, d, ..., q are unstarred atoms, is given by (50).

$$\phi_K = \frac{1}{\sqrt{2^n}} \sum_{R} (-1)^R R \mathcal{A} a^* \bar{b} c^* \bar{d} \ldots p^* \bar{q} \,. \qquad \text{(IC-4)}$$

R is the operator which interchanges the spin functions α and β of bonded atoms and $\mathcal{A}$ is the usual antisymmetrization and renormalization operator.

$$\mathcal{A} = \frac{1}{\sqrt{N!}} \sum_{P} (-1)^P P \,. \qquad \text{(IC-5)}$$

Equation IC-2 can now be written

$$\rho(r) = \frac{1}{2^n} \sum_{i,j} c_i c_j \sum_{R,Q} (-1)^{R+Q} \langle R a^* \bar{b} \ldots \bar{q} \,|\, \rho \,|\, Q \; a^* \bar{b} \ldots \bar{q} \rangle . \qquad \text{(IC-6)}$$

Since the orbitals a^*, b, ..., q are orthogonal and the operator ρ is a sum of one-electron operators, both spin and space functions must match, and any permutation of pairs of electrons in IC-6 will lead to a zero value for the matrix element. Thus we need only retain the identity permutation in IC-5. This simplification allows us to factor the functions corresponding to the structures ϕ_i and ϕ_j into a product of functions representing bonds between pairs of atoms. For example, we can now write

$$\phi_K = \frac{1}{\sqrt{2^n}} \{ [a^*(1) \bar{b}(2) - \bar{a}^*(1) b(2)] [c^*(3) \bar{d}(4) - \bar{c}^*(3) d(4)] \ldots m^*(m) \ldots [p^*(n-1) \bar{q}(n) - \bar{p}^*(n-1) q(n)] \} . \qquad \text{(IC-7)}$$

Assignment of the spins in the manner illustrated by IC-7 gives the proper phase to each canonical structure.

Let I(i) represent the distribution function for the electrons associated with those atoms making up a "closed" island in the superposition diagram of the structures ϕ_i and ϕ_j and let $d\tau(i)$ represent the element of volume for these electrons. If we wish to calculate the non-orthogonality integral between two structures, the quantity can be expressed as

$$\langle \phi_i | \phi_j \rangle = \frac{1}{2^n} \int I(1)\, d\tau_1 \int I(2)\, d\tau_2 \ldots \int I(m)\, d\tau_m \ldots \int I'\, d\tau' \qquad \text{(IC-8)}$$

and one can easily convince himself that

$$\int I(i)\, d\tau_i = 2$$

and, I' being the "open" island,

$$\int I'\, d\tau' = 1,$$

which yields the well-known result (50)

$$\langle \phi_i / \phi_j \rangle = \frac{1}{2^{n-m}} \quad . \qquad \text{(IC-9)}$$

The spin density matrix element between the structures ϕ_i and ϕ_j can be written

$$\langle \phi_i / \underset{\substack{k \\ \text{(electrons)}}}{\sum} \delta(r-r_k)\, S_{kz} / \phi_j \rangle = \underset{\substack{k \\ \text{(atoms)}}}{\sum} \langle \phi_i | \rho_k | \phi_j \rangle \quad , \qquad \text{(IC-10)}$$

and since we have already observed that only the identity permutation of IC-5 gives a non-vanishing result, we can associate electron k with atom k.

To derive IC-3 let us first consider the various cases which arise.

<u>Case I.</u> K is in the closed island I(k).

a) K is a starred atom (electron).

$$\langle \phi_i | \rho_k | \phi_j \rangle = \frac{1}{2^n} \int \rho_k \, I(K) \, d\tau_k \int I(1) \, d\tau_i \ldots \int I' d\tau'$$

$$= \frac{1}{2^{n-m+1}} \int \rho_k \, I_k \, d\tau_k \qquad \text{(IC-11)}$$

Let us write the integral $\int \rho_k I(K) \, d\tau_k$ in the following form

$$\int \rho_k \, I(k) \, d\tau_k = \langle u^*_k \bar{u}_i - \bar{u}^*_k u_i \,|\, \rho_k \,|\, u^*_k \bar{u}_j - \bar{u}^*_k u_j \rangle \cdot \int \prod_{\substack{\text{pairs } P \\ \text{of bonded atoms z } k,l}} \qquad \text{(IC-12)}$$

$$(u^*_p \bar{u}_{p+1} - \bar{u}^*_p u_{p+1}) \cdot \prod_{q \neq k, j} (u^*_q \bar{u}_{q+1} - \bar{u}^*_q u_{q+1}) \frac{d\tau}{d\tau_k}$$

Carrying out the operation of ρ_k and rewriting, we obtain

$$\int \rho_k \, I(K) \, d\tau_k = u^{*2}_k \int (\bar{u}_i \bar{u}_j - u_i u_j) \prod_p (u^*_p \bar{u}_{p+1} - \bar{u}^*_p u_{p+1}) \cdot \qquad \text{(IC-13)}$$

$$\prod_q (u^*_q \bar{u}_{q+1} - \bar{u}^*_q u_{q+1}) \frac{d\tau}{d\tau_k}$$

In the expanded form of the integral above there are only two terms which do not vanish by orthogonality of the spin function, namely

$$\int u^*_1 \bar{u}_2 \ldots \bar{u}_i \ldots \bar{u}_j \ldots u^*_{n-1} \bar{u}_n \frac{d\tau}{d\tau_k} \quad \text{and} \quad (-1)^{a-3} \int \bar{u}^*_1 u_2 \ldots u_i \ldots u_j \ldots \bar{u}_n \frac{d\tau}{d\tau_k}$$

where a is the number of pairs of bonded atoms in the superposition diagram. Since a is even, these two integrals have the same value and we arrive at the result

$$\langle \rho_k \rangle = \frac{1}{2^{n-m+1}} u_k^2 (1 - 1) = 0 . \qquad \text{(IC-14)}$$

b) K unstarred

$$\int \rho_k I(k) d\tau_k = u_k^2 \int (\bar{u}_i^* \bar{u}_j^* - u_i^* u_j^*) \pi_{P,Q} (u_p^* \bar{u}_{p+1} - \bar{u}_p^* u_{p+1})(u_q^* \bar{u}_{q+1} - \bar{u}_q^* u_{q+1}) \frac{d\tau}{d\tau_k}$$

(IC-15)

By exactly the same type of argument which held for the starred case we find that the two integrals have the same value and cancel each other

$$\langle \rho_k \rangle = \frac{1}{2^{n-m+1}} u_k^2 (1 - 1) = 0 . \qquad \text{(IC-16)}$$

<u>Case II.</u> K is in the open island I' .

a) K starred

Following equations IC-11 and IC-12 we are led to

$$\int \ldots \int \rho_k I' d\tau' = \frac{1}{2^{n-m}} \int \rho_k I' d\tau' \qquad \text{(IC-17)}$$

When IC-17 is rewritten in a form similar to IC-13 we find

$$\int \rho_k I' d\tau' = \frac{1}{2^{n-m}} \int \prod_{p \neq k, L, y} u_y^* (u_p^* \bar{u}_{p+1} - \bar{u}_p^* u_{p+1}) \prod_{q \; k, j, z} (u_q^* \bar{u}_{q+1} - \bar{u}_q^* u_{q+1}) u_z^* \frac{d\tau}{d\tau_k} .$$

$$\langle u_k^* \bar{u}_L - \bar{u}_k^* u_L \,|\, \rho_k \,|\, u_k^* \bar{u}_j - \bar{u}_k^* u_j \rangle$$

$$= \frac{u_k^{*2}}{2^{n-m}} \int (\bar{u}_L \bar{u}_j - u_L u_j) \prod_{p,q} (u_p^* \bar{u}_{p+1} - \bar{u}_p^* u_{p+1}) \cdot (u_q^* \bar{u}_{q+1} - \bar{u}_q^* u_{q+1}) u_y^* u_z^* \frac{d\tau}{d\tau_k} \tag{IC-18}$$

For this case we observe that the only term which does not vanish by spin orthogonality is $\int (u_1^*)^2 (\bar{u}_2)^2 \ldots (\bar{u}_L)^2 (\bar{u}_j)^2 \ldots (u_z^*)^2 (u_y^*)^2 \ldots (\bar{u}_n)^2 \frac{d\tau}{d\tau_k}$ which gives the result

$$\langle \phi_i | \rho_k | \phi_j \rangle = + \frac{u_k^{*2}}{2^{n-m}} \tag{IC-19}$$

b) K unstarred

By a completely analogous procedure we obtain

$$\langle \phi_i | \rho_k | \phi_j \rangle = \frac{u_k^2}{2^{n-m}} \int (u_L^* u_j^* - \bar{u}_L^* \bar{u}_j^*) \prod_{p,q} (u_p^* \bar{u}_{p+1} - \bar{u}_p^* u_{p+1}) u_y (u_q^* \bar{u}_{q+1} - \bar{u}_q^* u_{q+1}) u_z \frac{d\tau}{d\tau_k} \tag{IC-20}$$

and we recognize this integral as being the negative of IC-18, leading finally to

$$\langle \phi_i | \rho_k | \phi_j \rangle = - \frac{u_k^2}{2^{n-m}} \tag{IC-21}$$

which completes our derivation of IC-3.

The matrix of the Hamiltonian $| \mathcal{H}_{ij} - S_{ij} E |$ is constructed using the usual rules of valence bond theory (50). For our purposes a simplification can be made by observing the following relations:

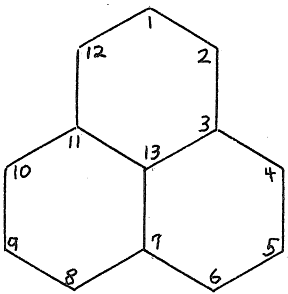
$$\mathcal{H}_{ij} = S_{ij} Q + h_{ij} \alpha \tag{IC-22}$$

$$E = Q + \epsilon \alpha$$

The matrix which we wish to solve for its lowest eigenvector takes the form $| h_{ij} - S_{ij} \epsilon |$.

Perinaphthenyl

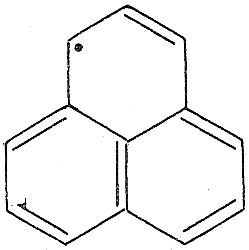
Sogo, Nakazaki and Calvin (23) observed that, upon standing for several hours, a solution of perinaphthene in carbon tetrachloride began to show a yellow color and the previously well resolved NMR spectrum of this solution lost its resolution. The ESR of the colored solution yielded a spectrum consisting of seven lines (intensity 1:6:15:20:15:6:1) each of which was further split into a quartet (intensity 1:3:3:1). This spectrum is interpreted as arising from the perinaphthenyl radical (I).



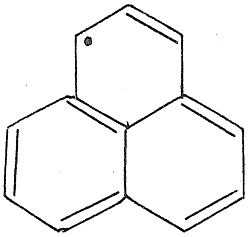
(I)

This molecule seemed to be a good example to test the predictions of valence bond theory for the width of the ESR spectrum indicated the presence of negative spin densities.

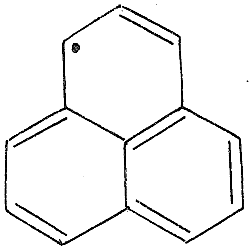
We must calculate the ground state electronic wave function, so we proceed to solve the secular equation arising from IC-22. It is assumed that (I) has D_{3h} symmetry. Since long-bond and ionic structures have been neglected, all of the principal structures can be generated from the four classes of structures:



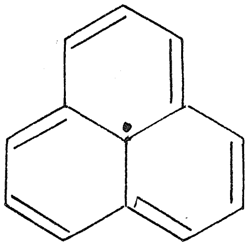
ϕ_1



ϕ_2



ϕ_3



ϕ_4

From the four ϕ_i we generate four totally symmetrical functions as follows:

$$\psi_i = \frac{1}{N_i} \sum_{j=1}^{3} C_j (1 + R) \phi_i \quad . \tag{IC-23}$$

In IC-23 N_i is a normalization factor, and C_1, C_2, C_3 are operators producing rotation of the structures ϕ_i of O, $\frac{2\pi}{3}$, and $-\frac{2\pi}{3}$ about the axis perpendicular to the plane of the molecule and passing through atom 13. R is the operation of rotation by π about an axis passing through atoms 1, 13, and 7.

Much of the labor involved in the calculation of the various matrix elements can be avoided by noting that, if M is an operator having the symmetry properties of the molecule, any matrix element of that operator can be written

$$\langle \psi_i | M | \psi_j \rangle = \frac{1}{N_i N_j} \langle \sum_L C_L (1 + R)\phi_i \Big| M \Big| \sum_K C_K (1 + R) \phi_j \rangle$$

$$= \frac{1}{N_i N_j} \sum_{K,L} (C_L C_K + C_L R C_K + C_L C_K R + C_L R C_K R) \cdot \qquad \text{(IC-24)}$$

$$\langle \phi_i | M | \phi_j \rangle$$

We now recall that

$$C_j R - R C_j = 0 \qquad j = 1, 2, 3. \qquad \text{(IC-25)}$$

and $R \cdot R = 1$,

and further that $\sum_{LK} C_L C_k = 3 \sum_L C_L$ (IC-26)

since the operators C form a complete subset. Thus equation IC-24 becomes

$$\langle \psi_i | M | \psi_j \rangle = \frac{(2)(3)}{N_i} \langle \phi_i | M / \psi_j \rangle \qquad \text{(IC-27)}$$

The secular determinant which we must solve for the ground state wave function is

$$\begin{vmatrix} (\frac{115}{38} - \epsilon) N_1^{-2} & (\frac{168}{3\sqrt{323}} - \frac{9}{\sqrt{323}} \epsilon) N_1^{-1} N_2^{-1} & (\frac{121}{2\sqrt{285}} - \frac{25}{2\sqrt{285}} \epsilon) N_1^{-1} N_3^{-1} & (\frac{48}{\sqrt{627}} - \frac{6}{\sqrt{627}} \epsilon) N_1^{-1} N_4^{-1} \\ (\frac{168}{3\sqrt{323}} - \frac{9}{\sqrt{323}} \epsilon) N_2^{-1} N_1^{-1} & (\frac{303}{102} - \epsilon) N_2^{-2} & (\frac{52}{\sqrt{255}} - \frac{10}{\sqrt{255}} \epsilon) N_2^{-1} N_3^{-1} & (\frac{111}{2\sqrt{561}} - \frac{33}{2\sqrt{561}} \epsilon) N_2^{-1} N_4^{-1} \\ (\frac{121}{2\sqrt{285}} - \frac{25}{2\sqrt{285}} \epsilon) N_3^{-1} N_1^{-1} & (\frac{52}{\sqrt{255}} - \frac{10}{\sqrt{255}} \epsilon) N_3^{-1} N_2^{-1} & (\frac{10}{3} - \epsilon) N_3^{-2} & (\frac{16}{\sqrt{55}} - \frac{3}{\sqrt{55}} \epsilon) N_3^{-1} N_4^{-1} \\ (\frac{48}{\sqrt{627}} - \frac{6}{\sqrt{627}} \epsilon) N_4^{-1} N_1^{-1} & (\frac{111}{2\sqrt{561}} - \frac{37}{2\sqrt{561}} \epsilon) N_4^{-1} N_2^{-1} & (\frac{16}{\sqrt{55}} - \frac{3}{\sqrt{55}} \epsilon) N_4^{-1} N_3^{-1} & (\frac{39}{22} - \epsilon) N_4^{-2} \end{vmatrix} = 0 \qquad \text{(IC-28)}$$

where $N_1 = \frac{3}{4} \sqrt{19}$

$N_2 = \frac{3}{4} \sqrt{17}$

$N_3 = \frac{3}{4} \sqrt{15}$

$N_4 = \frac{3}{4} \sqrt{33}$.

Solution of the resulting polynomial for its lowest root gives

$$\epsilon = 4.3757$$

or
$$E = Q + 4.3757\alpha .$$

Relative to structure ϕ_1, this represents a resonance energy of 2.8757α. This energy is also 1.0054α greater than the sum of the resonance energies of naphthalene and allyl:

$$\begin{array}{rlll} & \text{naphthalene} & = & 1.3703\ \alpha \\ + & \text{allyl} & = & \underline{0.5000\ \alpha} \\ & & & 1.8703\ \alpha \end{array}$$

Solution for the ratio of the coefficients of the ground state function gives:

$$\frac{c_2}{c_1} = 0.7827$$

$$\frac{c_3}{c_1} = 0.8788$$

$$\frac{c_4}{c_1} = 0.3804 .$$

The normalization equation gives us the values of these coefficients

$$\frac{1}{C_1^2} = \sum_{j,k} \frac{C_j}{C_1} \cdot \frac{C_k}{C_1} S_{jk} \qquad \text{(IC-29)}$$

Finally the ground state electronic wave function is found to be

$$\Psi = 0.3999\,\psi_1 + 0.3130\,\psi_2 + 0.3434\,\psi_3 + 0.1521\,\psi_4 . \qquad \text{(IC-30)}$$

In order to use IC-29 for the development of the matrix of the spin density operator, one must select linear combinations of the ρ's which exhibit the molecular symmetry. Those chosen are listed below:

$$\langle \psi_i | \rho_1 | \psi_j \rangle = \frac{6}{N_j} \langle \phi_i | \frac{\rho_1 + \rho_5 + \rho_9}{3} | \psi_j \rangle \qquad \text{(IC-31)}$$

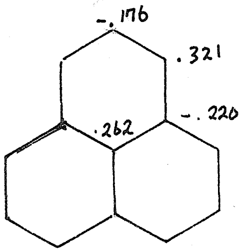
$$\langle \psi_i | \rho_2 | \psi_j \rangle = \frac{6}{N_j} \langle \phi_i | \frac{\rho_2 + \rho_4 + \rho_6 + \rho_8 + \rho_{10} + \rho_{12}}{6} | \psi_j \rangle \qquad \text{(IC-32)}$$

$$\langle \psi_i | \rho_3 | \psi_j \rangle = \frac{6}{N_j} \langle \phi_i | \frac{\rho_3 + \rho_7 + \rho_{11}}{3} | \psi_j \rangle \qquad \text{(IC-33)}$$

Use of these relations leads to the following spin density function for the perinaphthenyl radical

$$\rho(r) = (-.176)(u_1^2 + u_5^2 + u_9^2) + (.321)(u_2^2 + u_4^2 + u_6^2 + u_8^2 + u_{10}^2 + u_{12}^2) + (-.220)(u_3^2 + u_7^2 + u_{11}^2) + (.262)u_{13}^2 \qquad \text{(IC-34)}$$

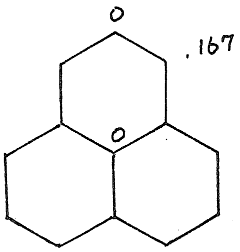
in which u_i is the atomic orbital centered on carbon atom i. The following diagram demonstrates the prediction of simple valence bond theory for the spin distribution of the perinaphthenyl radical.



The absolute values of the observed hyperfine coupling constants due to protons 1 and 2 of (I) are found to be $|a_1| = 2.2$, $|a_2| = 7.3$ gauss (23). If one employs the linear relation between spin density and proton coupling constant (3) with the value of the proportionality constant -22.5 gauss, the spin densities derived in this work lead to coupling constants $a_1 = -4.0$, $a_2 = +7.3$ gauss. The total spread of the spectrum is given by

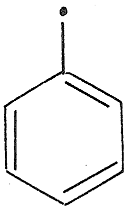
$$S = 6(7.3) + 4(4.0) = 55.8 \text{ gauss}$$

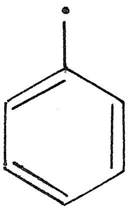
which is to be compared with the experimental value of 50.4 gauss. Simple molecular orbital theory without configuration interaction predicts the spin distribution which is displayed on the following diagram.

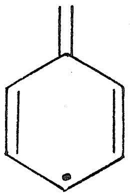


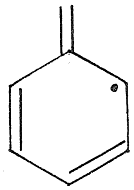
Benzyl

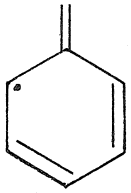
Pauling and Wheland (51) have treated the benzyl radical with simple valence bond theory and develop the necessary secular equation from the following set of canonical structures:


ϕ_1


ϕ_2


ϕ_3


ϕ_4


ϕ_5

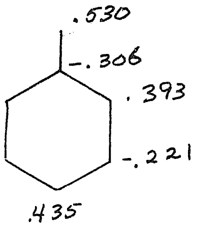
These authors make the assumption that the ground state function is of the form

$$\Psi = a(\phi_1 + \phi_2) + b(\phi_3 + \phi_4 + \phi_5) \tag{IC-34}$$

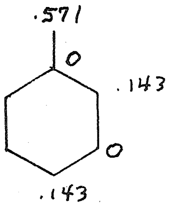
and report the ratio of coefficients $\frac{a}{b} = 1.0279$. Making use of the normalization equation IC-29 we obtain for the ground state function

$$\Psi = 0.3000(\phi_1 + \phi_2) + 0.2919\,(\phi_3 + \phi_4 + \phi_5)\,. \tag{IC-35}$$

Evaluating the matrix of the spin density operator leads to the diagram of the spin distribution for the benzyl radical



This can be compared to that predicted by simple molecular orbital theory (52)



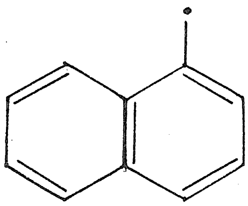
No experimental observation of the proton coupling constants in the molecule have been reported. However, we can get some idea of the ring proton couplings from the ESR of the nitrobenzene negative ion (67) in which $\frac{a_3}{a_3} = \frac{3.7}{0.65}$ and $\frac{a_3}{a_5} = 1$.

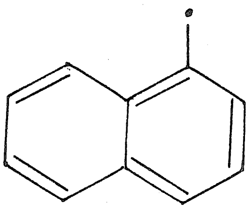
<u>α-Methylnaphthanyl</u>

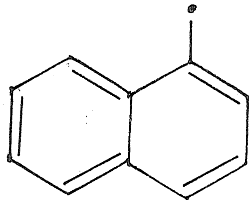
Again using the results of Pauling and Wheland (51) we obtain for this molecule

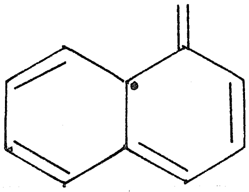
$$\Psi = 0.2685\ \phi_1 + 0.2370\ (\phi_2 + \phi_3) + 0.1589 \sum_{i=4}^{10} \phi_i \qquad \text{(IC-36)}$$

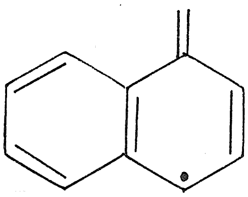
in which the canonical structures are

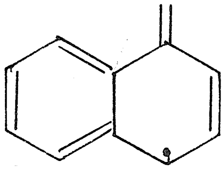

ϕ_1

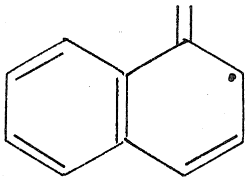

ϕ_2

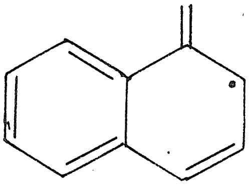

ϕ_3

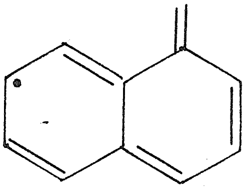

ϕ_4

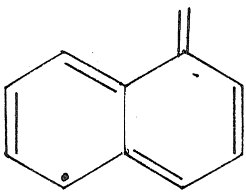

ϕ_5


ϕ_6

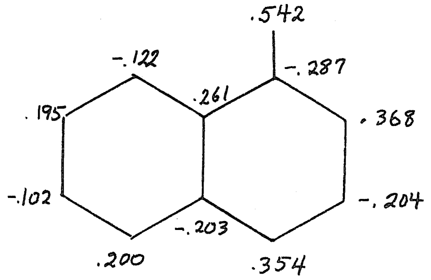

ϕ_7


ϕ_8

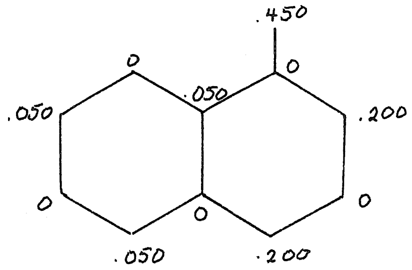

ϕ_9


ϕ_{10}

Evaluation of the spin density function leads to the spin distribution diagram



which is to be compared with that predicted by simple molecular orbital theory (52)



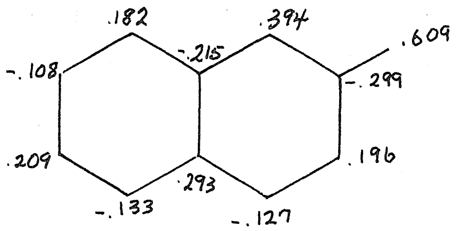
There are no experimental results for this molecule at all.

β-Methylnaphthanyl

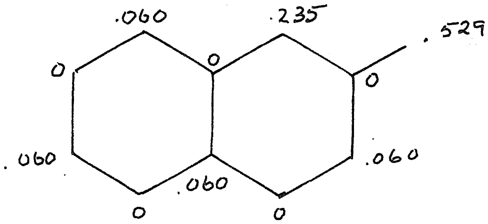
The canonical structures here are quite similar to those of α-methylnaphthanyl and will not be enumerated. From the ratio of coefficients reported by Pauling and Wheland (51) we determine the ground state function to be

$$\Psi = 0.2969\ \phi_1 + 0.2609\ (\phi_2 + \phi_3) + 0.1620 \sum_{i=4}^{9} \phi_i \qquad \text{(IC-39)}$$

The spin distribution diagram which is obtained with this function is



and that obtained with the use of simple molecular orbital theory (52) is



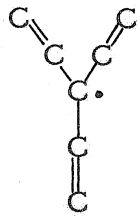
Again there are no experimental results available at this time.

Trivinylmethyl

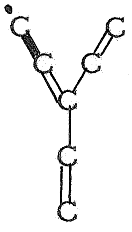
Symmetry requires that the ground state wave function be of the form

$$\Psi = a\phi_1 + b(\phi_2 + \phi_3 + \phi_4) \qquad \text{(IC-38)}$$

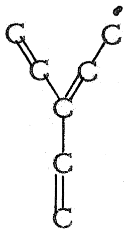
in which the principal structures ϕ_i are



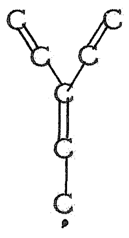
ϕ_1



ϕ_2



ϕ_3



ϕ_4

The secular determinant is developed using the usual rules of valence bond theory and is found to be

$$\begin{vmatrix} 1 - \epsilon & \frac{15}{4} - \frac{3}{2}\epsilon \\ \frac{15}{4} - \frac{3}{2}\epsilon & \frac{15}{2} - \frac{9}{2}\epsilon \end{vmatrix} = 0 \qquad \text{(IC-39)}$$

whose solutions are

$$\epsilon = \frac{1}{6}(1 \pm \sqrt{106}) \quad . \qquad \text{(IC-40)}$$

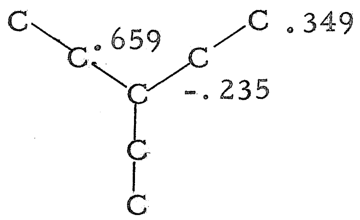
The lowest root corresponds to the energy

$$E = Q + 1.8826\,a \qquad \text{(IC-41)}$$

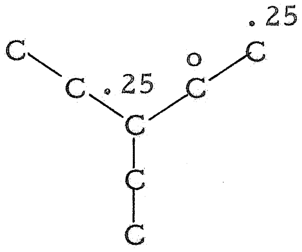
for which the eigenvector is

$$\Psi = 0.3531\,\phi_1 + 0.3381\,(\phi_2 + \phi_3 + \phi_4)\ . \qquad \text{(IC-42)}$$

With IC-42 we obtain the spin distribution



For this molecule simple molecular orbital theory (52) results in the diagram



Discussion

As very little experimental data is available concerning spin densities in odd-alternant free radicals, we are unable to give a detailed comparison of the predictions of this work with experiment. However, it does seem pertinent to mention some of the limitations which are inherent in the use of simple valence bond theory for estimation of proton coupling constants in these compounds.

Valence bond theory without the inclusion of long-bond or ionic structures is known to over-estimate the effect of electron correlation. Löwdin (26) has shown that there is a tendency for electrons of α spin to accumulate on certain atoms accompanied by the accumulation of electrons with β spin on their neighboring atoms in alternant hydrocarbons. However, simple valence bond theory assumes that this process is complete. Thus we can see qualitatively that this method will overestimate spin densities. Introduction of ionic structures into the ground state wave function will have the effect of placing two electrons with opposing spin on one atom and no electrons on its neighbor; neither of these effects produces net spin density at either atom. Unfortunately, the labor involved in the enumeration of all the ionic structures and calculation of the necessary matrix elements is prohibitive.

Also it has been shown that as the size of an aromatic hydrocarbon increases the contribution of the ionic structures to the ground state wave function becomes more and more important. The diagram in figure IC-1 is taken from the work of Pullman (52) and illustrates this effect.

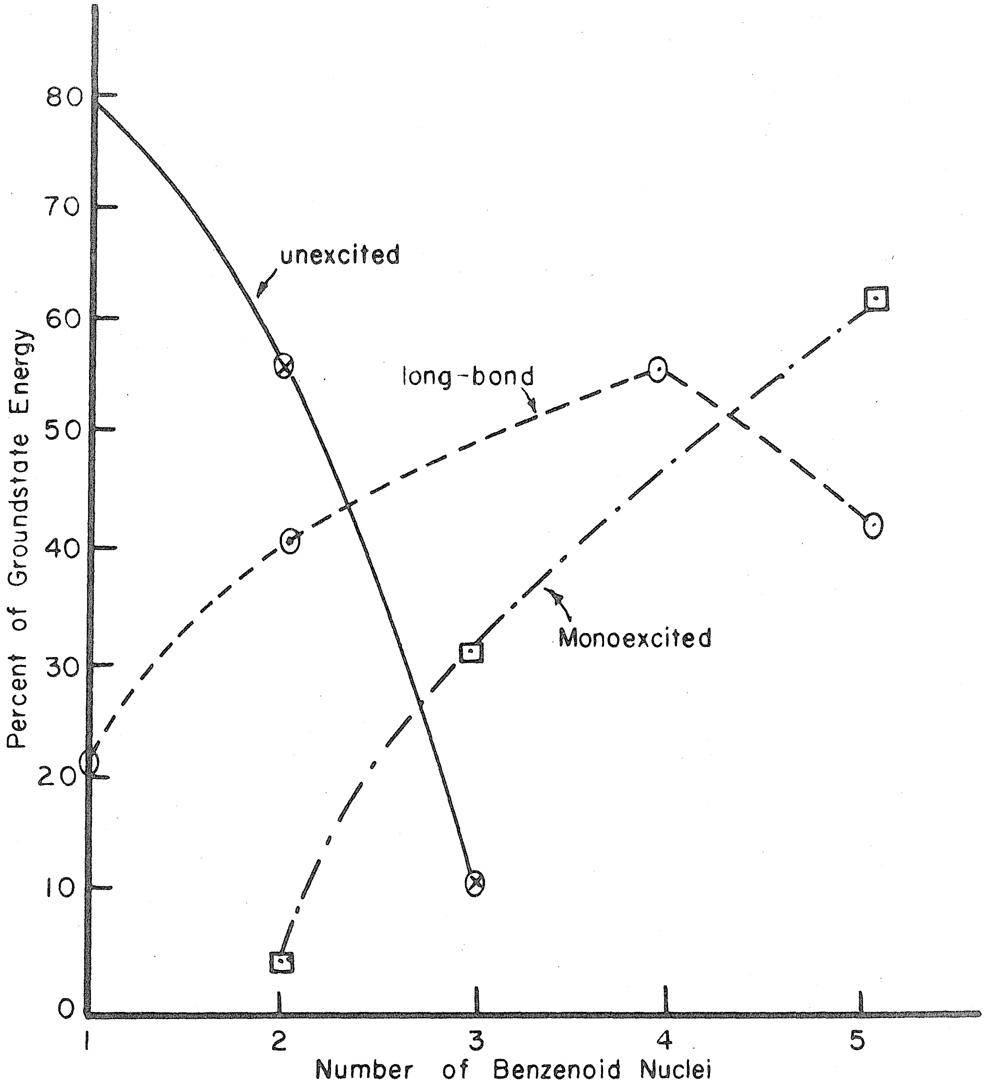


Fig. IC-1. Diagram showing increasing contribution to the groundstate energy of excited and long-bond structures as size of hydrocarbon increases. Reproduced from reference (53).

While these arguments tend to make the quantitative predictions of spin densities obtained from simple valence bond theory suspect, the conclusion that negative spin densities are a real phenomenon is not affected. Polar structures merely reduce the absolute amount of spin magnetization at a given position but can never cause the sign to change.

D. Relation between C^{13} Hyperfine Interaction and π-Electron Spin Density

Previously it was mentioned that proton hyperfine splittings of the ESR of π-electron radicals have provided a useful means for obtaining valuable information about the electronic structure of these molecules. McConnell (21) has shown that a particular proton coupling constant, a_H, in these molecules is linearly related to the diagonal element of the spin density matrix, ρ_{NN}, by the following approximate equality,

$$a_H \approx Q \rho_{NN} .$$

This relation affords a sensitive test of the accuracy of the ground state molecular wave function employed to describe the particular free radical, when a comparison of calculated and observed coupling constant is made.

Hyperfine splittings in these radicals due to magnetic nuclei other than protons are now becoming available experimentally. Adam and Weissman (40) have observed the splittings in the triphenylmethyl radicals due to C^{13} in the methyl position. Cole et al. (54) have obtained the coupling constant of the C^{13} methyl radical, and Tuttle and Weissman (55) have determined the coupling constant of α-C^{13} naphthalene negative ion. With spectrometers of increased sensitivity the C^{13} hyperfine coupling constants can be observed from that small amount of this isotope which is present in natural abundance. Recently McConnell and Fessenden (56) have measured the C^{13} splittings in X-irradiated malonic acid from natural abundance. Thus it is most desirable to have a theory by which these interactions can be related to the electronic structure of π-electron radicals. Especially is it desirable to be able to use splittings due to isotopes such as C^{13}, N^{14} or N^{15} and S^{35} as probes for the determination of the π-electron spin density at a position to which no proton is bonded.

In this section we shall present a theory which relates the coupling constant of a magnetic nucleus within the π-molecular framework itself to the π-spin density distribution. The relation will be shown to be a linear one if the spin densities at each neighbor are included. The necessary proportionality constants for C^{13} are evaluated semi-empirically. Numerical calculation of the coupling constant of the triphenylmethyl radical with C^{13} in the methyl position is carried out and comparison with experiment is made. The splittings due to C^{13} in benzene negative ion and in the β and γ positions of naphthalene negative ions and in the p-benzosemiquinones are predicted.

Calculation of Spin Density in the Molecular Plane

The usual description of a planar conjugated π-electron radical is in terms of π and σ orbitals, for which the π orbitals are antisymmetrical and the σ symmetrical upon reflection in the plane of the molecule. The simplest molecular orbital wave function which employs this description is the Slater determinant

$$\psi_o = |\sigma_1 \bar{\sigma}_1 \ldots \sigma_r \bar{\sigma}_r \pi_1 \bar{\pi}_1 \ldots \pi_n \bar{\pi}_n \pi_o| \ .$$

The r doubly occupied σ bonding orbitals and the corresponding r unoccupied σ^* antibonding orbitals are localized on the various single bonds in the molecule. That this restriction of localized orbitals is not a serious one is shown by the work of Lennard-Jones (57) and Aono (58). For the cases of the singly charged ions of even alternant hydrocarbons there will be n bonding and n antibonding LCAO π orbitals extending over the entire molecule, $2n$ being the number of atoms making up the molecular framework. There are n bonding, n antibonding and one non-bonding delocalized π orbitals for the neutral radical. The manner in which the π orbitals are filled with electrons has been given for these various cases in section A.

Inspection of ψ_o reveals that this function cannot contribute spin density in the molecular plane. It can be shown that the doubly occupied orbitals form a closed shell and make no contribution to the unpaired spin density at all, and π_o itself is made up of $2p_z$ atomic orbitals which mave a node in the molecular plane. Therefore, in constructing the ground state wave function, excited configurations must be introduced which will allow spin magnetization to be realized in the molecular plane. In the Introduction the proper excited configurations for the isolated C-H bond were enumerated. In the present work a generalization of the procedure for the isolated fragment is carried out, taking into account the presence of neighboring atoms from which the entire molecule is constructed. First order perturbation theory is used to treat the configuration interaction problem.

For the determination of the spin density at the protons, McConnell and Chesnut (3) propose two alternative methods for carrying out the perturbation calculation; one in which the series is thrown into closed form and the other in which enumeration of the most important excited states occurring in the expansion is carried out. We shall employ this latter alternative which is described in section VI of that paper.

ψ_o will not be taken as the zeroth order function in the perturbation procedure, but, instead, we will take the function Φ_o, a function which includes some π-π configuration interaction but no σ-π or σ-σ excited states. Hoijtink (59) has recently studied the π electron spin density problem with a π-π CI calculation which is similar in its conclusions to those of section A. The function Φ_o used here is quite similar to the function which is obtained by Hoijtink. If Φ_o is a reasonable starting function (in the sense of reference (3)) the ground state wave function to first order is given by

$$\Psi_{\text{ground state}} = \Phi_o - {\sum_i}' \frac{\langle \Phi_o | \mathscr{H} | \Phi_i \rangle}{E_i - E_o} \Phi_i \qquad \text{(ID-1)}$$

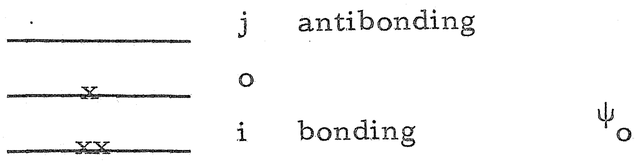
in which the Φ_i's are excited configurations of the σ and π electrons simultaneously, and $\mathscr{H}$ is the total Hamiltonian.

The spin density operator, ρ , is defined by I-3 , and the expectation value of this operator to first order is

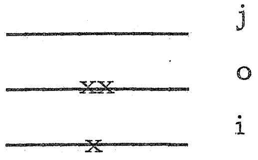
$$\rho(r) = \langle \Phi_o | \rho | \Phi_o \rangle - 2 {\sum_i}' \frac{\langle \Phi_o | \mathscr{H} | \Phi_i \rangle \langle \Phi_i | \rho | \Phi_o \rangle}{E_i - E_o} . \qquad \text{(ID-2)}$$

If we wish to calculate $\rho(r)$ in the plane of the molecule, we note first that the zeroth order matrix element, $\langle \Phi_o | \rho | \Phi_o \rangle$, vanishes everywhere in this plane. Since all π configurations making up Φ_o are constructed from atomic $2p_z$ orbitals which have nodes in this plane, there can be no contribution to the density in the plane from any pure π excited configuration.

Let us now enumerate explicitly those excited configurations which are included in the following treatment. π-π configuration interaction leads to the function Φ_o which is made up of four types of one-electron excited configurations which are to be mixed with the basic function ψ_o . The configurations are diagrammatically

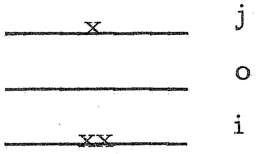


which corresponds to the Slater determinant $|\pi_i \bar{\pi}_i \pi_o|$. Here the orbital π_o is the orbital occupied by the unpaired electron in the basic Slater determinant. One must keep in mind the particular form of this orbital for the individual case: neutral radical, positive ion or negative ion. We shall include the doublet functions arising from one electron excitations which are represented by

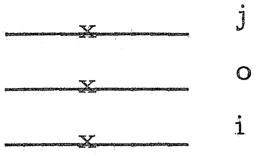


$$\psi_I = |\pi_i \pi_o \bar{\pi}_o|$$

$$\psi_{II} = |\pi_i \bar{\pi}_i \pi_j|$$



and the two doublets arising from



$$\psi_{III} = \frac{1}{\sqrt{2}} [|\pi_i \pi_o \bar{\pi}_j| - |\bar{\pi}_i \pi_o \pi_j|]$$

$$\psi_{IV} = \frac{1}{\sqrt{6}} [\,|\pi_j \pi_o \bar{\pi}_i| - |\pi_i \pi_o \bar{\pi}_j| + 2|\pi_i \bar{\pi}_o \pi_j|\,] .$$

Here again the convention is adopted of deleting from all Slater determinants those orbitals which are doubly occupied and form a closed shell. For example $\psi_I = |\sigma_1 \bar{\sigma}_1 \ldots \sigma_r \bar{\sigma}_r \pi_1 \bar{\pi}_1 \ldots \pi_i \ldots \pi_n \bar{\pi}_n \pi_o \bar{\pi}_o|$ is abbreviated $|\pi_i \pi_o \bar{\pi}_o|$.

If the individual π_k's are self consistent, it has been shown (59, 60) that the matrix elements of the Hamiltonian connecting ψ_o with the configurations ψ_I, ψ_{II} and ψ_{III} vanish as a result of the definition of self-consistency. Therefore the π-π CI problem in first order gives the function

$$\Phi_o = \psi_o + \sum_{i,j} \lambda_{ij}\, \psi_{ij} \qquad \text{where } \psi_{ij} \text{ is the function } \psi_{IV}.$$

There are several criteria which dictate the selection of σ-π excited functions Φ_i: (a) equation ID-2 requires that for a particular Φ_i to contribute to the spin density (to order λ), it must have matrix elements of the Hamiltonian and the spin density operator which are simultaneously different from zero; (b) the corresponding energy E_i must not be so large as to obviate its contribution to the perturbation expansion. With this restriction in mind we choose the members of the set of Φ_i's to be the following:

1. Doublets arising from excitation of an electron from a particular σ bonding to the corresponding σ^* antibonding orbital. There are two such doublets

   $$\Phi_{I\sigma} = \frac{1}{\sqrt{2}} \left[|\sigma_p \pi_o \bar{\sigma}^*_p| - |\bar{\sigma}_p \pi_o \sigma^*_p| \right]$$

   and

   $$\Phi_{II\sigma} = \frac{1}{\sqrt{6}} \left[|\sigma^*_p \pi_o \bar{\sigma}_p| - |\sigma_p \pi_o \bar{\sigma}^*_p| + 2|\sigma_p \bar{\pi}_o \sigma^*_p| \right] ,$$

2. Doublets arising from the simultaneous excitation of a particular σ_p bonding to the corresponding σ^*_p antibonding and of one electron from a π_i bonding to a π_j antibonding orbital. From five electrons in five different

orbitals five linearly independent orthonormalized doublets can be generated. Denoting the members of this group by $\Phi^{k}_{\sigma\pi}$ the following set of doublets is chosen

$$\Phi^{1}_{\sigma\pi} = \frac{1}{\sqrt{10}} \left[\mathrm{I} - \mathrm{II} + \mathrm{V} - 2\mathrm{VI} + \mathrm{VIII} - \mathrm{IX} + \mathrm{X} \right]$$

$$\Phi^{2}_{\sigma\pi} = \frac{1}{\sqrt{6}} \left[\mathrm{I} - \mathrm{II} - \mathrm{V} + \mathrm{VIII} + \mathrm{IX} - \mathrm{X} \right]$$

$$\Phi^{3}_{\sigma\pi} = \frac{1}{\sqrt{6}} \left[\mathrm{II} - \mathrm{II} - \mathrm{V} + \mathrm{VII} + \mathrm{VIII} - \mathrm{IX} \right]$$

$$\Phi^{4}_{\sigma\pi} = \frac{1}{\sqrt{12}} \left[\mathrm{I} - 2\,\mathrm{III} + \mathrm{IV} + \mathrm{VI} - 2\,\mathrm{VII} + \mathrm{X} \right]$$

$$\Phi^{5}_{\sigma\pi} = \frac{1}{\sqrt{60}} \left[3\,\mathrm{I} + 2\,\mathrm{II} - 5\,\mathrm{IV} - 2\,\mathrm{V} - \mathrm{VI} - 2\,\mathrm{VIII} + 2\,\mathrm{IX} + 3\mathrm{X} \right]$$

where

$$\mathrm{I} = |\bar{\pi}_i \; \bar{\sigma}_p \pi_o \; \sigma^*_p \pi_j|$$

$$\mathrm{II} = |\bar{\pi}_i \; \sigma_p \bar{\pi}_o \; \sigma^*_p \pi_j|$$

$$\mathrm{III} = |\bar{\pi}_i \; \sigma_p \pi_o \; \bar{\sigma}^*_p \pi_j|$$

$$\mathrm{IV} = |\bar{\pi}_i \; \sigma_p \pi_o \; \sigma^*_p \bar{\pi}_j|$$

$$\mathrm{V} = |\pi_i \; \sigma_p \bar{\pi}_o \; \bar{\sigma}^*_p \pi_j|$$

$$\mathrm{VI} = |\pi_i \; \bar{\sigma}_p \pi_o \; \bar{\sigma}^*_p \pi_j|$$

$$\mathrm{VII} = |\pi_i \; \bar{\sigma}_p \pi_o \; \sigma^*_p \bar{\pi}_j|$$

$$\mathrm{VIII} = |\pi_i \; \sigma_p \bar{\pi}_o \; \bar{\sigma}^*_p \pi_j|$$

$$\mathrm{IX} = |\pi_i \; \sigma_p \bar{\pi}_o \; \bar{\sigma}^*_p \pi_j|$$

$$\mathrm{X} = |\pi_i \; \sigma_p \pi_o \; \bar{\sigma}^*_p \bar{\pi}_j| \; .$$

We exclude in both these cases the excitation of one electron from a σ_p orbital localized between atoms p and q to a σ^*_r anti-bonding orbital localized between atoms r and s. Of the two doublets of type 1 only $\Phi_{II\sigma}$ contributes to the spin density to order λ. Also it can be shown that of the doublets of type 2, only $\Phi^{4}_{\sigma\pi}$ satisfies both criterion (a) and (b). We then are able to omit the superfluous superscripts and subscripts of the two contributing doublets, merely writing $\Phi_{\sigma}(p)$ and $\Phi_{\sigma\pi}(ijp)$. Functions which will emanate from excitation of an electron from either σ_p to π_j or σ^*_p to π_i need not be included. Matrix elements of the Hamiltonian between these states and Φ_o vanish when the component molecular orbitals are self-consistent.

With these configurations now at hand, we can evaluate the various matrix elements of the Hamiltonian and the spin density operator (in the molecular plane) which occur in equation ID-2.

$$\begin{aligned}
\langle \psi_o | \mathcal{H} | \Phi_{\sigma}(p) \rangle &= -\frac{3}{\sqrt{6}} \left\}\begin{matrix} o & \sigma_p \\ o & \sigma^*_p \end{matrix}\right. \\
\langle \psi_{ij} | \mathcal{H} | \Phi_{\sigma}(p) \rangle &= -\left\}\begin{matrix} i & \sigma_p \\ i & \sigma^*_p \end{matrix}\right. \\
\langle \psi_o | \mathcal{H} | \Phi_{\sigma\pi}(ijp) \rangle &= \frac{6}{\sqrt{12}} \left\}\begin{matrix} i & \sigma^*_p \\ j & \sigma_p \end{matrix}\right. \\
\langle \psi_o | \rho | \Phi_{\sigma}(p) \rangle &= \sqrt{\frac{2}{3}} \quad \sigma_p(r) \quad \sigma^*_p(r) \\
\langle \psi_{ij} | \rho | \Phi_{\sigma\pi}(ijp) \rangle &= -\sqrt{\frac{2}{3}} \quad \sigma_p(r) \quad \sigma^*_p(r) \\
\langle \psi_o | \rho | \psi_{ij} \rangle &= 0
\end{aligned} \tag{ID-3}$$

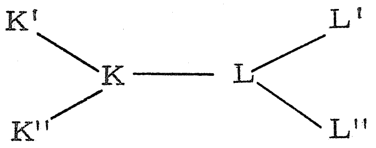
Substitution of these matric elements into equation ID-2 leads to the spin density in the molecular plane. Since the point in the plane is completely arbitrary at this point, it can be specified to be the nucleus itself. Following the notation of McConnell and Chesnut (3) where $\delta(N)$ is the spin density at the nucleus N, we have

$$\delta(N) = 2(\Delta E_{ave})^{-1} \sum_{p} \sigma_p(N)\,\sigma_p^*(N) \Big[\zeta^{o\;\sigma_p}_{o\;\sigma_p^*} + \sqrt{\frac{2}{3}} \sum_{i,j} \lambda_{ij} \left(\zeta^{i\;\sigma_p}_{j\;\sigma_p^*} + \zeta^{i\;\sigma_p^*}_{j\;\sigma_p} \right) \Big] . \qquad \text{(ID-4)}$$

Neglect of excitations $\sigma_p \rightarrow \sigma_r$ results in additivity of the spin density at the nucleus with respect to the index p. According to the hypothesis of the localized character of the σ orbitals, it is necessary to retain in the summation over p in equation ID-4 only those σ orbitals which link a particular nucleus to its neighbors. Thus, when N is a proton, there will be only one term, but when N is a carbon atom in sp^2 hybridization, we must retain three such terms.

Special Cases

Equation ID-4 will now be specialized for evaluation of the coupling constants due to in-plane protons and to C^{13}. To aid in the development of a relation with which these cases can be treated simultaneously, let us consider a fragment made up of six atoms



in which the various atoms, K...L'', can be either carbon or hydrogen.

π orbitals can extend over all these six atoms if the coefficient of such an orbital is equated to zero at the position of a hydrogen. The contributions to the two-electron integrals in ID-4 from these six atoms are retained. Thus these integrals can be decomposed into the component atomic orbitals as follows

$$\begin{aligned} \mathcal{J}^{o\ \sigma_p}_{o\ \sigma_p^*} &= \sum_{m,n} c_{om}\, c_{on}\, (m\,\sigma_p | n\,\sigma_p^*) \\ \mathcal{J}^{i\ \sigma_p}_{j\ \sigma_p^*} = \mathcal{J}^{i\ \sigma_p^*}_{j\ \sigma_p} &= \sum_{m,n} c_{im}\, c_{jn}\, (m\,\sigma_p | n\,\sigma_p^*) \end{aligned} \tag{ID-5}$$

where c_{ab} is the coefficient of the $2p_z$ carbon orbital centered on atom b which belongs to the LCAO MO π_a, and the other quantities have been previously defined. Then for atom K, that contribution to $\delta_p(K)$ resulting from just that σ bond connecting atoms K and L, σ_p, is

$$\begin{aligned} \delta_p(K) = &- 2(\Delta E_{\text{ave }p})^{-1}\, \sigma_p(K)\, \sigma_p^*(K) \Big\{ \big[c_{oK}^2 (K\,\sigma_p | K\,\sigma_p^*) + \\ & c_{oL}^2 (L\,\sigma_p | L\,\sigma_p^*) + c_{oL}\, c_{oK} ((K\,\sigma_p | L\,\sigma_p^*) + (L\,\sigma_p | K\,\sigma_p^*)) \big] \\ & + \sqrt{\frac{2}{3}} \sum_{i,j} 2\lambda_{ij} \big[c_{iK}\, c_{jK} (K\,\sigma_p | K\,\sigma_p^*) + c_{iL}\, c_{jL} (L\,\sigma_p | L\,\sigma_p^*) \\ & + c_{iK}\, c_{jL} (K\,\sigma_p | L\,\sigma_p^*) + c_{iL}\, c_{jK} (L\,\sigma_p | K\,\sigma_p^*) \big] \Big\} . \end{aligned} \tag{ID-6}$$

Of course, similar contributions from the other σ bonds between K and its neighbors must be included in the final determination of $\delta(K)$.

In the final equation for the spin density at an atom, atomic integrals of the type $(K\sigma_p | L\sigma^*_p)$, $(L\sigma_p | L' \;{}^*_p)$, and $(L\sigma_p | L'\sigma^*_p)$ are neglected because of the large distance between centers.

Equation ID-6 can be further simplified by employing Mulliken's approximation (61) for integrals of the type $(K\sigma_p | L\sigma^*_p)$ and $(L\sigma_p | K\sigma^*_p)$

$$(K\sigma_p | L\sigma^*_p) = \frac{1}{2} S_{KL} \left[(K\sigma_p | K\sigma^*_p) + (L\sigma_p | L\sigma^*_p) \right] \qquad \text{(ID-7)}$$

in which $S_{KL} = \langle K | L \rangle$. If

$$\sigma_p = \frac{t_K + t_L}{[2(1+S_o)]^{\frac{1}{2}}}$$

$$\sigma^*_p = \frac{t_K - t_L}{[2(1-S_o)]^{\frac{1}{2}}}$$

in which t_K is the atomic orbital centered on atom K and t_L on atom L which make up the sigma bond and the overlap integral S_o is $\langle t_K | t_L \rangle$, it can be further shown that

$$(L\sigma_p | L\sigma^*_p) = -(K\sigma_p | K\sigma^*_p) \, . \qquad \text{(ID-8)}$$

We shall be concerned both with sigma bonds between carbon and hydrogen and between carbon and carbon; one will be designated σ_{CH} and the other σ_{CC}, and the average excitation energies are $\Delta E_{ave\ CH}$ and $\Delta E_{ave\ CC}$.

Making use of the Mulliken approximation equation ID-6 becomes

$$\delta(K) = -2(\Delta E_{ave})^{-1} \sigma_p(K) \sigma^*_p(K) (K\sigma_p | K\sigma^*_p) \Big\{ \Big[D^K_{oo} + 2\sqrt{\tfrac{2}{3}} \sum_{i,j} \lambda_{ij} D^K_{ij} \Big] - \Big[D^L_{oo} + 2\sqrt{\tfrac{2}{3}} \sum_{i,j} \lambda_{ij} D^L_{ij} \Big] \Big\} \qquad \text{(ID-9)}$$

in which

$$D^K_{ij} = c_{iK}\, c_{jK} + \frac{1}{2}\, S_{KL}\, (c_{iK}\, c_{jL} + c_{jK}\, c_{iL})\,.$$

The quantity $D^K_{oo} + 2\sqrt{\frac{2}{3}} \sum_{i,j} \lambda_{ij}\, D^K_{ij}$ represents the π-electronic spin density at atom K, denoted now by ρ'_{KK}, and the corresponding quantity with superscript L, the spin density at its neighbor, ρ'_{LL}.

Now that equations are available for the spin densities in the plane, we make use of equation 4 of McConnell and Chesnut (3), $a_K = \frac{8\pi g\beta}{3h}\ \delta(K)$ to calculate the coupling constant for the various cases which are now enumerated.

Case I. K = H; L = C.

$$a_H = Q\rho'_{LL} \qquad \text{(ID-10)}$$

$$Q = -\left(\frac{8\pi g\beta}{3h}\right) |1s(o)|^2 \left(\frac{\mu_H}{I}\right) (\Delta E_{ave\ CH})^{-1} \frac{(\pi\sigma_{CH} | \pi\sigma^*_{CH})}{(1-S^2_{oCH})^{\frac{1}{2}}} \qquad \text{(ID-11)}$$

Q is the proton coupling constant of the hypothetical C-H fragment (see equation 34 of reference 3) and has the experimental value of -23 gauss (38).

Case II. K = C^{13}; K' = K'' = L = H.

$$a_{C^{13}} = 3Q'\rho'_{KK} \qquad \text{(ID-12)}$$

$$Q' = +\frac{1}{3}\left(\frac{8\pi g\beta}{3h}\right) |2s(o)|^2 \left(\frac{\mu_{C^{13}}}{I}\right) \frac{(\pi\sigma_{CH} | \pi\sigma^*_{CH})}{(1-S^2_{oCH})^{\frac{1}{2}}} (\Delta E_{ave\ CH})^{-1}$$

(ID-13)

A comparison of ID-10 and ID-11 yields

$$\frac{Q'}{Q} = -\frac{1}{3}\frac{a_{C^{13}}}{a_H} = -\frac{400}{502}$$

$$Q' \approx +18 \text{ gauss}$$

$a_{C^{13}}$ has been evaluated using the Hartree-Fock 2s orbital for carbon determined by Torrance (62). However, a direct experimental evaluation of Q' is obtained from the isotropic splittings of the ESR of the C^{13} methyl radical (54).

$$Q' = \frac{41 + 5}{3} \approx 14 \text{ gauss} .$$

<u>Case III.</u> $K = C^{13};\ K' = K'' = H;\ L = C$.

$$a_{C^{13}} = 2\,Q'\,\rho'_{KK} - Q''\,(\rho'_{KK} - \rho'_{LL}) \tag{ID-14}$$

$$Q'' = -\frac{1}{3}\left(\frac{8\pi g\beta}{3h}\right) |2s(o)|^2 \frac{\mu_{C^{13}}}{I} (\Delta E_{\text{ave CC}})^{-1} \frac{(\pi\sigma_{CC}\,|\,\pi\sigma^*_{CC})}{(1-S^2_{oCC})^{\frac{1}{2}}} \tag{ID-15}$$

Comparing equations ID-13 and ID-15 we have

$$\frac{Q''}{Q'} = -\frac{\Delta E_{\text{ave CH}}}{\Delta E_{\text{ave CC}}} \cdot \left(\frac{1-S^2_{oCH}}{1-S^2_{oCC}}\right)^{\frac{1}{2}} \approx -1 . \tag{ID-16}$$

If the assumption is made that the quantities in ID-16 are all the same in magnitude (i.e. a C-C σ bond is very much the same as a C-H σ bond), then the calculated value of Q'' is -18 gauss, from Torrance's wave function. Experimental estimates of this quantity depend on accurate knowledge of the π electron spin densities. However, in the spirit of the assumption about the similarity of a C-C and a C-H bond, we can take as an experimental value for Q'' one-third of the coupling constant of C^{13}-methyl radical, - 14 gauss.

Case IV. $K = C^{13}$; $K' = K'' = C$; $L = H$.

$$a_{C^{13}} = Q'\rho'_{KK} - Q''(2\rho'_{KK} - \rho'_{K'K'}) \tag{ID-17}$$

When the experimental coupling constant for the α position of naphthalene negative ion ($a_{C^{13}} \doteq 7.1$ gauss (55)) is combined with the spin densities deduced from experiment (63), equation ID-17 can be used to estimate Q''. The spin densities, assuming $Q = -23$ gauss, are $\rho_\alpha = 0.193$, $\rho_\beta = 0.072$ and $\rho_\gamma = -0.030$ which with $Q' = 14$ gauss give the value $Q'' = -13$ gauss.

Case V. $K = C^{13}$; $K' = K'' = L = C$.

$$a_{C^{13}} = -3Q''(\rho'_{KK} - \rho'_{LL}) \tag{ID-18}$$

Numerical Calculations

Having made a rather incomplete empirical estimate of Q' and Q'', we can now compare the results of this theory with the experimental coupling constant in triphenylmethyl and make some predictions for cases which seem likely to have experimental data within the near future.

Experimental spin densities for the triphenylmethyl radical are unavailable, but we can compare the results given by various theoretical treatments. We summarize these spin densities below

Method	Methyl Carbon	Neighbor	$a_{C^{13}}$	Reference
Simple MO	0.307	0.00	12.6	Section A
Valence Bond	0.564	-0.230	33	(40)
Valence Bond (with twist)	0.616	-0.226	34.5	(40)
MAO	0.360	-0.065	17.9	Section A
Hartree-Fock	0.413	-0.045	19.2	(64)
Anisotropic Coupling	0.68	0.00	28.6	(40)
Experimental			26	(40)

Calculated coupling constants were arrived at assuming that $Q' = -Q'' = 14$ gauss. Since both theoretical spin densities and the values of the necessary constants are uncertain, the comparison above only shows that the predicted coupling constants are of the correct order of magnitude.

Predictions for interesting cases for which experimental data should soon be available are

Naphthalene negative ion, β position	+0.4 gauss
Naphthalene negative ion, α position	-6.6 gauss
Benzene negative ion	+2.1 gauss
p-Benzosemiquinone (C=O)	-0.6 gauss *
p-Benzosemiquinone (C-H)	+0.5 gauss *

*Calculated spin densities from the work of Bersohn (8)

Discussion

Equations have been derived in a simple way which emphasize the importance of the π electron spin density at a neighboring atom for the coupling constant of the atom itself. Thus if the spin density at the neighbor, is negative in sign, the coupling constant which is measured is increased. The analysis of the diagonal component of the nuclear coupling tensor between C^{13} and the odd electron in malonic acid radical by McConnell and Fessenden (56) shows clearly that the sign of Q' is positive. Electronic theory of σ bonds gives much support to the assignment of a negative Q''. Analysis of the anisotropic coupling of the proton and electron in X-irradiated malonic acid single crystals (65) shows that the sign of Q (proton constant) is negative, and there should not be such a difference between a C-H bond and a C-C σ bond as to cause an opposite sign for Q''.

There are several approximations in this present theory which have been made unnecessary by the recent work of McLachlan *et al.* (66), who have developed equations which give the same conclusions as this work, but the calculation is performed in a much more general way. The exact form of the excited wave function was not required, nor was it necessary to invoke any approximate method for evaluating the molecular integrals.

Numerical calculations and predictions have been included here for the purpose of illustrating the way the theoretical formulae can be used. We want to emphasize that the numerical values of the necessary constants are not to be taken as final. Experimental data is still rather sparse, but accurate determination of these constants will make it possible to evaluate the π electron spin density at positions where no proton is bonded. Further, it is probably a bad assumption that the sigma bonds connecting an atom to its neighbors are independent, and a complete theory, when enough experimental data is at hand, must account for interactions between these bonds.

APPENDIX TO SECTION IA

Relaxation of the assumption of a single splitting parameter leads to the more general form of T_o

$$T_{o'} = \left| (a_1\phi_1 + b_1\phi_1{}')\ldots(a_n\phi_n + b_n\phi_{n'})\phi_o \right.$$
$$\left. (a_1\bar{\phi}_1 - b_1\bar{\phi}_1{}')\ldots(a_n\bar{\phi}_n - b_n\bar{\phi}_{n'}) \right| \qquad \text{(AIA-1)}$$

Application of the same procedure described in the text has the effect of leading to different coefficients for the various functions which arise from the expansion and projection of T_o.

The molecular orbital spin density now takes on the form

$$\rho(r) = (N'')^{-1}\Big\{ \phi_o\phi_o + \sum_i \frac{b_i}{a_i}\,\phi_i\phi_{i'} + \frac{1}{9}\sum_i \left(\frac{b_i}{a_i}\right)^{*2} \cdot$$
$$[4\phi_i\phi_i + 4\,\phi_{i'}\phi_{i'} - 2\phi_o\phi_o] + \frac{8}{9}\sum_{i\neq j}\left(\frac{b_i}{a_i}\right)\left(\frac{b_j}{a_j}\right)^2 \phi_i\phi_{i'}$$
$$+ \frac{4}{3}\sum_{i\neq j}\left(\frac{b_i}{a_i}\right)^2\left(\frac{b_j}{a_j}\right)\phi_o\phi_o + \frac{4}{3}\sum_i\left(\frac{b_i}{a_i}\right)^3 \phi_i\phi_{i'} + \sum_i\left(\frac{b_{i'}}{a_i}\right)^4 \phi_o\phi_o \Big\}$$

$$\text{(AIA-2)}$$

in which $N'' = 1 + \frac{2}{3}\sum_i\left(\frac{b_i}{a_i}\right)^2 + \frac{4}{3}\sum_{i\neq j}\left(\frac{b_{i'}}{a_{i'}}\right)^2\left(\frac{b_j}{a_j}\right)^2 + \sum_i\left(\frac{b_{i'}}{a_{i'}}\right)^4 .$

The formulae for the atomic orbital spin density which correspond to equations IA-40 and IA-41 are

$$\rho_A(r) = (N'') \Big\{ c_{oA}^2 - \frac{2}{9} \sum_i \left(\frac{b_i}{a_i}\right)^2 c_{oA}^2 + \frac{4}{3} \sum_{i \neq j} \left(\frac{b_i}{a_i}\right)^2 \left(\frac{b_j}{a_j}\right)^2 c_{oA}^2$$

$$+ \sum_i \left(\frac{b_i}{a_i}\right)^4 c_{oA}^2 + \sum_i c_{iA}^2 \Big[\frac{4}{3} \left(\frac{b_i}{a_i}\right) + \frac{8}{9} \left(\frac{b_i}{a_i}\right)^2$$

$$+ \frac{8}{9} \left(\frac{b_i}{a_i}\right)^2 \sum_{i \neq j} \left(\frac{b_j}{a_j}\right) + \frac{4}{3} \left(\frac{b_i}{a_i}\right)^3 \Big] \Big\} \chi_A^2(r) \qquad \text{(AIA-3)}$$

and

$$\rho_B(r) = (N'')^{-1} \sum_i c_{iB}^2 \Big[-\frac{4}{3} \left(\frac{b_i}{a_i}\right) + \frac{8}{9} \left(\frac{b_i}{a_i}\right)^2 - \frac{4}{3} \left(\frac{b_i}{a_i}\right)^3$$

$$- \frac{8}{9} \sum_{i \neq j} \left(\frac{b_i}{a_i}\right) \left(\frac{b_j}{a_j}\right)^2 \Big] \chi_B^2(r) \ . \qquad \text{(AIA-4)}$$

To determine the sign of $\frac{b_i}{a_i}$ the same type of argument as proposed in the text can be applied,

$$\Psi_{GS} = \psi_o + \sum_{k=1}^{n} \lambda_k \psi_k$$

where

$$\lambda_k = - \frac{\mathcal{H}_{ok}}{E_k - E_o} \qquad \text{(AIA-5)}$$

and

$$\mathcal{H}_{ok} = - \sqrt{\frac{3}{2}} \ \zeta_{ko}^{ko} \ . \qquad \text{(AIA-6)}$$

λ_k, thus $\frac{b_k}{a_k}$, is a positive quantity because of the positive value of ζ^{ko}_{ko}.

Inclusion of different parameters has the effect of weighting the different configurations differently, which is certainly the more reasonable case. We note that the conclusion of negative spin density at the unstarred atom is still valid in this more general treatment.

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Section II

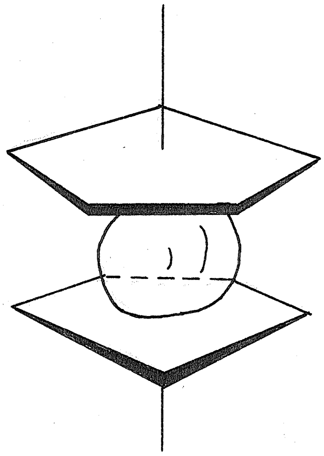
ELECTRON RESONANCE STUDIES OF SOME SANDWICH COMPOUNDS

Introduction

The unusual structure and bonding of the "sandwich" compounds have stimulated a large number of experimental and theoretical studies of the behavior of the various transition metal ion analogues of ferrocene (1). The vast majority of the previous experimental investigations has been concerned with the preparation and characterization of these substances. In this section the results of ESR experiments with pure nickelocene (powder), pure cobaltocene (powder) and vanadocene dissolved in ferrocene (dilute single crystal) will be described. Only qualitative conclusions about the "spin Hamiltonian" for the powders can be made, but the single crystal experiments with vanadocene allow a more detailed analysis of the ground electronic state of this compound to be made. This information, coupled with the solution ESR spectra obtained by Porterfield (2), permits the evaluation of the zero-field splitting parameter of V^{+2} in the cylindrical electric field of the cyclopentadienyl rings.

Since this series of molecules is relatively new and unusual, a short review of the current ideas about their structure and bonding seems appropriate. The first real confirmation of the "sandwich" configuration of the rings with the metal ion as filling followed from the X-ray crystallographic determination of the structure of ferrocene by

Dunitz and Orgel (3). The molecular structure which they found is shown below.



Any explication of the bonding of the sandwich compounds must account for their relative stability, the aromaticity of the rings and the magnetic susceptibility of each cogener. Dunitz and Orgel (3) made the proposal that these properties are consistent with bonds involving the π orbitals of the rings and 3s, 3p and 3d atomic orbitals of the transition metal ion. In the neutral molecule the metal is present as the dipositive ion, and two covalent bonds connect it to the π molecular orbital system of the rings. Overlap occurs between the highest bonding orbital of the rings and the $3d_{\pm 1}$ atomic orbital of the metal. Thus for ferrocene one may assign the electrons as follows:

$$(A)\ (C)\ (B)^4\ (H)^2\ (D)^4$$

where

A - argon core of metal

C - core of filled molecular orbitals of rings

B - bonding orbital between de_{1g} (metal) and cpe_{1g} (rings)

H - hybrid between metal 3s and $3d_o$

D - other 3d orbitals of the metal.

The electronic configuration of any other metal sandwich compound can be derived by adding or removing electrons and by making allowance for Hund's rule of maximum multiplicity. While this picture is quite qualitative, it does account for the aromaticity of the rings and the multiplicity (magnetic susceptibility) of most of these compounds.

Robertson (1) has considered the theory of the magnetic behavior of the sandwich compounds as it relates to ESR experiments. We shall review his predictions and make comparison to the experimental situation when possible in a later section.

Experimental

Materials

Nickelocene and cobaltocene were prepared by the method of Wilkinson (4), and no particular modification of the procedure was necessary. Reagent grade starting materials were used and at all times the cyclopentadiene was freshly distilled. In both these cases the product was purified by extensive sublimation (until no residue remained), but no analysis was carried out. Nickelocene is a dark green crystalline substance which acquires a white film of oxidation product upon prolonged contact with air. Cobaltocene is a similar material almost black in crystalline form but dissolving in benzene to give a blue color in dilute solution.

Wilkinson's method for the preparation of vanadocene was also employed (5), but since the details given are at most sketchy and the preparation itself far from trivial, the technique which finally proved successful will be recorded. The overall course of the reaction is

$VCl_3 + Na(C_5H_5)_2 \rightarrow V(C_5H_5)_2 + NaCl +$ oxidation products

and the VCl_3 is obtained by the thermal decomposition of VCl_4 (6).

Reagent grade V_2O_5 was intimately mixed with an equal weight of carbon and placed in a glass tube (30 mm; 2 ft) adapted as a furnace with wrapped Nichrome wire and asbestos tape. Inlets for both chlorine and nitrogen were provided and at the exit a liquid air trap was attached by means of a ball joint. After preliminary heating and flushing with tank nitrogen to rid the mixture of adsorbed water, tank chlorine was introduced. At the temperature used, 300°C, the products distilled into the trap which was maintained at 0°C:

$$8\,C + 15\,Cl_2 + 2\,V_2O_5 \rightarrow 2\,VCl_4 + 2\,VOCl_3 + 8\,COCl_2 \quad .$$

Separation of VCl_4 and $VOCl_3$ was unnecessary because at the temperature of the subsequent thermal decomposition of VCl_4, the $VOCl_3$ volatilized from the reaction. This mixture was refluxed under a stream of dry nitrogen at 150°C for approximately 48 hours, and the resulting VCl_3 was used without further purification. $2\,VCl_4 \underset{\Delta}{\longrightarrow} 2\,VCl_3 + Cl_2\uparrow$.

The solvent for the final reaction was dimethoxyethane. Every care must be taken to avoid the presence of water in the reaction; so that the solvent was used immediately after its distillation from $LiAlH_4$. Freshly distilled cyclopentadiene was introduced in two fold excess to finely chopped sodium. After stirring for several hours to complete the formation of the salt, VCl_3 was added and the reaction allowed to proceed under nitrogen for 3-4 hours. It was found expedient to use a two fold excess of $Na(C_5H_5)_2$. After completion of the reaction, the mixture was pumped to dryness and the product separated by immediate vacuum sublimation from the original reaction vessel at 75° C at a pressure of 10^{-4} mm Hg.

Vanadocene is a lustrous deep purple solid which decomposes instantly on contact with air to a dark brown material. The purified product was sealed under vacuum to be opened and handled in a nitrogen filled dry box.

Crystal Growth

In order to achieve a spectrum of vanadocene whose fine structure is not obscured by intermolecular exchange effects, the molecule must be incorporated into a host lattice as a substitutional impurity. Requirements for a host lattice include diamagnetism, a known crystal structure and a molecular structure similar enough to the impurity to allow substitution in regular lattice sites. After unsuccessfully attempting to substitute sandwich compounds into such materials as durene or naphthalene, it was decided to use as the diamagnetic host ferrocene itself. Since the great sensitivity of vanadocene to water and air were well known to us at this time, coprecipitation was not attempted, and the crystals were grown by slow cosublimation from a constant temperature bath maintained at 37°C. The crystals which were obtained had fairly well developed faces but often appeared to be twinned.

ESR Spectra

Neither nickelocene nor cobaltocene give a measurable ESR signal at room temperature or liquid nitrogen temperature. A cavity which operated at liquid helium temperature was constructed. Although the design of this cavity is rather esoteric because it was originally designed for single crystal experiments at helium temperatures, it was not used for this purpose and the modifications necessary for crystal reorientation are superfluous for this discussion; so this equipment will not be described in detail. The cylindrical cavity operated at X-band wavelengths (9.4 Kmc), and detection was effected with the usual Varian equipment using 400 cps magnetic field modulation. The dewar system was designed and built by Dr. T. Cole and its description is to be found in his thesis (7). For the vanadocene spectra which was obtained at room temperature, a k-band spectrometer (22.5 Kmc) of conventional design constructed by Dr. R. W. Fessenden was employed. The cylindrical cavity was detachable so that crystals could be mounted in the dry box, and precaution was taken to avoid the leaking of air into the cavity. Varian equipment was used to phase-sensitive-detect the signal, and magnetic field modulation was again at 400 cps. After a crystal was mounted in the dry box in the desired orientation by eye, the angle between the magnetic field vector and the perpendicular crystal axis was measured on the vernier of the rotatable magnet.

Figure II-1 shows the spectrum of nickelocene powder at 4.2° K and figure II-2 that of cobaltocene powder at the same temperature. Calibration was carried out externally by measuring the separation between hyperfine peaks of a dilute $MnSO_4$ solution and internally with the free radical, diphenyl picryl hydrazyl (DPPH). In figure II-3 illustrative spectra of vanadocene in ferrocene at various angles of the magnetic field and some vector in the (100) crystal face, when this face is oriented parallel to the floor of the laboratory (plane of rotation of H_o) are represented. In figure II-4 the magnetic field at which a line occurs is plotted versus the angle which the magnetic field vector makes with the vector described above. The angular variation for the orientation of the crystal with its (100) face perpendicular to the laboratory floor is depicted in figure II-5. The relative intensities of the lines from the first orientations is given in table II-1. It should be emphasized that these crystal orientations are very approximate due to the great difficulty of handling the crystals with the heavy rubber gloves of the dry box.

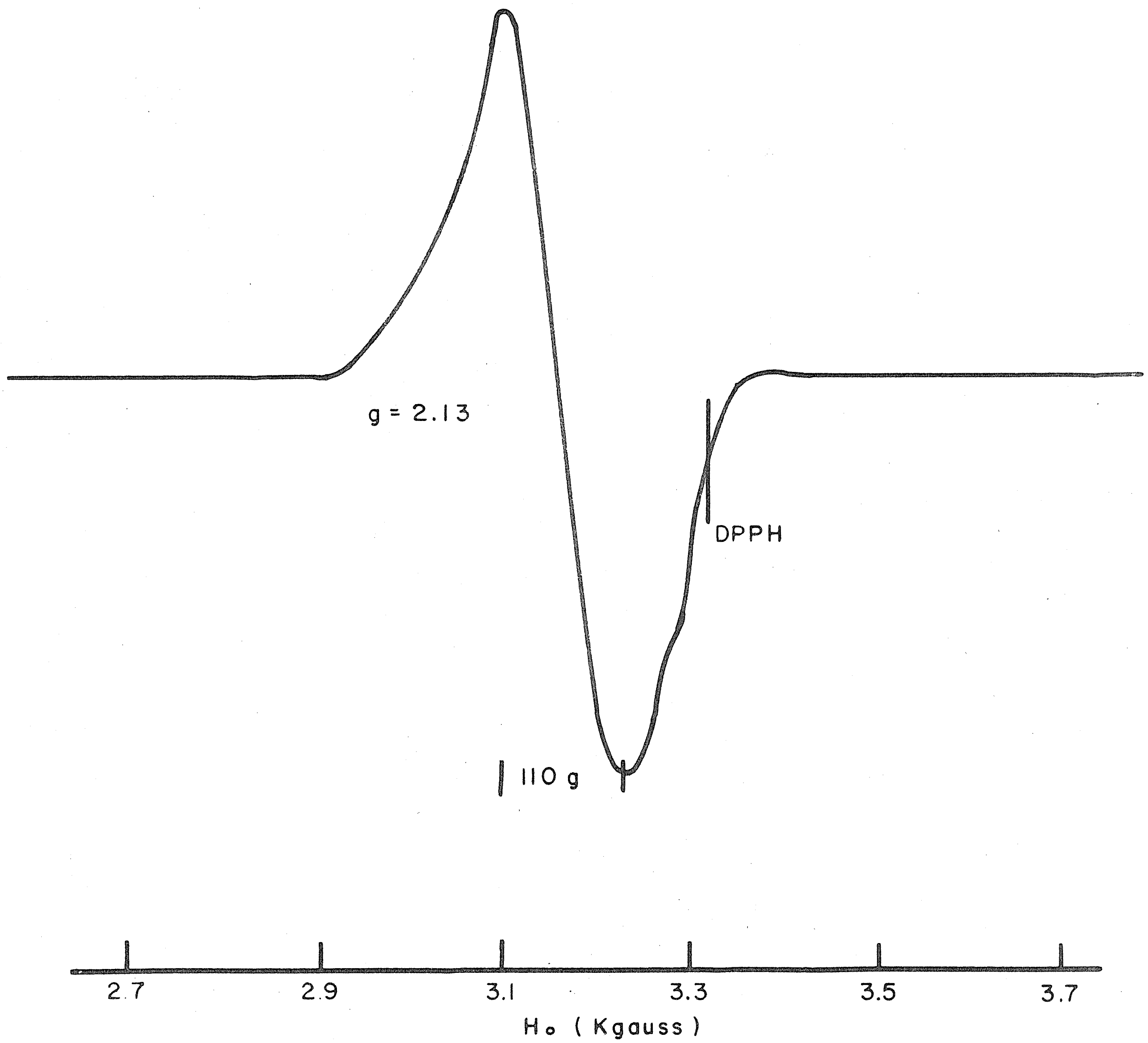


Fig. II-1. Powder spectrum of nickelocene at 4.2°K. Frequency of incident radiation 9.4 Kmc. $\frac{S}{N} = 20$.

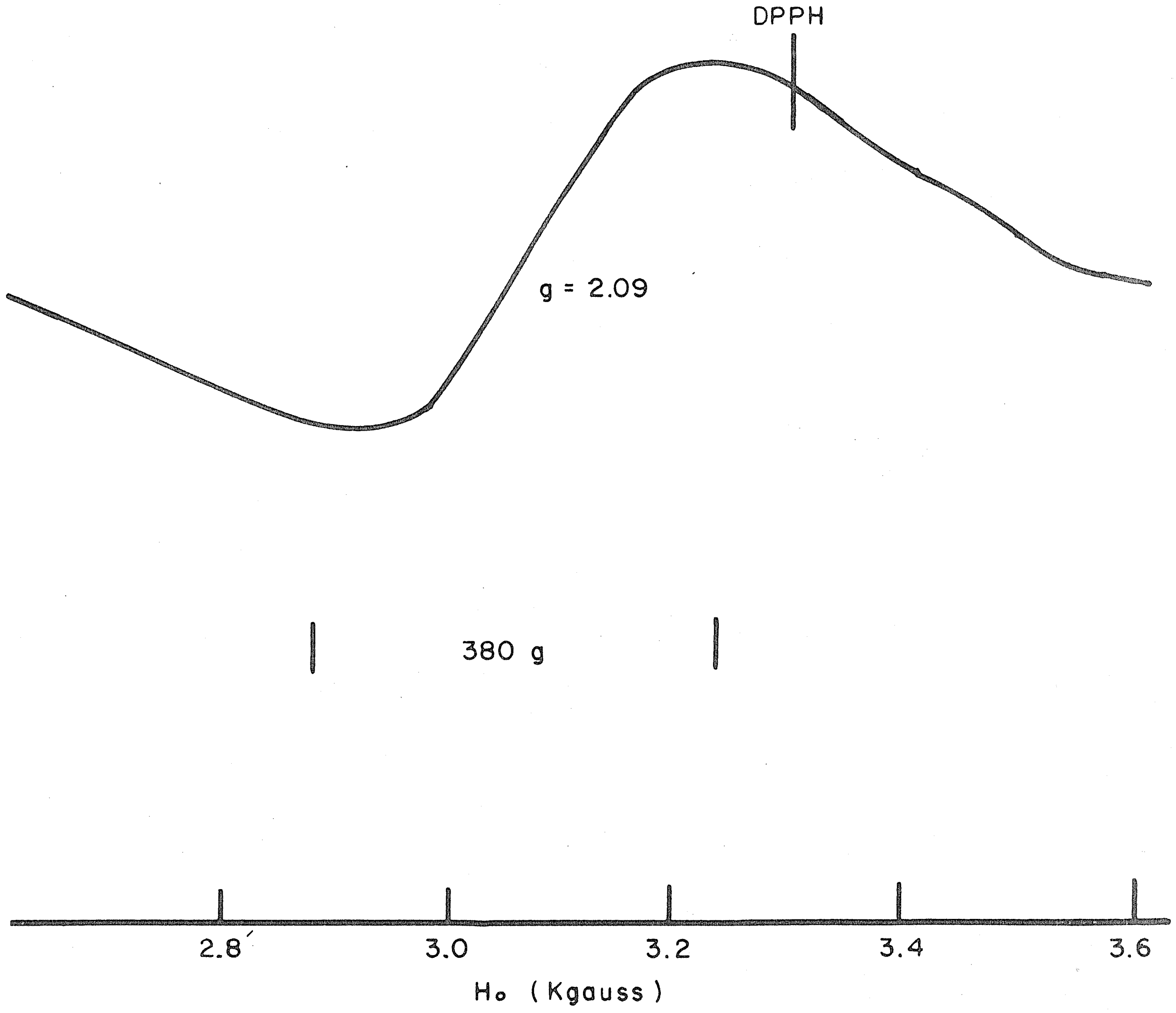


Fig. 11-2. Powder spectrum of cobaltocene at 4.2°K. Frequency of incident radiation 9.4 Kmc. $\frac{S}{N} = 7.$

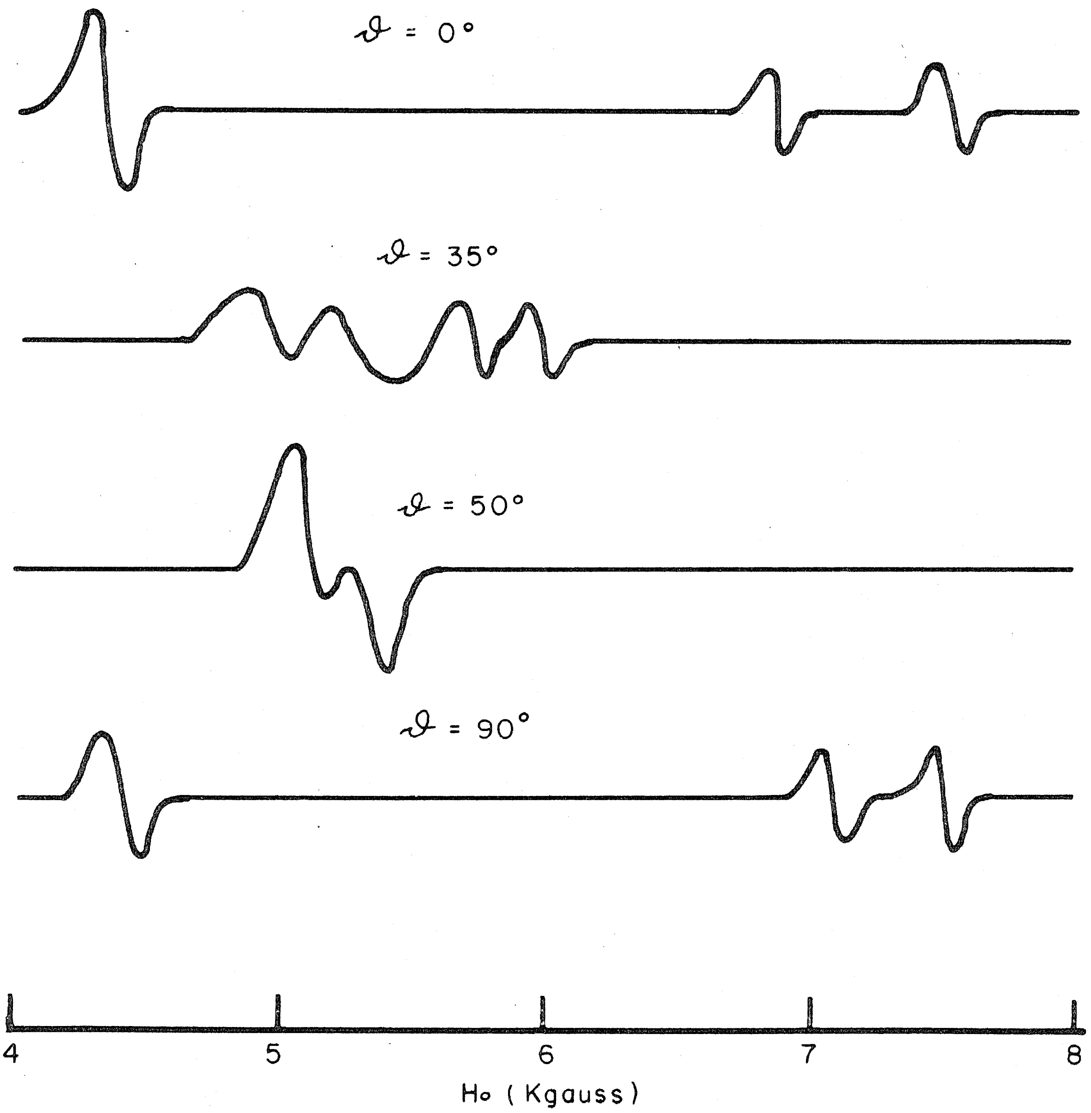


Fig. II-3. Illustrative spectra of vanadocene dissolved in a crystal of ferrocene. ϑ measures the angle between H_0 and a vector in the (100) plane. (100) is coplanar with the plane of rotation of H_0. Frequency of incident radiation 22.5 Kmc. $\frac{S}{N}$ = 10.

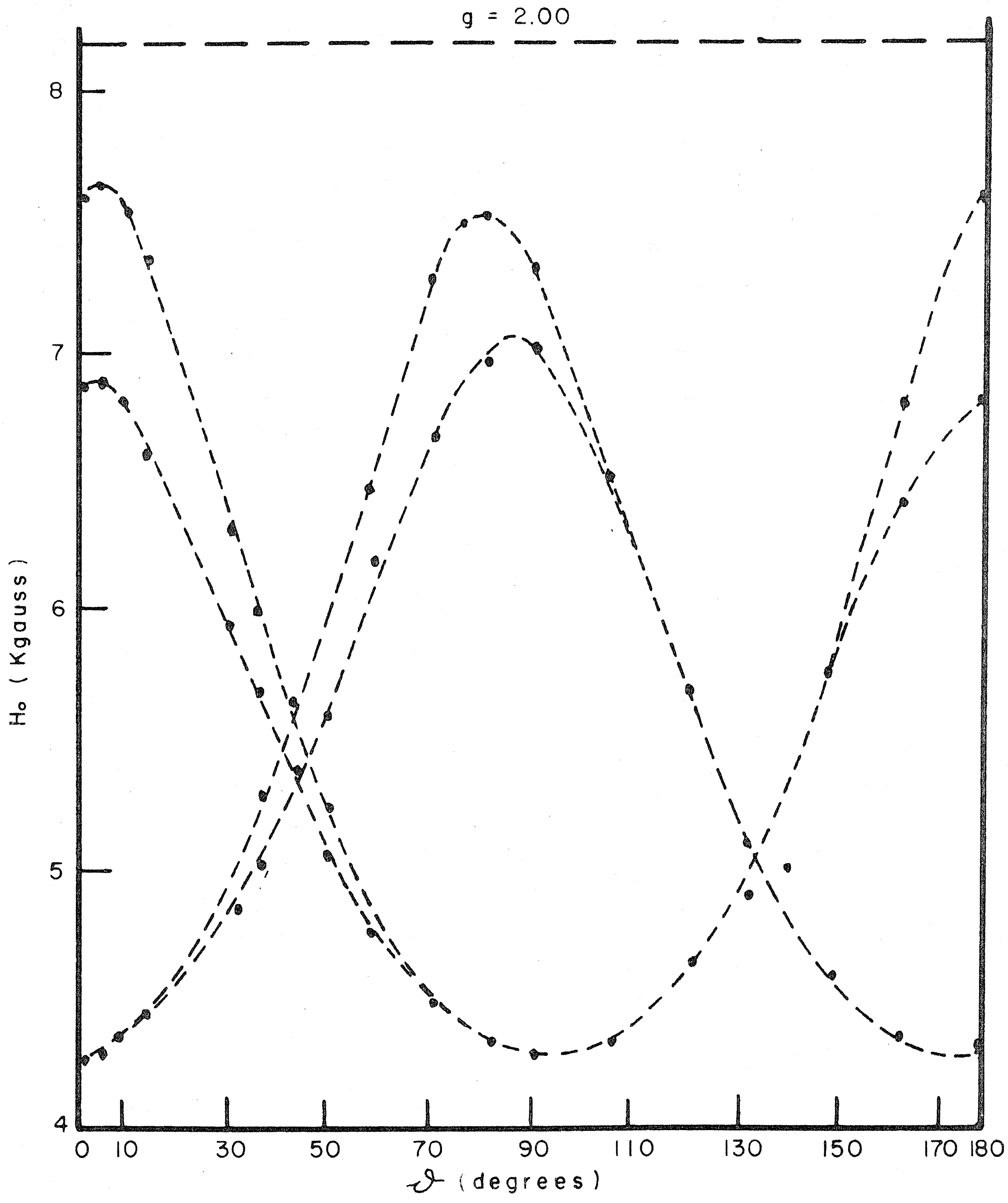


Fig. II-4 The angular variation of the spectrum when (100) is coplanar with the plane of rotation to H_o.

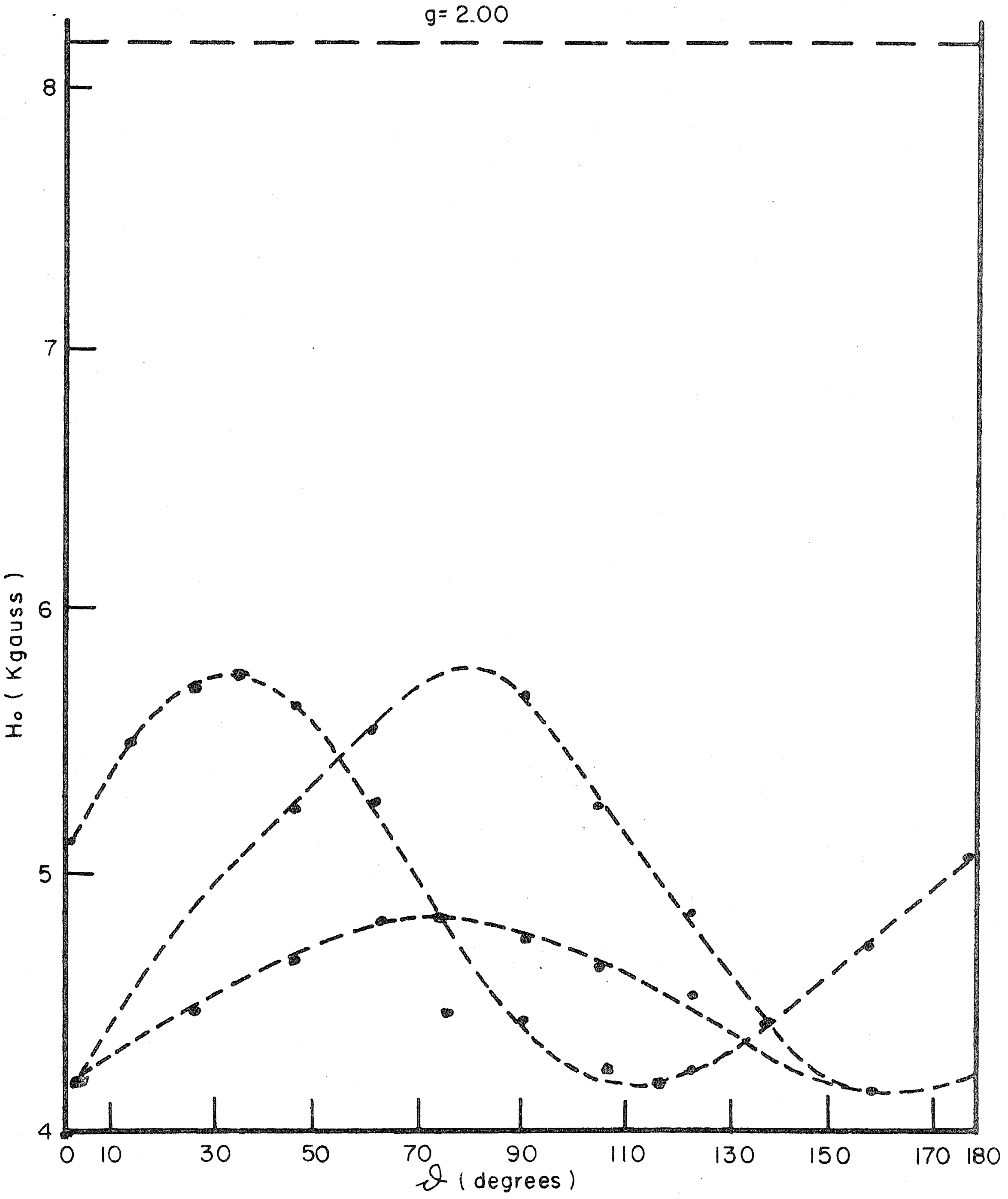


Fig. 11-5. The angular variation of the spectrum when (100) is perpendicular to the pland of rotation of H_0.

Table II-1

Illustrative Resonances When (100) Is Coplanar with Plane of H_o

	H_{res}	Intensity*
0°	7550 gauss	4
	6825	4
	4275	14
10°	7550	5
	6825	7
	4350	17
30°	6330	5
	5925	7
	4825	10
40°	6650	8
	6360	12
	6225	4
60°	6475	5
	6100	7
	4750	15
80°	7475	6
	6930	3
	4350	21
120°	5700	12
	4675	17
150°	5550	8 (broad)
	4500	13

*Peak heights in cm.

Also optical goniometry was completely impossible because the contact with air would have decomposed the sample. The faces were assigned using the crystallographic information given by Pfab and Fischer (8). Magnetic field calibration was carried out with a Sensitive Research Instruments fluxmeter (Model FS) and the internal marker DPPH.

Theoretical Background

Spin Hamiltonian

Experimental results of ESR are usually reported in terms of the parameters which occur in the so-called "spin Hamiltonian". We shall sketch the development of this method for representing the energy and eigenfunctions of magnetic electrons in an ion situated in a crystalline electric field and show its form necessary for the compounds we are concerned with.

Abragan and Pryce (9) express the different factors which contribute to the total energy of an ion in a crystal as follows:

$$\mathcal{H} = \mathcal{H}_F + \mathcal{H}_{CF} + \mathcal{H}_{LS} + \mathcal{H}_H + \mathcal{H}_{SS} + \mathcal{H}_N + \gamma\beta_n H \cdot I \qquad \text{(II-1)}$$

$$\mathcal{H} = \mathcal{H}_F + \mathcal{H}_{CF} + \mathcal{H}' \qquad \text{(II-2)}$$

where $\mathcal{H}_F$ - - energy of the free ion

$\mathcal{H}_{CF}$ - - energy of interaction with the crystal field

$\mathcal{H}_{LS}$ - - spin-orbit interaction, $\lambda L \cdot S$

$\mathcal{H}$ H - - interaction with the external field, $\beta(L + 2S) \cdot H$

$\mathcal{H}_{SS}$ - - electron-spin electron-spin interaction,

$$4\beta^2 \sum_{j,k} \left[\frac{S_j \cdot S_k}{r_{jk}^3} - \frac{3(r_{jk} \cdot S_j)(r_{jk} \cdot S_k)}{r_{jk}^5} \right]$$

$\mathcal{H}_N$ - - interaction (magnetic and quadrupole) of nucleus with field due to electron

$\gamma \beta_n H \cdot I$ - - direct interaction of nuclear moment with field.

The perturbation Hamiltonian $\mathcal{H}'$ will be reduced to the form

$$\mathcal{H}'_{spin} = S \cdot D \cdot S + H \cdot g \cdot S + S \cdot T \cdot I + I \cdot P \cdot I - \gamma \beta_n H \cdot I - \beta^2 H \cdot \Lambda \cdot H \qquad \text{(II-3)}$$

in which D, g, T, P, and Λ are tensors and the eigenvalues of II-3 are determined by spin variables alone. Experimental data is to be expressed in terms of the principal values of these tensors. This is the most general form of the energy , and for our purposes it will be necessary to retain only the spin-orbit and Zeeman terms of II-1

$$\mathcal{H}' = \lambda L \cdot S + \beta (L + 2S) \cdot H . \qquad \text{(II-4)}$$

We now restrict ourselves to states arising from the ground term (lowest eigenstate of $\mathcal{H}_F$) and to a ground state (lowest eigenstate of $\mathcal{H}_{CF}$) which is an orbital singlet. The first restriction assures us that we are dealing with eigenstates of L and S, and the latter allows the energy to be computed without the necessity of resorting to a secular equation with the various possibilities of orbital degeneracy. These two assumptions are plausible since the separation of various terms is of the order of 10^{+5} cm^{-1} and the "quenching of orbital angular momentum" by crystalline fields is a familiar phenomenon in the first row transition metal ions. It will be found that these conditions are indeed fulfilled for the cases of nickelocene and vanadocene, but that the ground state of cobaltocene is probably nearly degenerate.

The whole advantage of a spin Hamiltonian is that the energy of the system can be computed from matrix elements involving spin variables alone. Thus we will "integrate out" the orbital momenta variables which occur in the set of states $|o\rangle, \ldots, |n\rangle$. The energy to first order is given by

$$\begin{aligned} W^1 &= \langle o | \mathcal{H}' | o \rangle \\ &= 2\beta H \cdot S \end{aligned} \tag{II-5}$$

since by hypothesis $\langle o | L | o \rangle = 0$. To second order the energy is

$$W^2 = - \sum_{n \neq o} \frac{\langle o | \beta(L + 2S) \cdot H + L \cdot S | n \rangle \langle n | \beta(L + 2S) \cdot H + L \cdot S | o \rangle}{E_n - E_o} \tag{II-6}$$

$$= - \sum_{n \neq o} \sum_{\substack{i,j \\ = x,y,z}} \frac{\langle o | L_i | n \rangle \langle n | L_j | o \rangle \; (\lambda S_j + \beta H_j)(\lambda S_i + \beta H_i)}{E_n - E_o} \; . \tag{II-7}$$

Making the substitution

$$\Lambda_{ij} = \sum_{n \neq o} \frac{\langle o | L_i | n \rangle \langle n | L_j | o \rangle}{E_n - E_o} = \Lambda_{ji}$$

and combining the first order energy, the desired result is

$$\mathcal{H}_{\text{spin}} = \sum_{i=x,y,z} 2\beta H_i S_i - \sum_{i,j=x,y,z} \Lambda_{ij}(\lambda^2 S_i S_j + \beta^2 H_i H_j + 2\lambda\beta H_i S_j) \qquad \text{(II-8)}$$

which is equivalent to

$$\mathcal{H}_{\text{spin}} = \beta H \cdot g \cdot S + S \cdot D \cdot S + \beta^2 H \cdot \Lambda \cdot H \ . \qquad \text{(II-9)}$$

Λ_{ij} is a symmetric dyadic since $\langle o | L | n \rangle$ is imaginary and equal to the negative of $\langle n | L | o \rangle$ and can thus be diagonalized. Following Robertson (1), the zero field splitting term can be written

$$\Lambda_{xx} S_x^2 + \Lambda_{yy} S_y^2 + \Lambda_{zz} S_z^2 = \frac{1}{3}(\Lambda_{xx} + \Lambda_{yy} + \Lambda_{zz}) S \cdot (S+1) + \frac{1}{2}(\Lambda_{xx} - \Lambda_{yy})(S_x^2 - S_y^2) + [\Lambda_{zz} - \frac{1}{2}(\Lambda_{xx} + \Lambda_{yy})] \ [S_z^2 - \frac{1}{3} S(S+1)] \ . \qquad \text{(II-10)}$$

The spin Hamiltonian now has taken on its familiar form

$$\mathcal{H}_{\text{spin}} = g_z \beta H_z S_z + g_x \beta H_x S_x + g_y \beta H_y S_y + D[S_z^2 - \frac{1}{3} S(S+1)] + E(S_x^2 - S_y^2) \ . \qquad \text{(II-11)}$$

and for a crystalline field of axial symmetry is given by

$$\mathcal{H}_{\text{spin}} = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + D[S_z^2 - \frac{1}{3} S(S+1)] \ . \qquad \text{(II-12)}$$

A bit of discussion of the various quantities which are introduced by this method seems warranted. Spin-orbit coupling vanishes in first order, but the term $\lambda^2 \Lambda_{ij} S_i S_j$ is the manifestation of this effect in second order and gives rise to the zero-field splitting as

$$D = -\lambda^2 [\Lambda_{zz} - \frac{1}{2}(\Lambda_{xx} + \Lambda_{yy})] . \qquad \text{(II-13)}$$

There will also be a contribution to the zero field splitting from the electron-spin electron-spin interaction in II-1. However, this quantity is rather difficult to evaluate and is claimed to be usually small compared to the spin-orbit interaction (9); so it will be neglected here. The anisotropy of the g-factor is also determined by the tensor

$$g_i = 2(1 - \lambda \Lambda_{ii}) \qquad i = x, y, z ; \qquad \text{(II-14)}$$

so that for the Hamiltonian II-4, D and g_i are related by the equation

$$D = -\frac{\lambda}{2} (g_{\parallel} - g_{\perp}) . \qquad \text{(II-15)}$$

The spin independent term $\beta^2 \Lambda_{ij} H_i H_j$ gives rise to temperature independent paramagnetism.

It should be mentioned here that, for the case of a near-degenerate orbital ground state (cobaltocene), formulae resembling those which have just been developed can be written in terms of a fictitious spin. We shall not dwell on this possibility.

In a recent paper Schulz-DuBois reports the results of a calculation of the eigenvalues and eigenvectors of II-12 for Cr^{+3} (10). This ion is isoelectronic with V^{+2} so that these results may be used directly in the interpretation of the vanadocene spectra. The Hamiltonian II-12 is referred to a coordinate system determined by the internal field, and it is convenient to transform this equation to a coordinate system which has for its z-axis the magnetic field vector. The result of this transformation to a spherical system in which the angle ϑ is measured from H_o to the axial crystalline field vector is given by

$$\mathcal{H} = (g_{\parallel}\cos^2\vartheta + g_{\perp}\sin^2\vartheta)\beta H S_z + D(\cos^2\vartheta - \frac{1}{2}\sin^2\vartheta)\cdot$$

$$[S_z^2 - \frac{1}{3}S(S+1)] + D\frac{1}{2}\cos\vartheta\sin\vartheta\,[(S_zS_+ + S_+S_z) + (S_zS_- + S_-S_z)]$$

$$+ D\sin^2\vartheta\,(S_+^2 + S_-^2)\,. \qquad \text{(II-16)}$$

The solution of the fourth order secular equation

$$|\langle n\,|\,\mathcal{H} - W\,|\,m\rangle| = 0 \qquad \text{(II-17)}$$

$$n, m = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$$

is carried out numerically, and the eigenvalues and eigenvectors are plotted as a function of the parameter $\dfrac{(g_{\parallel}\cos^2\vartheta + g_{\perp}\sin^2\vartheta)\beta H}{D}$ at ϑ intervals of 10°. In figures II-6 and II-7 the plots of these quantities at $\vartheta = 0^\circ$ and $\vartheta = 90^\circ$ are reproduced from this paper. Eigenvalues are described in terms of fictitious quantum numbers $\frac{\bar{3}}{2}, \frac{\bar{1}}{2}, -\frac{\bar{1}}{2}, -\frac{\bar{3}}{2}$, such that at any magnetic field strength $\frac{\bar{3}}{2}$ labels

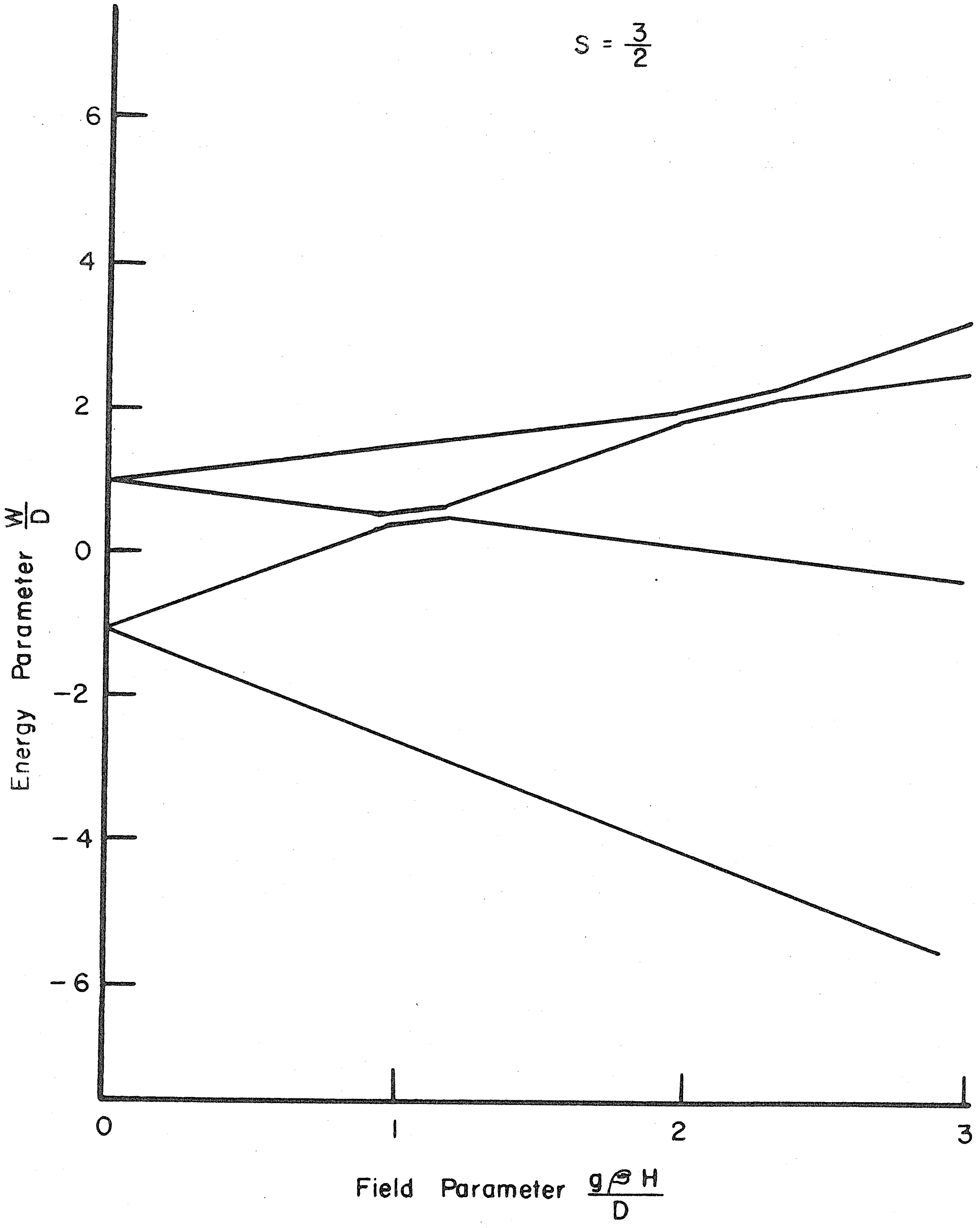


Fig. II-6 Energy levels of (II-16) as a function of magnetic field at $\vartheta = 0°$. Reproduced from reference (10). The sign of D is taken negative.

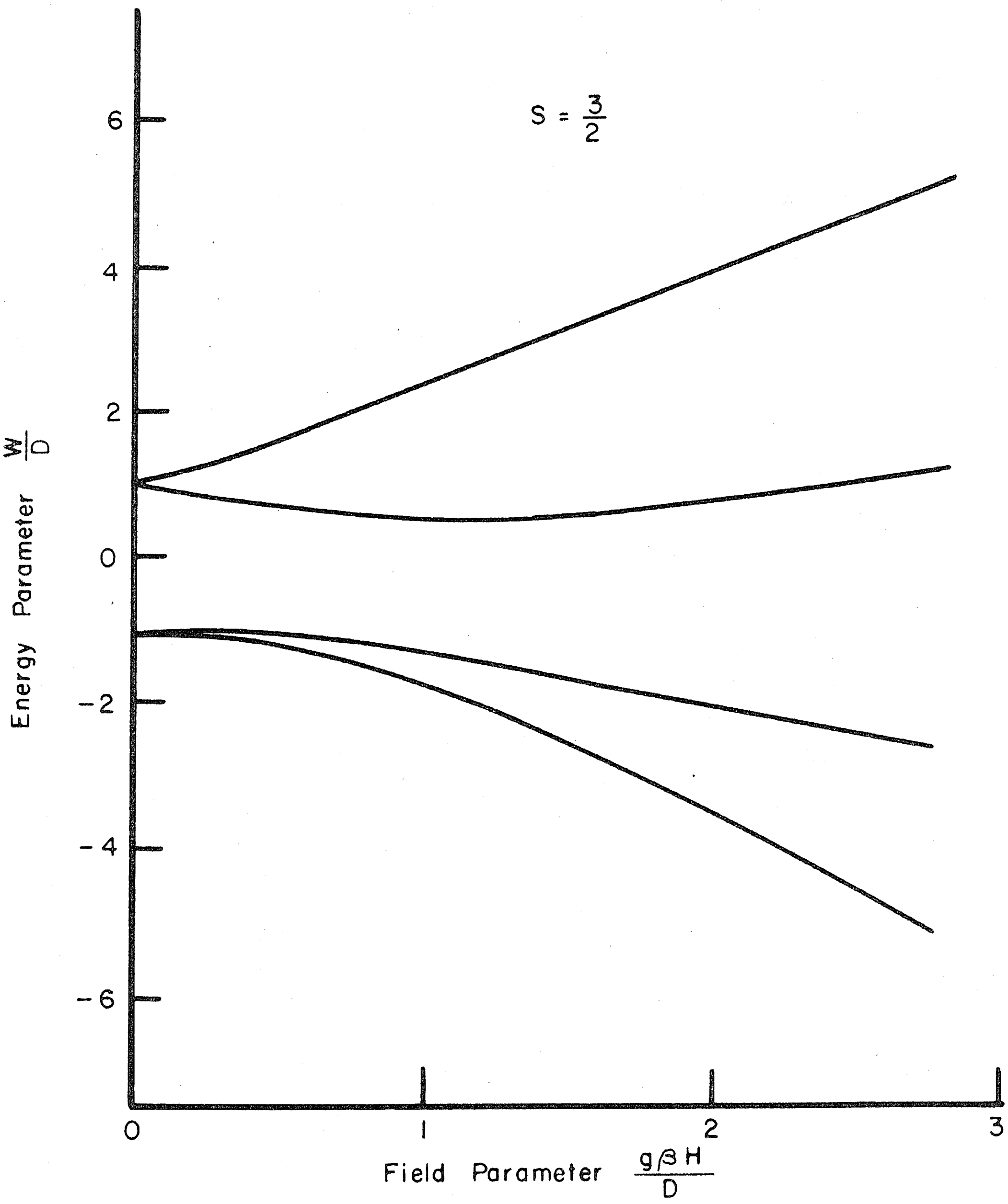


Fig. II-7 Energy levels of (II-16) as a function of magnetic field at $\vartheta = 90°$. Reproduced from reference (10). The sign of D is taken to be negative.

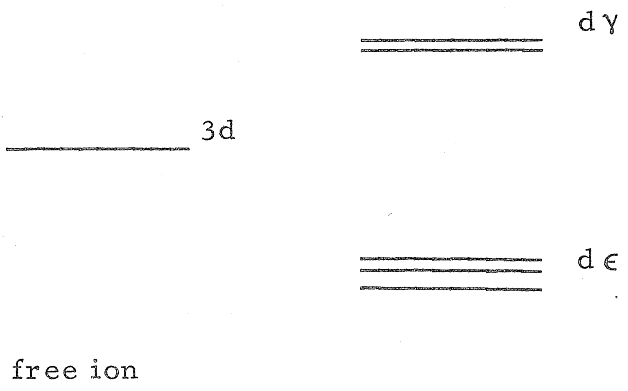
the highest level and $-\frac{\bar{3}}{2}$ labels the lowest. Naturally, these are not pure states, in general, but are given in terms of the high field eigenstates $|m\rangle$ by the equation

$$|\bar{n}\rangle = \sum_{m=-\frac{3}{2}}^{\frac{3}{2}} a(\bar{n}; m)\, |m\rangle \qquad \text{(II-18)}$$

The selection rules for the absorption of emission of radiation are $\Delta S_m = 0, \pm 1$ but not $\Delta S_{\bar{n}} = 0, \pm 1$. We shall make a good deal of use of these results in the interpretation of the vanadocene spectra.

Crystal Field Theory

Robertson (1) has discussed the crystal field theory of the sandwich compounds and can account for the observed magnetic susceptibility (of all except $Ti(C_5H_5)_2$ and $Mn(C_5H_5)_2$ by strong crystal field theory. Under the perturbation of the cylindrical electric field of the rings, the 3d levels of the transition metal ion are initially split as follows



The multiplicity of the ground state can be arrived at by putting the appropriate number of d electrons into this scheme, treating the dγ and dϵ levels as individual groups for the application of Hund's rule. For examples V^{+2} in vanadocene has its ground state schematically represented by

$V(C_5H_5)_2$

$S = \frac{3}{2}$

$L = 0$

and, after inverting the level diagram to consider two positive holes as equivalent to $3d^8$, nickelocene is given by

$S = 1$

$L = 0$

$Ni(C_5H_5)_2$

Of course, the two degenerate subgroups will subsequently be further split by the crystalline field, spin-orbit, etc. Since the 3d orbitals of the metal ion are involved with bonding with the rings, the dγ and dϵ are no longer pure atomic orbitals but include the effects of interaction with the rings.

Interpretation of Spectra

Nickelocene

The important experimental facts which are derived from the powder spectrum of nickelocene can be summarized as follows:

1. There is only one line.
2. No signal is found at room temperature either in the powder or in dilute liquid solution or in a diluted single crystal.
3. The line is only slightly anisotropic.
4. The effective g-factor is 2.13.
5. The line width at 4.2°K is 110 gauss.
6. A violent phase transition slightly above liquid nitrogen temperatures insures a truly polycrystalline sample.

It must be realized at the outset that very little quantitative information can be realized from a powder spectrum. What follows is an attempt to enumerate the factors which influence the powder spectrum of nickelocene and to construct various plausible sets of these factors which can explain the observed facts.

First a brief review of the results of previous ESR experiments with Ni^{+2} in various salts is given. The zero field splitting parameter, D, varies from $-3.5\ cm^{-1}$ in $NiSO_4 \cdot 7H_2O$ to $-0.5\ cm^{-1}$ in $NiSiF_6 \cdot 6H_2O$. The g-factors of salts which have been studied are isotropic and lie in the range 2.14 - 2.30. In several compounds the rhombic component of the crystal field must be included, and E is generally of the order 0.1 - 1.0 cm^{-1} when it was necessary. Resonance absorption was observable at room temperature in all the cases reported by Bowers and Owen (11) and by Ingram (12). An interesting observation is made for the case of $NiSiF_6 \cdot 6H_2O$ that the parameter D decreases with decreasing temperature, being reduced in magnitude by a factor of four on going from room temperature to 14°K (13).

The eigenvalues of the spin Hamiltonian II-12 for which S = 1 are given by the roots of

$$W^3 + 2D\,W^2 + (4D^2 - g^2\beta^2H^2)\,W - 2D\,g^2\beta^2H^2\sin^2\vartheta = 0. \qquad \text{(II-19)}$$

To derive II-19 from the equations of reference (13) we have made the assumption that the g-factor is isotropic. II-19 is not factorable for a general angle between H_o and the axial crystalline field vector; however, for $\vartheta = 0°$ and $\vartheta = 90°$ factorization is possible, yielding the roots

$$\vartheta = 0° \qquad \begin{aligned} W_1 &= 0 \\ W_2 &= g\beta H - D \\ W_3 &= -g\beta H - D \end{aligned} \qquad \text{(II-20)}$$

$$\vartheta = 90° \qquad \begin{aligned} W_1 &= -D \\ W_2 &= -\frac{1}{2}\left[D - (D^2 + 4g^2\beta^2H^2)^{\frac{1}{2}}\right] \\ W_3 &= -\frac{1}{2}\left[D + (D^2 + 4g^2\beta^2H^2)^{\frac{1}{2}}\right]. \end{aligned} \qquad \text{(II-21)}$$

The variation of these eigenvalues with H_o is depicted in figure II-8.

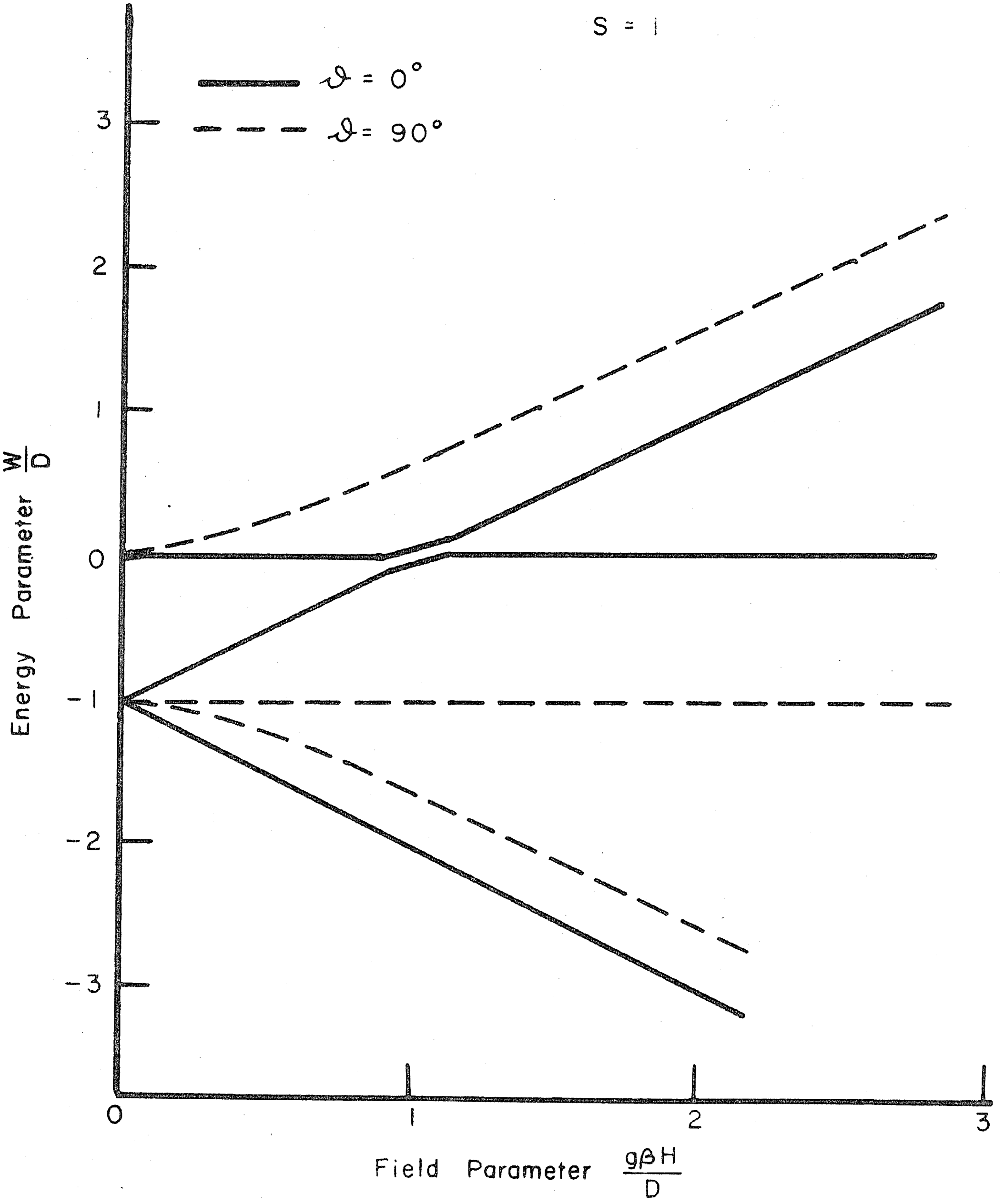


Fig. 11-8 Energy levels of (11-19) as a function of magnetic field. The sign of D is taken to be negative.

With this background we can now investigate the following possible effects on the powder spectrum of nickelocene.

Anisotropic g-factor

At room temperature in a powder this effect could lead to a very broad signal (of width $(g_{\parallel} - g_{\perp})\beta H$) which may be obscured by electronic noise. Since the - ϑ of a particular crystallite is random, a distribution of individual lines would make up the single broad absorption seen by the spectrometer. In dilute benzene solution, the spin-lattice relaxation time, T_{1e}, must be shorter than the time for molecular tumbling (10^{-11} sec) in order that a g-factor anisotropy be operative (14,15). Typical values of T_{1e} lie between 10^{-8} and 10^{-10} sec for transition metal ions in solution. Assuming for the moment that this condition is satisfied, transitions in a diluted and pure single crystal should be observable at room temperature, and, in fact, they were not found.

Further, the temperature effect of nickelocene could be explained by assuming low lying orbital states which become depopulated at helium temperature. However, in octahedrally complexed Ni^{+2} the nearest orbital state lies about $10^4 cm^{-1}$ above the ground singlet (11). The fact that previous ESR experiments have found a finite zero field splitting but an isotropic g-factor may seem mutually excluded by equation II-15 . However, for Ni^{+2} D is probably determined more by the electron-spin electron-spin interaction than by the second order spin-orbit coupling (9), and in the derivation of II-15 this effect was neglected.

It now seems safe to conclude that an anisotropic g-factor alone cannot explain our results and, based on previous experimental and theoretical conclusions, is quite an unattractive possibility.

Zero Field Splitting

In order to use the level diagram in figure II-8 for discussion of a powder spectrum, the reader must attempt to visualize the gross effects of averaging this scheme over angle. A series of guesses of what the powder spectrum of nickelocene would look like at various magnitudes of the parameter $\frac{D}{h\nu}$, in which $h\nu$ is the energy of the incident radiation follows. For simplicity we shall assume that the g-factor is isotropic and that the broadening effects of the dipole-dipole and isotropic exchange interactions are small.

i. $\frac{D}{h\nu} = 0$

Only one line will be observed for this case because the levels in figure II-8 are completely symmetrical. This possibility accounts for the occurrence of only one line, but it cannot explain the absence of absorption at room and liquid nitrogen temperatures.

ii. $\frac{D}{h\nu} > 0$

At small values of this parameter (0.1 - 0.5) two lines will be seen separated in field by approximately the value of the splitting parameter expressed in gauss, but as this ratio increases in value the high field component of this doublet will be unattainable at the magnetic field available for our experiment (7500 gauss).

iii. $\frac{D}{h\nu} >> 1$

For this case the spin will be too tightly coupled to the internal crystal field requiring very large magnetic fields to split the Zeeman levels sufficiently to allow resonance absorption. Of course these transitions are allowed but will not be seen at the magnetic fields attainable with the magnet which was used.

Isotropic Exchange Interaction

Pryce and Stevens (16) have shown that for non-equivalent ions in a crystal the term $\sum_{i,j} A_{ij} S_i \cdot S_j$ should produce a broadening of the ESR absorption line. This will be in addition to the "natural" line width caused by the dipole-dipole interaction and the averaging of the spectra from various ϑ's in a powder sample. It is difficult to imagine that A_{ij} is a strong function of temperature unless the phase transition which $Ni(C_5H_5)_2$ undergoes in some way causes the various Ni^{+2} ions to come into closer proximity with one another at low temperature. Even if this is the case, the effect is working in the wrong direction to explain the absence of an absorption at room temperature and its presence at 4.2°K.

The fact that the line width is only 110 gauss indicates that this effect is very small. $(Ni(NH_3)_6Br_2$ has a polycrystalline line width at room temperature of 1200 gauss (17)). Actually, it is attractive to invoke the "exchange narrowing" concept of the Van Vleck theory for nuclear resonance (18). Pryce and Stevens do believe that there will be an effect on the fourth moment of a spectrum from isotropic exchange between non-equivalent ions but are unable to estimate its magnitude. At any rate, the broadening of the second moment is clear and must be taken here in the absence of a more complete theory to be the dominant process. This all leads us to conclude that the intermolecular exchange parameter is probably quite small for nickelocene and that no important features of the powder spectrum have been obscured.

There are other effects such as rhombic components to the crystal field which will not be discussed because the data certainly does not warrant such detail.

Conclusions

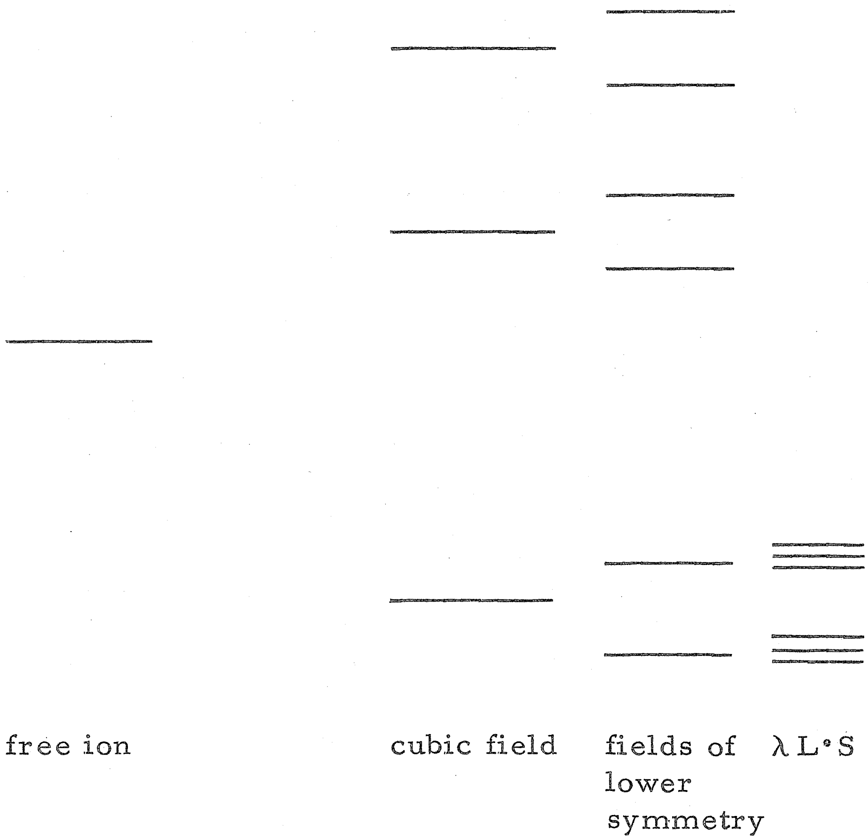
The most attractive set of assumptions which account for the experimental facts enumerated at the beginning of this discussion are:

1. The g-factor is isotropic.
2. At room temperature D is larger than the incident radiation, but D decreases with decreasing temperature; so that at helium temperature it is of the same magnitude as the microwave radiation, i.e. $|D| \approx 0.3 \text{cm}^{-1}$.
3. Isotropic exchange broadening is small.

We certainly have not proved that this model for nickelocene is superior to that of a low lying orbital state, but our choice is prompted by previous theory and experiments and by the fact that the room temperature magnetic susceptibility yields a "spin-only" magnetic moment (19). Proof of this model would come from experiments at room temperature at a higher frequency.

Cobaltocene

Ingram (12) gives as the energy level diagram for Co^{+2} in a crystal the following.



The ground state is nearly orbitally degenerate.

The data for cobaltocene substantiates the conclusion that for this compound there are orbital states lying close to the ground state. The situation for cobaltocene is further complicated by the fact that the g-factor is probably very anisotropic (1). Our powder spectrum is consistent with low lying orbital states and an anisotropic g-factor, since the width even at low temperatures is great, and no signal was found at room temperature.

Vanadocene

The experimental facts which are most important to any interpretation are summarized below:

1. The angular dependence and intensities of the various resonance lines given in figures II-4 and II-5 and in table II-1.
2. No more than four lines were ever observed at any angle with the magnetic fields available.
3. No lines appear at high fields ($g^{eff} < 2$).
4. ESR of vanadocene in dilute benzene solution occurs at $g = 2.0$.

We shall again employ the procedure of enumerating the various possibilities and choosing the one which best fits the data.

Previous ESR results for V^{+2} and Cr^{+3} can be summarized as follows (11,12):

1. $|D|$ is of the order 0.1 - 1.0 cm^{-1}.
2. $g_{\parallel}$ and $g_{\perp}$ differ by about 1% or less and are in value slightly less than 2.00.

3. Rhombic components of the crystal field are usually unnecessary.

For example, the spin Hamiltonian parameters for Cr^{+3} in ruby at room temperature are (10):

$D = -0.916\ cm^{-1}$

$g_{\parallel} = 1.9840$

$g_{\perp} = 1.9867$

and for Cr^{+3} in emerald also at room temperature (20),

$D = -0.895\ cm^{-1}$

$g_{\parallel} = 1.973$

$g_{\perp} = 1.970$.

In both these cases no rhombic component of the crystal field was found.

The discussion of the vanadocene spectra which will follow is based initially on three assumptions.

(a) The ESR spectra which are observed arise from V^{+2} for which $S = \frac{3}{2}$.

(b) The vanadocene molecule is oriented in the host lattice in the same manner as the ferrocene itself.

(c) The g-factor is approximately isotropic and has the value 2.00.

Assumption (a) essentially requires that the ground state ($S = \frac{3}{2}$ from the magnetic susceptibility (21)) is not appreciably altered when the vanadocene molecule is placed into a crystal of ferrocene. Assumption

(c) is based on the results of previous experiments with the same and isoelectronic ions and is necessary because experiments at only one frequency were performed.

Assumption (b) has a good deal of experimental justification. Weiss and Fischer (22) have performed the crystal structure determination of vanadocene and find a structure similar in all respects to that of ferrocene (3, 23). The unit cell dimensions are compared below.

$Fe(C_5H_5)_2$	$V(C_5H_5)_2$
a = 5.95 Å	a = 5.88 Å
b = 7.59 Å	b = 8.02 Å
c = 10.56 Å	c = 10.82 Å
β = 121°	β = 121.3°
Vol. = 202 $Å^3$	Vol. = 218 $Å^3$

The unit cell of ferrocene is depicted in figure II-9 and is taken from the paper by Pfab and Fischer (8). The five-fold axis lies approximately on the b-c diagonal [011]; so that when the (100) plane is coplanar with the plane of rotation of H_o, we expect the angular variation of the spectra of one molecule in the unit cell to be about 90° of phase with that of the other. When the (100) plane is perpendicular to the plane of rotation of H_o, the molecules will be magnetically equivalent when H_o is perpendicular to (100), but at other angles the spectra of the two molecules will again be out of phase.

Zero Field Splitting

The reader should now recall figures II-6 and II-7 in which

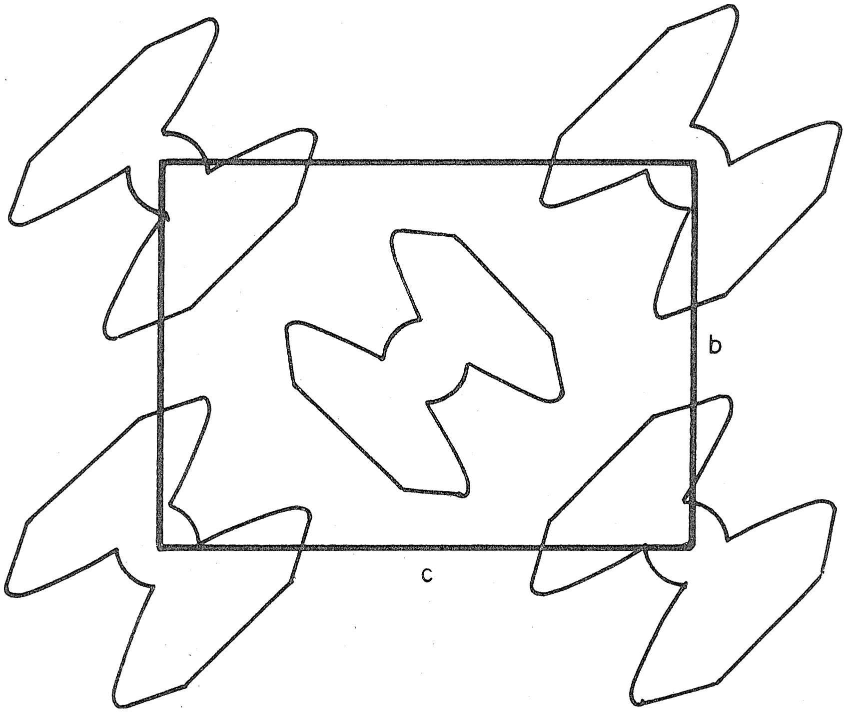


Fig. II-9. Unit cell of ferrocene. Cut parallel to (100). Reproduced from reference (24).

the energy levels for the spin Hamiltonian II-16 are sketched for $\vartheta = 0°$ and $\vartheta = 90°$. Inspection of these plots reveals that for $\frac{D}{h\nu} < 1$ three transitions are allowed at $\vartheta = 0°$ and six are possible and $\vartheta = 90°$ (for each molecule). Clearly this case is not a possibility for vanadocene purely from the number of lines expected. For $\frac{D}{h\nu} \gtrsim 1$ and at $\vartheta = 0°$, the allowed transitions are $(\frac{\bar{1}}{2} \rightarrow \frac{\bar{3}}{2})$ at $g^{eff} = 2$ and $(\frac{\bar{1}}{2} \rightarrow \frac{\bar{3}}{2})$ at $g^{eff} = \frac{2}{3}$ (but this latter transition occurs at a higher magnetic field than was attainable in our experiment). At $\vartheta = 90°$ $(\frac{\bar{1}}{2} \rightarrow \frac{\bar{3}}{2})$ and $(-\frac{\bar{3}}{2} \rightarrow -\frac{\bar{1}}{2})$ are possible; so that for this range of the zero field splitting parameter a reasonable number of lines is predicted, and this case must be examined in careful detail.

The case in point is illustrated by the angular variation in figure II-10 of the spectra arising from Cr^{+3} in ruby for which $\frac{D}{h\nu} = 1.1$. The scales of the plot given in Schulz-DuBois' paper (10) have been multiplied by the appropriate factor such that this diagram may be compared directly to our experiment. The computed intensities of each transition are given in table II-2 at angle intervals of 10°.

The most conspicuous difference between this plot and the experimental curve in figure II-4 is the absence of strong lines at high fields (10-15 K gauss) in our experiment. Due to mounting uncertainties the magnetic field probably never attained a configuration parallel to the molecular figure axis, i.e., $\vartheta = 0°$. Suppose that the b-c plane made an angle α with the plane of rotation of H_o. Then the real angle ϑ' between H_o and the figure axis is given in terms of the apparent

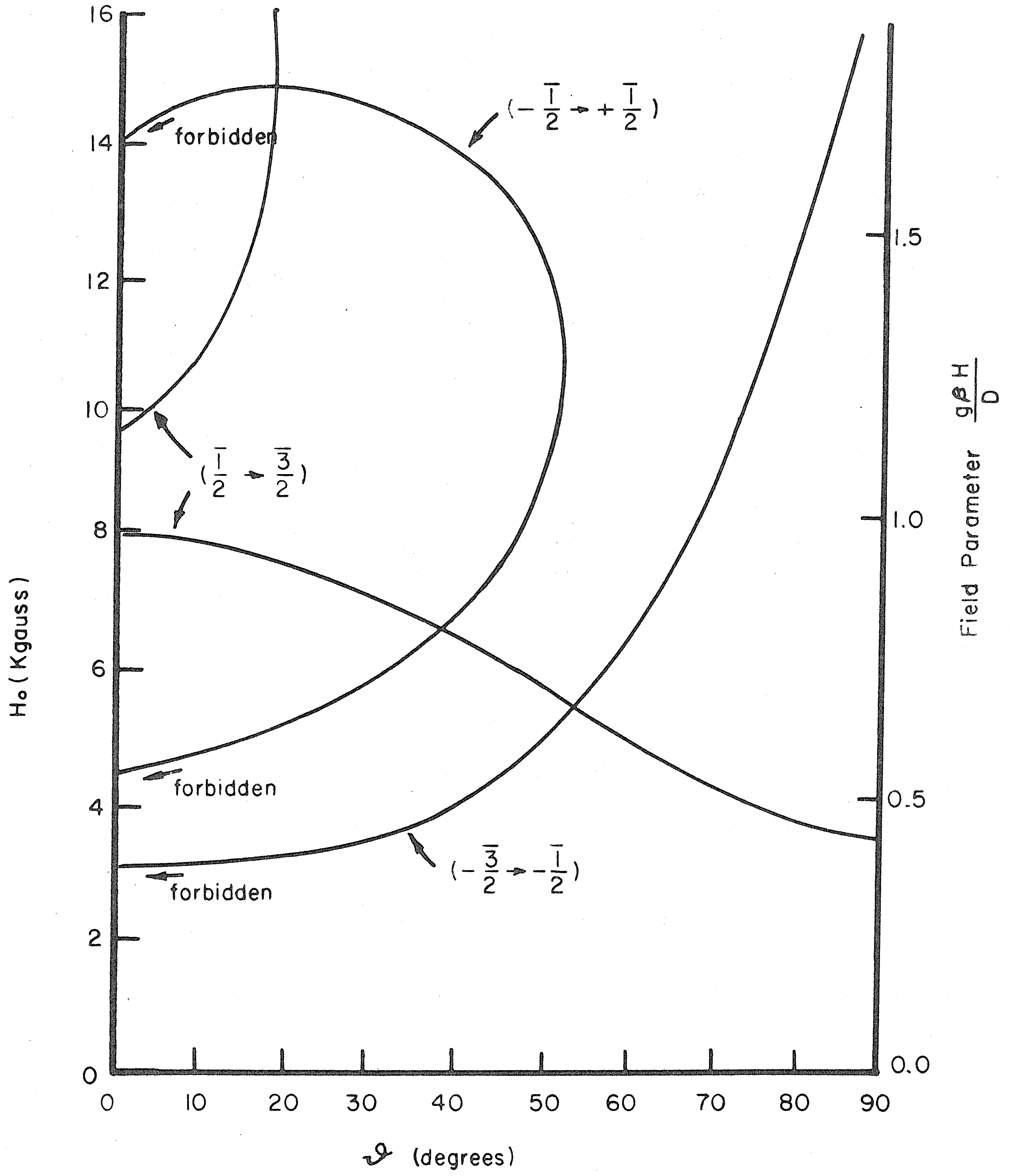


Fig. 11-10. Angular variation of Cr^{+3} in ruby. $\frac{D}{h\nu} = 1.1$. Reproduced from reference (10).

Table II-2

Calculated Relative Intensities

	$(+\frac{\bar{1}}{2} \rightarrow +\frac{\bar{3}}{2})$	$(+\frac{\bar{1}}{2} \rightarrow +\frac{\bar{3}}{2})$	$(-\frac{\bar{1}}{2} \rightarrow +\frac{\bar{1}}{2})$	$(-\frac{\bar{3}}{2} \rightarrow -\frac{\bar{1}}{2})$
0°	1000	1000	0	0
10°	750	250	10	1
20°	450	0	90	5
30°	425	0	80	10
40°	400	0	5	25
50°	380	0	1	50
60°	360	0	0	100
70°	350	0	0	300
80°	345	0	0	900
90°	340	0	0	1000

angle ϑ read on the vernier by the equation

$$\cos \vartheta' = \cos \alpha \cos \vartheta \ . \tag{II-22}$$

Equation II-22 shows that the angle ϑ' must attain a 90° value during any rotation by π of H_o. Thus, the absence of the strong absorptions $(\frac{1}{2} \rightarrow \frac{3}{2})$ at $g^{eff} < 2$ and at $g^{eff} = 2$ is not surprising, but nonoccurrence of lines which have the intensity or angular behavior of the $(-\frac{3}{2} \rightarrow -\frac{1}{2})$ transition must be taken as evidence that for vanadocene $\frac{D}{h\nu} > 1$.

There is a definite similarity of the various continuous curves of the figure II-4 to that of the $(\frac{1}{2} \rightarrow \frac{3}{2})$ transition both in relative intensities and angular dependence. Geusic *et al.* (20) find a single anisotropic line, $(\frac{1}{2} \rightarrow \frac{3}{2})$, for Cr^{+3} in emerald at the incident frequency of 9.3 Kmc. For this system the zero field splitting is quite large ($|2D| = 52$ Kmc), and the other allowed transitions occur at too high a magnetic field to see in their experiment (24). These authors give the perturbation formula for the effective g-factor of the observed absorption when $\frac{D}{h\nu} > 1$

$$g^{eff} = [g_{\parallel}^2 + (4g_{\perp}^2 - g_{\parallel}^2) \sin^2 \vartheta]^{\frac{1}{2}} [1 - \frac{1}{2} (\frac{g_{\perp} \beta H}{2D})^2 F(\vartheta)] \tag{II-23}$$

where

$$F(\vartheta) = \frac{3 \sin^2 \vartheta \ (\sin^2 \vartheta - \frac{1}{3})}{\sin^2 \vartheta + \frac{1}{3}} \ .$$

Specialization of II-23 to 0° and to 90° results in the equations

$$g^{eff}\ (0°) = g_{\parallel} \qquad \text{(II-24)}$$

and

$$g^{eff}\ (90°) = 2g_{\perp}\ [1 - \frac{3}{4}\ (\frac{g_{\perp}\ \beta H}{2D})^2\ ]\ . \qquad \text{(II-25)}$$

From figure II-4 all the continuous curves have the same minimum in magnetic field of 4250 gauss, yielding the value g^{eff} (90°) = 3.85. Figure II-11 shows the comparison of the calculated spectral angular dependence and the experimental points when equation II-23 is used. The angle α necessary to account for the maximum in magnetic field of each continuous curve is reported. It is felt that the agreement is satisfactory both in angular variation and relative intensities (comparing tables II-1 and II-2). Substituting the experimental value of g^{eff} (90°) and invoking assumption (c), the parameter $|D|$ can be computed and is found to be: $|D|$ = 25 Kmc.

If one supposes for the moment that all the lines which are observed arise from the $(\frac{\bar{1}}{2} \rightarrow \frac{\bar{3}}{2})$ transition, the question is immediately raised: How can there possibly be a maximum of four lines when there are only magnetically two non-equivalent molecules in the unit cell? The answer to this question cannot be unequivocably proven from this work, but there is a distinct possibility that the crystal studied was not single. As was mentioned in the experimental section, many of the crystals which resulted from the growth by sublimation appeared distinctly to be twinned. However, one cannot say with certainty that the

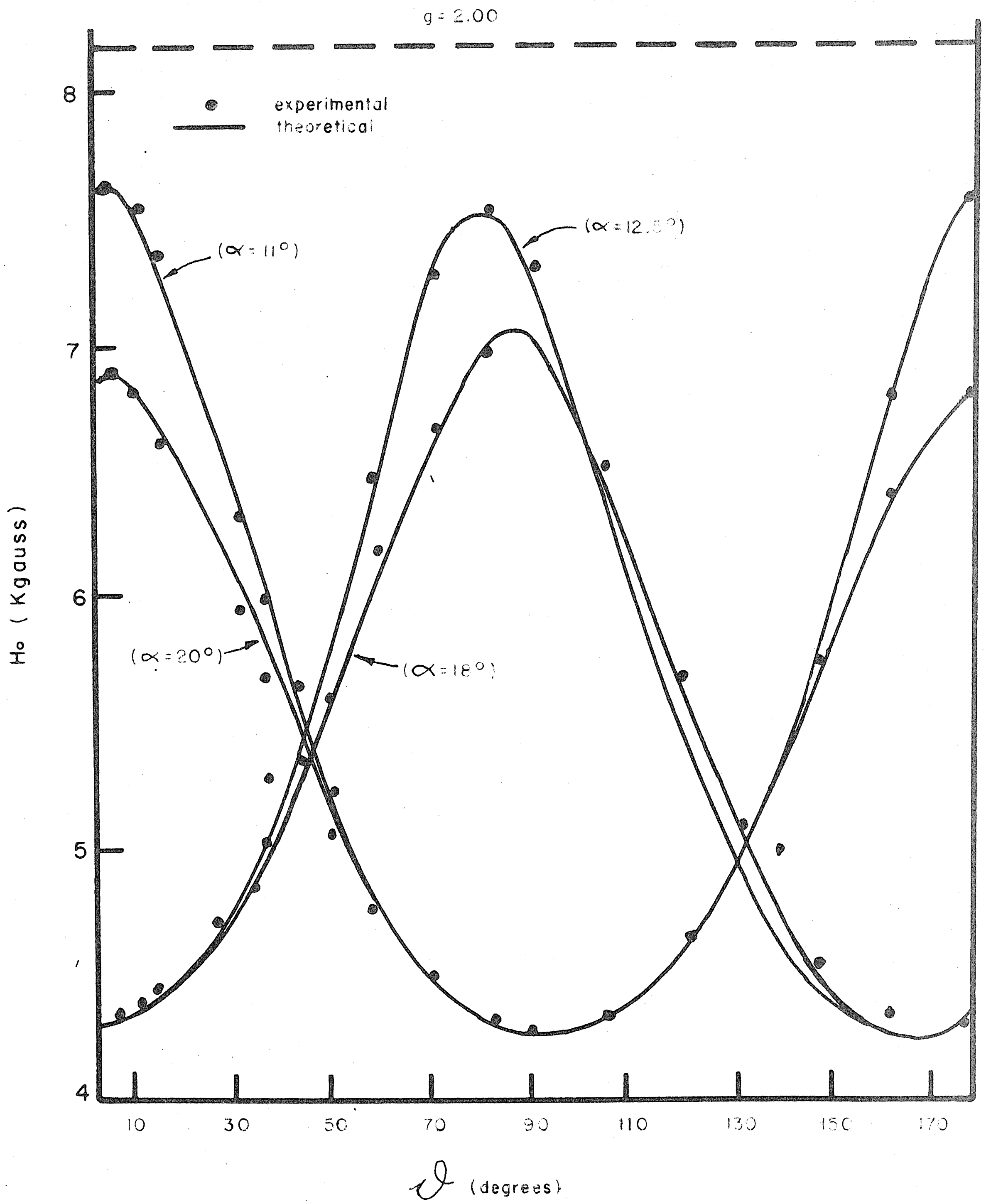


Fig. II-11. Comparison of experimental data to theoretical curve given by equation (II-23). α is the angle necessary to account for maximum in H_o.

particular crystal chosen for the experiments was twinned or not. If the crystal was a twin, then the one member was probably so oriented that its (100) plane makes the angle 30° (or 10°) with the (100) plane of the other.

Some support to the supposition that the crystal was a twin is provided in figure II-5 in which the spectral angular variation from the same crystal reoriented such that the (100) face is perpendicular to the plane of rotation is recorded. The important aspects of this plot are:

1. The various maxima occur at much lower field.
2. The distance between maxima (in angular units) has markedly decreased.
3. The magnetic field at which minima occur has not changed from that of figure II-4, within experimental error.

The first of these experimental features suggests that the reorientation has indeed been such as to increase the angle α between the plane of intersection of the molecular axes of the two molecules and the plane of rotation of H_o. Thus the approach of g^{eff} to $g_{\parallel}$ is less than the previous orientation. It is shown in the appendix that the second observation is what would be expected as (100) becomes more nearly perpendicular to the plane of H_o. It is shown that, if the angular distance between maxima is Γ, Γ increases from 0° when the two planes are perpendicular to a maximum $\cos \Gamma = -\cos \chi$ when the two are coplanar; χ is the angle between the figure axes of two molecules.

The third experimental aspect strengthens the assertion that all the lines come from the $(\frac{\bar{1}}{2} \rightarrow \frac{\bar{3}}{2})$ transition.

Since the vast majority of previous experimental studies of V^{+2} and isoelectronic ions have found it unnecessary to include components of the crystal field lower than tetragonal and since the sandwich molecule has a natural cylindrical symmetry (1), we shall not explore the possibility of rhombic components to II-12.

Conclusions

At least one subsidiary assumption has been made to make coherence from the ESR of vanadocene.

(d) Two of the continuous "curves" of figure II-5 are associated with the $(\frac{1}{2} \rightarrow \frac{3}{2})$ transition, one from each non-equivalent molecule.

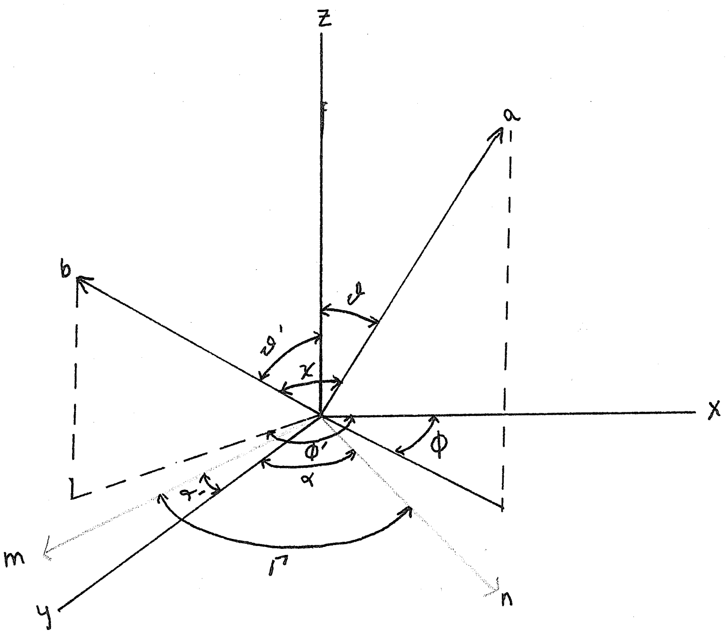
At this point there are several possibilities to account for the other two "curves".

1. Somehow they originate from the $(-\frac{\bar{3}}{2} \rightarrow -\frac{\bar{1}}{2})$ transitions of the two molecules.

2. The crystal is twinned such that $\angle (100):(100)' = 30°$ (or 10°), and the experimental plot in figure II-4 is made up of the spectral angular dependence of the $(\frac{1}{2} \rightarrow \frac{3}{2})$ transition of <u>four</u> non-equivalent molecules.

It is important to point out that the reported value of the splitting parameter, $|D|$, does not depend on these latter two possibilities, only on assumption (d), which itself is implied by assumption (a). It is felt that the agreement of the calculated and experimental spectra is sufficiently excellent to be good evidence for the correctness of assumption (d) and that the behavior of the spectra on reorientation of the crystal makes the latter possibility much more attractive than the former.

APPENDIX TO SECTION II



Suppose that the vectors m and n are perpendicular to the molecular axes a and b and that they both lie in the xy plane. Γ is the angle between m and n in the xy plane and χ is the angle between a and b. a makes the angle ϑ and b the angle ϑ' with the z-axis. We then desire Γ as a function of ϑ and ϑ'. ϕ and ϕ' are the azimuthal angles of a and b, and α and α' measure the angles between m and n and the z-axis.

$$a = a(k\cos\vartheta + i\sin\vartheta\sin\phi + j\sin\vartheta\cos\phi) \tag{AII-1}$$

$$b = b(k\cos\vartheta' - i\sin\vartheta'\sin\phi' + j\sin\vartheta'\cos\phi') \tag{AII-2}$$

$$m = m(-i\sin\alpha + j\cos\alpha) \tag{AII-3}$$

$$n = n(i\sin\alpha' + j\cos\alpha') \tag{AII-4}$$

$$m \cdot n = mn\cos(\alpha + \alpha') = mn\cos\Gamma \tag{AII-5}$$

$$a \cdot m = am\sin\vartheta \cos(\alpha + \phi) = 0 \tag{AII-6}$$

or

$$\alpha + \phi = \frac{\pi}{2} \tag{AII-7}$$

$$b \cdot n = bn\sin\vartheta' \cos(\alpha' + \phi') = 0 \tag{AII-8}$$

or

$$\alpha' + \phi' = \frac{\pi}{2} \tag{AII-9}$$

Combining AII-7 and AII-9 we find

$$\phi + \phi' = \pi - \Gamma \tag{AII-10}$$

$$a \cdot b = ab\,[\cos\vartheta \cos\vartheta' - \sin\vartheta \sin\vartheta' \cos(\phi + \phi')] . \tag{AII-11}$$

which is equivalent to

$$\cos\chi = \cos\vartheta \cos\vartheta' - \sin\vartheta \sin\vartheta' \cos\Gamma . \tag{AII-12}$$

Γ is a maximum when $\vartheta = \vartheta' = \frac{\pi}{2}$ and is given by

$$\cos\Gamma = -\cos\chi . \tag{AII-13}$$

Γ is a minimum when $\vartheta + \vartheta' = \chi$ which from AII-10 gives the value $\Gamma = 0°$.

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PROPOSITIONS

1. On the basis of the method of alternant orbitals described in Section I-A of this thesis, spin densities in linear polyene radicals tend to be nearly uniform on unstarred atoms, thus supporting the assumption of Hanna and McConnell (1).

From the molecular orbital treatment of these molecules (2) the energies and atomic orbitals are given by

$$\epsilon_j = 2\beta \cos\left(\frac{j\pi}{M+2}\right)$$

$$C_j^r = \sqrt{\frac{2}{M+2}} \sin\left(\frac{jr\pi}{M+2}\right)$$

where j refers to the molecular orbital, r the serial number of the carbon atom and M + 1 is the total number of carbon atoms, hence the number of molecular orbitals.

If the approximate formula (IA-56) is used to estimate spin densities, we find

$$\rho_A = \frac{2}{M+2}\left[1 + \frac{MK}{2}\right]$$

$$\rho_B = -K$$

which says that the spin density on all starred atoms is the same and positive and the spin density at unstarred atoms is uniform and negative in sign. The constant K is $\dfrac{1}{6 \sum_{j=1}^{M/2} \cos\left(\frac{j\pi}{M+2}\right)}$.

If one uses the more general formulas of the Appendix to Section I, the spin densities are no longer uniform on the two sets of atoms, but there is a slight build-up of spin at the ends of the radical.

$$\rho_A = \frac{2}{M+2}\left[1 + \frac{2}{3}K'\right]$$

$$\rho_B = -\frac{2}{M+2}K'$$

$$K' = \sum_{j=1}^{M/2} \frac{\sin^2\left(\frac{jr\pi}{M+2}\right)}{\cos\left(\frac{j\pi}{M+2}\right)}$$

2. The ultraviolet and visible spectra of various alkali metal cyclopentadienides in ether solution should be studied, and special care should be taken to determine if the intense violet color is due to a charge transfer transition of an ion pair.

The reason why these ions are interesting is that from the simple molecular orbital point of view they are isoelectronic with benzene which is known to absorb in the uv. Admittedly simple molecular orbital theory is unreliable in prediction of the position of spectral transitions, but the more general method of Pariser and Parr (3), which works well for benzene, is inconclusive. It is not understood how basic integrals for benzene should be changed for the charged cyclopentadienide ion since there are more than one electron per atomic orbital.

It is then at least possible that the spectral transition has been shifted to longer wave lengths by absorption via charge transfer in an ion pair. Although no spectra for this species have been reported in the literature, a dilute ($\sim 10^{-3}$M) solution is not translucent. This is evidence of a very intense transition which is a characteristic of a charge transfer transition (4).

These observations and ideas are consistent with the color and intensity of a charge transfer absorption. They can be checked experimentally by looking for a deviation from Beer's Law in diluted samples. Also one would expect a change in the C-H stretching frequency due to ion pair formation, and this would again be observed in dilution experiments. There would probably be a lack of vibrational fine structure if the transition arises from an ion pair.

3. The proton magnetic resonance shifts in nickelocene have been interpreted in terms of a mechanism by which the unpaired electron on the nickel jumps out on to the rings and interacts with the proton via σ-π exchange (5). An alternate explanation could be that the interaction is a direct one with non-vanishing 3d electron density at the proton position. I propose that this alternate mechanism is about 10^{-3} too small to account for the observed shift.

Slater orbitals (6) are known to give a poor description of the electronic wave function close to the nucleus but are often used for problems in which the behavior of the wave function far from the origin is important. I have evaluated the amplitude of the appropriate 3d

Slater type atomic orbital at the coordinates and find that the resulting shift in the proton resonance is much too small.

4. Recently Kim and Sugawara (7) reported the proton resonance of the waters in the compound $NiCl_2 \cdot 6H_2O$ from room temperature to liquid helium temperatures. At about 6°K they note the complete disappearance of the signal from their polycrystalline sample. I believe that this disappearance of signal is due to a transition of the salt from the paramagnetic to the antiferromagnetic state.

The exchange field at the proton in the antiferromagnetic state is much larger than the dipolar field in the paramagnetic state. Thus in a powder sample absorption will take place over a very wide range of the applied magnetic field and could easily be obscured by electronic noise. To test this hypothesis the experiment should be repeated with a single crystal, and the electronics should be geared to allow the wide sweeps necessary to follow the large shift near and through the transition. Analysis of the anisotropy of the proton resonance in the antiferromagnetic state might lead to the determination of the proton positions (8).

5. In their rush to carry out ESR experiments with transition metal ions in various crystalline fields, physicists have often neglected ions which are of considerable chemical interest. Such a case is Ag^{++}. This ion is probably of the configuration d^9 (the magnetic susceptibility of many complexes is very similar to the corresponding compounds of

Cu^{++}), and the moments of many complexes are only slightly higher than those given by the spin-only formula for one unpaired electron. Although many compounds of this ion are quite unstable with respect to reduction, most of the complexes with things like nitrogen bases are quite stable (9). The trouble with doing ESR experiments with these compounds is that the availability of diamagnetic host crystals with a known crystal structure is limited. However, the crystals of nickel bis-salicylaldehyde-imine and palladium bis-acetylacetonate are known (10, 11). It is proposed that the corresponding Ag(II) compounds be made and their ESR spectra as substitional impurities be observed. Hyperfine splittings due to H^1 and N^{14} are to be expected, and perhaps one can see the interactions of the Ag^{107} and Ag^{109} isotopes.

6. It is proposed that the 370-300 mμ band in solutions containing cupric nitrate and thiocyanate ion has been incorrectly assigned by Tanaka and Takamura (12). These authors maintain that the 300 mμ band in a solution containing only $Cu(NO_3)_2$ is characteristic of the free Cu^{++} ion. However, in the careful survey of the aqueous absorption of various cupric salts Bjerrum et al. (13) report no band that occurs at this low wave length. It seems almost certain that this absorption is due to the nitrate ion (14).

When SCN^- is added to the solution another very strong band appears to grow from the nitrate peak, but this is interpreted as an enhancement of a cupric absorption via interaction with the thiocyanate.

I believe that the opposite interpretation of enhancement and shifting of the uv absorption of the thiocyanate by the copper is correct. This behavior has been observed in nickel and cobalt thiocyanate solutions for instance (15).

It was this peak which was employed to determine the stability constants of the various complexes, $Cu(SCN)_n^{2-n}$. These numbers should remain valid in this alternate interpretation. However, the reported decrease of ϵ_{max} in going from the complex with $n = 3$ to $n = 4$ should be reinvestigated.

7. The zero field transition in peroxylamine disulfonate in solution should be relatively easy to observe. The transition in zero applied magnetic field is between the $F = \frac{3}{2}$ and the $F = \frac{1}{2}$ state, and the expected transition frequency is a simple matter to deduce. For an ion in solution the Hamiltonian in zero field is $a \underset{\sim}{I} \cdot \underset{\sim}{S}$, in which a is the isotropic electron-nuclear coupling constant. Neither I nor S is a good quantum number, but their sum, the total angular momentum F, is. Performing the usual trick, the eigenvalues of the Hamiltonian are given by

$$a \underset{\sim}{I} \cdot \underset{\sim}{S} = \frac{a}{2} \left[F(F+1) - I(I+1) - S(S+1) \right]$$

and for the case of one electron and a nucleus of spin 1 are $-a$ and $\frac{a}{2}$. The transition frequency is the three-halves the isotropic hyperfine interaction which is 36 Mc. The value 54 Mc is in good agreement with the number obtained by extrapolation of resonances at finite fields (16, 17).

8. It is proposed that experiments be carried out to determine the presence or absence of a diamagnetic dimer of ClO_2. The recent establishment of the equilibrium in the isoelectronic system $2SO_2^- \rightleftharpoons S_2O_4^=$ (18) makes the possibility of dimerization in chlorine dioxide quite attractive. The bonding can be rationalized on the same grounds (19), and the Cl-Cl bond may be even stronger than the S-S bond, since the coulombic repulsion of two negative charges is not present in $(ClO_2)_2$.

When the literature on ClO_2 is reviewed, several experimental facts appear to substantiate the postulated equilibrium. The magnetic susceptibility in CCl_4 solution (at the one concentration studied) corresponds to a moment due to less than one unpaired electron (20). Any orbital contribution would increase the observed moment. Further, there is a low frequency band in the infra red (22) which could not be assigned (every other transition was accounted for). Since this peak was observed in various samples prepared in different ways, it was not attributed to impurity.

Several experiments might be useful in this study. Of course, observation of the chlorine NMR would be ideal because the rate of exchange might be estimated. However, the quadrupole broadening would probably obviate this experiment. A concentration study of the magnetic susceptibility would permit the evaluation of the equilibrium constant. Also, a study of the excess sound absorption necessary to break up the dimer might make an ultrasonics experiment feasible (22).

9. The O^{17} chemical shift of the nitrite ion with respect to the nitrate ion is 260 ppm and in the paramagnetic direction (23). The direction and order of magnitude of this shift can be accounted for in terms of the energies of the $n \rightarrow \pi$ transitions of these two ions.

The chemical shift of an atom in two different molecules is made up of two parts. The difference of electron density near the atom is called the diamagnetic contribution and the second is a paramagnetic term which arises from the hindrance to Larmor precession of electrons due to there being more than one positive attracting center in a molecule (24).

We can write the chemical shift of O^{17} between nitrite and nitrate as

$$\Delta \sigma = \Delta \sigma_d + \Delta \sigma_p \text{ .}$$

First I argue that the difference in electron density at the oxygens is not too great in the two ions. As an example of the order of magnitude of this effect, the much bigger increase in electron density at the fluorine in going from F_2 to F^- gives a diamagnetic contribution to the chemical shift of only about 10 ppm (25). Since the change in density in our case is certainly less than the fluorine, I believe that it is reasonable to neglect the diamagnetic contribution to the shift.

For our purposes the paramagnetic part can be written

$$\Delta\sigma_p = C\left\{\sum \frac{M_{NO_3^-}}{\Delta E_{NO_3^-}} - \sum \frac{M_{NO_2^-}}{\Delta E_{NO_2^-}}\right\}$$

where M is a matrix element between the ground and excited states which will contain the average value of $\left\langle \frac{1}{r^3} \right\rangle$ and of angular momentum operators. I now assume that the $n \rightarrow \pi$ transition involving the lone pair oxygen orbitals make the most important contributions to the sums. $\pi \rightarrow \pi$ transitions are not effective since the matrix elements vanish when the ground and excited atomic orbitals are the same. It is further argued that the matrix elements themselves will differ only in coefficients of atomic orbitals since the pertinent ground and excited AO's in nitrate and nitrite are the same for both ions (nonbonding σ and antibonding π). With these assumptions we write the equation

$$\Delta\sigma_p \cong C\, M_{NO_3^-}\left\{\frac{1}{\Delta E_{NO_3^-}} - \left(\frac{C_{NO_2^-}}{C_{NO_3^-}}\right)_{l.p.} \cdot \left(\frac{C_{NO_2^-}}{C_{NO_3^-}}\right)_{\pi} \cdot \frac{1}{\Delta E_{NO_2^-}}\right\}$$

The values of the energy denominators are taken from spectroscopic data available in the literature. Sidman (26) assigns the 3500 Å band in nitrite to the transition which we need. McConnell (27) assigns the 3000 Å band of nitrate to the $n \rightarrow \pi$ transition, but recently Sayre (28) claims that this is a $\pi \rightarrow \pi$ transition. The next band in nitrate comes in at 2100 Å. To make the calculation as bad as possible let us take the lower energy to be the necessary $n \rightarrow \pi$ frequency. At any rate, it seems clear that nitrate absorbs at a higher energy than nitrite, and the direction of the chemical shift is accounted for.

To get a rough order of magnitude of this shift we proceed by assuming that the AO coefficient ratio does not differ much from unity. The necessary matrix elements between an $2p_Z$ and an $2p_\sigma$ atomic orbital have been evaluated by Saika and Slichter (29), and we compare our case to theirs by making estimates of $\left\langle \frac{1}{r^3} \right\rangle$ for oxygen. Unfortunately, the number which we want has not been explicitly evaluated, but by comparing the numbers which are available for various first row elements (30, 31), it is observed that these quantities vary approximately with the cube of Z (this is generous in the wrong direction). When all the numbers are plugged in, the magnitude of the chemical shift comes out 150 ppm and in the paramagnetic direction.

10. There are at least two very fast electron exchange reactions which should be studied with the NMR technique (32).

$MnO_4^{=} \rightleftarrows MnO_4^{-}$ has a half time of about 3 sec under conditions of very low total manganese concentration ($\sim 10^{-5}$) and low base strength (~ 0.15) (33). When either of these two conditions is altered to greater concentration, the reaction becomes immeasurably fast with standard techniques. It is proposed that by upping the concentrations (one would have to have a lot more Mn to see NMR anyway) there is a good chance that the broadening of the NMR of MnO_4^- would be of sufficient magnitude to permit estimation of the lifetime of the two species. MnO_4^- exhibits a temperature independent paramagnetism, but I believe that the broadening in absence of MnO_4^- could be subtracted out with all the other unknown contributions to T_2.

The other case is the $Co^{++} \rightleftarrows Co^{+++}$ exchange in acid solution. This reaction is slow enough under certain conditions to allow analysis by the usual isotope methods (34) (total concentration $Co \sim 10^{-3}M$, 1M in $HClO_4$; half time ~ 4.5 min). So it is seen that the rate must be greatly increased in order that the NMR technique would be feasible. Giuliano and McConnell (35) find that the exchange reaction between vanadium (IV) and (V) is too slow at relatively low acid concentration to allow analysis. However, when $[H^+]$ is about 7F, the broadening of the NMR is sufficient. Since it would be of interest to see if there are other similar reactions with this big H^+ catalysis, it seems to me that the Co experiment is worth a try. There may be another problem in this business which is the oxidation of water. The only hope is that the rate of this reaction is very much slower than the exchange reaction.

11. In Section I-D of this thesis formulas for the spin density at a C^{13} nucleus in a π molecular radical are derived assuming that the $\sigma - \pi$ exchange interaction mixes in excited triplet components of the σ bond. It might be imagined that the process involving the excitation of a carbon 1s electron to the antibonding level might be as effective

since while the energy denominator is much greater so is the density of a 1s electron at the nucleus. From the following calculation it is proposed that this process is at least an order of magnitude smaller than the usual 2s polarization.

Calling the proportionality constant for this latter process Q''', the ratio of this to the quantity Q' (given in equation ID-13) is

$$\frac{Q'''}{Q'} = \frac{\left\{ \frac{|1s(0)\ 2s(0)|}{\Delta E_{1s\to\sigma^*}} \quad (\pi\ 1s \mid \pi\sigma^*) \right\}}{\left\{ \frac{|2s(0)|^2}{\Delta E_{\sigma\to\sigma^*}} \quad (\pi\ \sigma \mid \pi\sigma^*) \right\}}$$

We take the Hartree 1s function for carbon in the sp^2 hybridization and the value of the energy gap between 1s and 2s from the calculation of Torrance (36). The exchange integrals in the ratio can be partially estimated from the tables of Roothaan (37). When these numbers are plugged in, we find the ratio to be

$$\frac{Q'''}{Q'} \simeq \frac{10\text{ ev}}{600\text{ ev}} \cdot \sqrt{\frac{750}{38}} \cdot \frac{0.0187 - J_{1s\sigma}}{0.0170 - J_{c\pi}} \quad \frac{1}{(1+5)^{1/2}} \simeq 0.05 \, .$$

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