A THEORETICAL STUDY OF THE ELECTRON SPIN RESONANCE SPECTRA OF CYCLOHEPTATRIENYL

Thesis by

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ABSTRACT

The ESR spectra of the cycloheptatrienyl radical (CHT) have been studied theoretically, and the orbital degeneracy of the ground state of CHT has been decisively confirmed. The static Jahn-Teller effect and out-of-plane puckering do not occur. The spin densities have been calculated according to the prescriptions of the simple Hückel, approximate UHF-LCAO-MO, Pariser-Parr and valence bond theories. The modifications of the dynamic Jahn-Teller effect and of the unusually strong coupling between the CHT molecule and the lattice through the crystal field have been discussed. The hyperfine structure of the high temperature spectra in naphthalene has been quantitatively explained, and the hyperfine structure of the low temperature spectra in naphthalene has been semi-quantitatively explained. The pi-electron contribution to the spectroscopic splitting factor, g_{zz}, has been estimated and shown to account for the low temperature polycrystalline g-factors. The role of the spin-orbit interaction in inducing spin-lattice relaxation has been examined in the light of the strong lattice-CHT coupling.

ACKNOWLEDGMENTS

The appearance of only one name on the title page of this thesis is misleading. This thesis is in fact the result of the efforts of many persons.

It could not have been possible in the first place without the love, support and encouragement of my wife, Ruth, and my son Robert, and my mother and father.

For the suggestion of the cycloheptatrienyl problem and for many patient discussions and invaluable suggestions, I am greatly indebted to Professor Harden M. McConnell.

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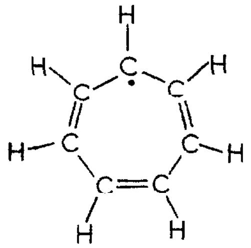
INTRODUCTION



The cycloheptatrienyl radical (CHT), C_7H_7, was first studied by Hückel (1) in 1931. In the Hückel theory, as well as in the valence bond theory, planar heptagonal CHT has a ground state which because of symmetry is orbitally degenerate. In 1937, Jahn and Teller (2) formulated their famous theorem: non-linear molecules whose ground states are orbitally degenerate because of symmetry will distort so as to remove both the symmetry and the degeneracy. Since 1937, the questions

Is CHT a planar, regular heptagon?

Does CHT have an orbitally degenerate ground state?

Does CHT undergo a Jahn-Teller distortion?

have received much theoretical attention, but until now have not been unambiguously answered.

The recent electron spin resonance (ESR) study of CHT in this laboratory by David E. Wood (3) has made it possible to answer these questions. In this thesis, we shall show that the answers to these questions are:

CHT is a planar molecule with the symmetry of a regular heptagon.

The ground state of CHT is orbitally degenerate.

The degeneracy is lifted not by a static Jahn-Teller distortion but by the crystalline electric field.

Several special consequences of the degeneracy will be investigated in detail. These include:

the very unusual coupling between the CHT molecule and the crystal;

the effect of this coupling on the spin-lattice relaxation time through the spin-orbit interaction;

the unusually important pi-electron contribution to the g-tensor.

The thesis will begin with a brief summary of the experimental ESR results on CHT. This will be followed by a review of the theory of the spin Hamiltonian and the spin density matrix. The spin Hamiltonian and the spin density matrix act as a liaison between theory and experiment. Next, various approximate methods of solving the Schrödinger equation will be applied to CHT. Since CHT is both a very simple non-alternant hydrocarbon and has a degenerate ground state, it provides a basic test of the various approximate methods. The predictions of the approximate theories are then modified to account for the dynamic Jahn-Teller effect. The effect of a crystal field is investigated. The numerical computations of spectra and the matching of the theory to experiment are described. Finally, the pi-electron contribution to the g-tensor, and the effect of the degeneracy on the spin-lattice relaxation time are derived.

A. EXPERIMENTAL RESULTS

Wood (3) has examined the ESR spectra of CHT in several matrices: naphthalene, thiourea, cycloheptatriene, and argon. The spectra in each matrix may be divided into two groups: high temperature spectra and low temperature spectra. The high temperature spectra all have eight equally spaced lines with relative intensities 1:7:21:35:35:21:7:1. The splitting between the lines varies from 3.5 to 4 gauss, and in single-crystal samples is significantly (but not greatly) anisotropic. The low temperature spectra are extremely anisotropic, and in single crystal naphthalene samples, the apparent number of lines varies from three to seven. The low temperature spectra vary greatly from one matrix to the next and are very easy to saturate, in contrast to the high temperature spectra which are difficult to saturate. The transition from high to low temperature spectra occurs within a temperature range of a few degrees Kelvin, and the transition temperatures in naphthalene, thiourea, and cycloheptatriene are 20°, 40°, and 13° K, respectively. In an argon matrix, no transition from the high temperature spectrum was observed down to a temperature of about 5° K.

Following are some g-values reported for the low temperature spectra.

g-value	matrix	
$2.0023 \pm .0002$	thiourea	(polycrystalline)
$2.0035 \pm .0004$	naphthalene	(parallel to a-axis)
$1.9985^{+.0015}_{-.0003}$	cycloheptatriene	(polycrystalline)

B. THE SPIN HAMILTONIAN

All the properties of CHT are contained in its exact Hamiltonian, H, and the associated Schrödinger equation,

$$H \phi = i \hbar \frac{\partial \phi}{\partial t} \qquad (1)$$

The spin Hamiltonian, H_{sh}, is a Hamiltonian depending explicitly on only spin operators, and whose energy spectrum in the ESR region is identical with that of H. H_{sh} is both a convenient way to summarize the magnetic properties of H and an indispensable computational device in the interpretation of experimental ESR spectra. In this section, it is shown how to derive the spin Hamiltonian from the exact Hamiltonian.

The exact Hamiltonian may be written as the sum of four terms:

$$H = H_e + H_{so} + H_m + H_{rest} \qquad (2)$$

H_e represents the usual non-relativistic Hamiltonian (in the absence of a magnetic field); H_{so} represents the spin-orbit interaction, H_m the magnetic terms other than the spin-orbit interaction. H_{rest} contains all the remaining terms in H, and for our purposes may be neglected.

Since H_e is much larger than H_{so} and H_m, the latter two may be treated mathematically as perturbations on the problem defined by H_e. The solution of the Schrödinger equation for H_e is discussed in Sections D-G. The spin-orbit interaction is dealt with in Sections R and S. In this section we are concerned explicitly with the magnetic terms of the Hamiltonian, H_m.

H_m is split into four parts*

$$H_m = H_z + H_{hf} + H_{ss} + H_{ohf} \tag{3}$$

The largest part of H_m is the Zeeman interaction of the electron with the external magnetic field $\underset{\sim}{H}$:

$$H_z = |\beta| \sum_{\text{electrons, } i} (\underset{\sim}{l}_i + g\underset{\sim}{s}_i)\cdot\underset{\sim}{H} \tag{4}$$

H_{hf} represents the hyperfine interaction. (For convenience, the Zeeman terms for the nuclei have been included in the electron-proton hyperfine interaction.) H_{ss} represents the electron spin-spin interaction, and H_{ohf} the orbital hyperfine interaction.

$$\begin{aligned} H_{hf} = & -g_e g_p|\beta|\beta_N \sum_{\substack{\text{electrons, } i \\ \text{protons, } j}} r_{ij}^{-5}\, \underset{\sim}{s}_i\cdot(\underset{\sim}{r}_{ij}^2 - 3\underset{\sim}{r}_{ij}\underset{\sim}{r}_{ij})\cdot\underset{\sim}{I}_j \\ & + (8\pi/3)\, g_e g_p|\beta|\beta_N \sum_{ij} \delta(\underset{\sim}{r}_i - \underset{\sim}{r}_j)\, \underset{\sim}{s}_i\cdot\underset{\sim}{I}_j \\ & - g_p\beta_N \sum_j \underset{\sim}{I}_j\cdot\underset{\sim}{H} \end{aligned} \tag{5}$$

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*For an excellent discussion of the important terms in the Hamiltonian, see Bethe and Salpeter (4).

$$H_{ss} = g_e^2\beta^2 \sum_{\substack{\text{electrons}\\ i<j}} r_{ij}^{-5}\, \underset{\sim}{s}_i \cdot (r_{ij}^2 - 3\underset{\sim}{r}_{ij}\underset{\sim}{r}_{ij}) \cdot \underset{\sim}{s}_j \qquad (6)$$

$$H_{ohf} = -g_p\beta_N \sum_{i,j} \underset{\sim}{l}_i \cdot r_{ij}^{-5}\, (r_{ij}^2 - 3\underset{\sim}{r}_{ij}\underset{\sim}{r}_{ij}) \cdot \underset{\sim}{I}_j \qquad (7)$$

The various symbols used on the right hand side of Equations 4-7 all have their usual meanings.

The ground state of H_e is assumed to have no orbital degeneracy, (for CHT it is necessary to include the effect of the crystal field to insure non-degeneracy), but does have two-fold electron-spin degeneracy, and $2^7 = 128$-fold proton-spin degeneracy. H_m lifts this 256-fold degeneracy. In ESR spectroscopy, one observes transitions among these 256 levels in which the energy differences are of the order of $2\,|\beta|\,|\underset{\sim}{H}|$. The energy levels are calculated to first order perturbation theory, by diagonalizing the 256x256 matrix of H_m with respect to the ground state space of H_e.

Parts of H_m are immediately seen to be zero. H_{ohf} and the orbital part of H_z are zero because the H_e ground state is orbitally non-degenerate. $\langle H_{ss}\rangle = 0$ because the ground state is a doublet (electron-spin). (See Proposition No. 1). Effectively, H_m reduces to

$$H_m = g|\beta|\, \underset{\sim}{S}\cdot\underset{\sim}{H} + H_{hf} \qquad (8)$$

The only non-zero part of H_m which depends on electron space-coordinates is H_{hf}. This spatial dependence is not difficult to eliminate, especially if the formalism is developed as follows.

Define $\underset{\approx}{h}_d(ij)$, and $h_c(ij)$ by

$$\underset{\approx}{h}_d(ij) = -g_e g_p|\beta|\beta_N\, r_{ij}^{-5}\, (r_{ij}^{2} - 3\underset{\sim}{r}_{ij}\underset{\sim}{r}_{ij}) \tag{9}$$

$$h_c(ij) = (8\pi/3)\, g_e g_p|\beta|\beta_N\, \delta(\underset{\sim}{r}_{ij}) \tag{10}$$

Expressed in terms of h_c and $\underset{\approx}{h}_d$, H_{hf} becomes

$$\begin{aligned} H_{hf} = {} & -g_p\beta_N \sum_j \underset{\sim}{I}_j\cdot\underset{\sim}{H} \\ & + \sum_{i,j} \left\{ \underset{\sim}{s}_i\cdot\underset{\approx}{h}_d(ij)\cdot\underset{\sim}{I}_j + \underset{\sim}{s}_i\cdot\underset{\sim}{I}_j\, h_c(ij) \right\} \end{aligned} \tag{11}$$

Consider the eigenfunctions of H_e. Each of the 256 functions can be written in the form

$$\Psi = \phi(\pm\tfrac{1}{2})\sigma_1\sigma_2\sigma_3\sigma_4\sigma_5\sigma_6\sigma_7 \tag{12}$$

$\phi(\pm\frac{1}{2})$ is the antisymmetric electron space and spin dependent ground-state eigenfunction of H_e with $S = \frac{1}{2}$, $S_z = \pm\frac{1}{2}$. σ_i is a proton spin function (α or β) for proton i. The spin density (5), $\rho(\underset{\sim}{r})$, is defined from $\phi(+\frac{1}{2})$ by

$$\rho(\underset{\sim}{r}) = \left(\phi(+\tfrac{1}{2}),\ \sum_i 2s_{iz}\delta(\underset{\sim}{r}-\underset{\sim}{r}_i)\, \phi(+\tfrac{1}{2}) \right) \tag{13}$$

The spin density also appears from Ψ in the following three ways:

$$\rho(\underset{\sim}{r}) = \pm\left(\Psi(\pm\tfrac{1}{2}),\ \sum_i 2s_{iz}\delta(\underset{\sim}{r}-\underset{\sim}{r}_i)\Psi(\pm\tfrac{1}{2}) \right) \tag{14}$$

$$\rho(\underset{\sim}{r}) = (\Psi(\pm\tfrac{1}{2}),\ \sum_{i} 2s_{ix}\delta(\underset{\sim}{r}-\underset{\sim}{r}_i)\Psi(\mp\tfrac{1}{2})\ ) \qquad (15)$$

$$\rho(\underset{\sim}{r}) = \pm i(\Psi(\pm\tfrac{1}{2}),\ \sum_{i} 2s_{iy}\delta(\underset{\sim}{r}-\underset{\sim}{r}_i)\Psi(\mp\tfrac{1}{2})\ ) \qquad (16)$$

Using the Equations 9-16, the general matrix element of $H_{hf'}$ can be written

$$(\ \Psi(s),\ H_{hf}\Psi(s')\ ) + (\ \Psi(s),\ \Sigma_j\, g_p\,\beta_N\, \underset{\sim}{I}_j\cdot\underset{\sim}{H}\Psi(s')\ ) \qquad (17)$$

$$= (\ \Psi(s), \sum_{i,j}\ (\underset{\sim}{s}_i\cdot\underset{\approx}{h}_d(ij)\cdot\underset{\sim}{I}_j + \underset{\sim}{s}_i\cdot\underset{\sim}{I}_j\ h_c(ij)\ )\Psi(s')\ )$$

$$= (\ \Psi(s), \sum_{j}\ (\underset{\sim}{S}\cdot\int\rho(\underset{\sim}{r})\ \underset{\approx}{h}_d(j)\ dV\cdot\underset{\sim}{I}_j$$

$$+\ \underset{\sim}{S}\cdot\underset{\sim}{I}_j\int\rho(\underset{\sim}{r})\ h_c(j)\ dV\ )\ \Psi(s')\ ) \qquad (18)^*$$

Equation 18 is the key to removing the dependence of H_{hf} on electron space coordinates. If we denote the isotropic proton hyperfine coupling constant by a_j

$$a_j = \int\rho(\underset{\sim}{r})\ h_c(j)\ dV \qquad (19)^*$$

$$= (8\pi/3)\ g_e g_p|\beta|\beta_N\ \rho(\underset{\sim}{r}_j) \qquad (20)$$

and the anisotropic hyperfine coupling tensor by $\underset{\approx}{T}_j$

$$\underset{\approx}{T}_j = \int\rho(\underset{\sim}{r})\ \underset{\approx}{h}_d(j)\ dV \qquad (21)^*$$

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*When the electronic coordinates, $\underset{\sim}{r}_i$, in $h_c(ij)$ and $\underset{\approx}{h}_d(ij)$ are not given a subscript, we shall write $h_c(j)$ and $\underset{\approx}{h}_d(j)$.

then the 256x256 matrix of H_m is identical with that of

$$H_{sh} = g_e|\beta|\underset{\sim}{S}\cdot\underset{\sim}{H} - \sum_j (g_p\beta_N \underset{\sim}{H} - \underset{\sim}{S}\cdot\underset{\approx}{T}_j - a_j\underset{\sim}{S})\cdot\underset{\sim}{I}_j \tag{22}$$

H_{sh} is called the spin Hamiltonian; it depends only on spin operators, and is an extremely convenient meeting ground between theory and experiment. On the one hand, H_{sh} provides an elegant way to report experimental results, i.e., through the isotropic coupling constants a_j, and the traceless, anisotropic coupling tensors $\underset{\approx}{T}_j$. On the other hand, H_{sh} is an equally elegant form for reporting theoretical results.

C. THE SPIN DENSITY MATRIX

Although the entire spin Hamiltonian is needed to describe the ESR spectrum, the spin properties unique to the electronic wavefunction are embodied in the spin density $\rho(\underset{\sim}{r})$. A particularly useful generalization of $\rho(\underset{\sim}{r})$ is the spin density matrix (5).

$$\begin{aligned}\rho(\underset{\sim}{r}',\underset{\sim}{r}) = \int & d\sigma_1 dV_2 d\sigma_2 \ldots dV_n d\sigma_n \phi(\tfrac{1}{2})^*(\underset{\sim}{r}',\underset{\sim}{r}_2,\ldots,\underset{\sim}{r}_n) \\ & \cdot 2ns_{1z}\phi(\tfrac{1}{2})(\underset{\sim}{r},\underset{\sim}{r}_2,\ldots,\underset{\sim}{r}_n)\end{aligned} \tag{23}$$

Furthermore, if $\{a_i\}$ is a complete set of one-electron space functions, then it is possible to express the spin density matrix as

$$\rho(\underset{\sim}{r}',\underset{\sim}{r}) = \sum_{i,j} \rho_{ij} a_i(\underset{\sim}{r})\, a_j(\underset{\sim}{r}')^* \tag{24}$$

The spin density is obtained by setting $\underset{\sim}{r}' = \underset{\sim}{r}$.

$$\rho(\underset{\sim}{r}) = \rho(\underset{\sim}{r},\underset{\sim}{r}) \tag{25}$$

D. THE SIMPLE HUCKEL MOLECULAR ORBITAL THEORY

The simple Hückel Molecular Orbital theory (1) (SHMO) is a highly approximate method for solving the Schrödinger equation for a planar, conjugated molecule (6). The first approximation of SHMO theory is to disregard all electrons except the so-called pi-electrons. The second approximation made is that the pi-electrons do not correlate. Thus, the pi-electron Hamiltonian, H_e, becomes the sum of one-electron terms:

$$H_e = \sum_{\text{pi electrons, } i} h(i) \tag{26}$$

h(n) acts only on electron n, and is called the effective one-electron Hamiltonian. Later approximations make a precise definition of h(n) unnecessary.

As a consequence of the second, non-interacting particle approximation, the wave functions $\phi(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots, \underset{\sim}{r}_7)$ (CHT has seven pi electrons) can be written in the form

$$\phi = \hat{A}\, M_1\sigma_1 M_2\sigma_2 \ldots M_7\sigma_7 \tag{27}$$

We use the convention that the ith spin-orbital to appear is a function of the coordinates of electron i. $\hat{A}$ denotes the antisymmetrization operator, so that ϕ satisfies the Pauli principle. σ_n denotes a spin function (α or β). The molecular orbitals, M_i, are eigenfunctions of h with energy e_i.

$$h\, M_i = e_i\, M_i \tag{28}$$

The energy of $\emptyset$ is $e_1 + e_2 + \ldots + e_7$.

The third approximation of the SHMO theory is to approximate each molecular orbital as a linear combination of atomic orbitals (LCAO).

$$M_i(\underset{\sim}{r}) = \sum_{\text{nuclei, } j} c_j^i \, a_j(\underset{\sim}{r}) \tag{29}$$

For CHT, the sum is over the seven carbon atoms whose position vectors are designated $\underset{\sim}{r}_j$. a_j is to be regarded as a Slater $2p_z$- type atomic orbital centered on the carbon nucleus at $\underset{\sim}{r}_j$. The c_j^i are chosen so that the total energy of $\emptyset$ is a minimum, which implies that the c_j^i satisfy the eigenvalue equations

$$\sum_m h_{lm} \, c_m^i = e_i \sum_m S_{lm} \, c_m^i \tag{30}$$

where

$$h_{lm} = (a_l, ha_m) \tag{31}$$

$$S_{lm} = (a_l, a_m) \tag{32}$$

Finally, the following mathematical assumptions are made:

$$S_{lm} = \delta_{lm} \tag{33}$$

$$h_{mm} = \alpha \text{ , independent of m} \tag{34}$$

$$h_{lm} = \beta \text{ , if l and m are nearest neighbors; independent of l and m} \tag{35}$$

$$h_{lm} = 0, \quad l \neq m, \text{ l and m not nearest neighbors} \tag{36}$$

Within this framework, the c_j^i are independent of α and β, and the one-electron energies have the form $e_i = \alpha + k_i\beta$, where k_i is independent of α and β.

For CHT, the molecular orbitals are determined by symmetry* (1):

$$\left.\begin{aligned} M_m(\underset{\sim}{r}) &= 7^{-\frac{1}{2}} \sum_{n=1}^{7} \exp(2\pi imn/7)\ a_n(\underset{\sim}{r}) \\ e_m &= \alpha + 2\beta\cos(2\pi m/7) \end{aligned}\right\} m = 0, \pm 1, \pm 2, \pm 3 \qquad (37)$$

The wavefunction of the form of Equation 27, with the lowest energy is

$$\phi = \hat{A}\ M_0\alpha\, M_0\beta\, M_1\alpha\, M_1\beta\, M_{-1}\alpha\ M_{-1}\beta\, M_{(2)}\sigma \qquad (38)$$

In addition to the two-fold spin degeneracy, the ground state is orbitally two-fold degenerate with symmetry E''_2. σ represents an arbitrary linear combination of α and β for electron #7, and $M_{(2)}$ stands for an arbitrary linear combination of $M_{\pm 2}$.

If $M_{(2)}$ is required to be real, then it must have the form

$$M_{\theta_{om}} = 2^{-\frac{1}{2}}(\exp(i\theta_{om})\ M_2 + \exp(-i\theta_{om})\ M_{-2}) \qquad (39)$$

where θ_{om} will be called the orbital mixing parameter.

In Sections B and C, it was shown how to incorporate the electronic wavefunction into the spin Hamiltonian via the spin density. Later, only the diagonal elements of the spin

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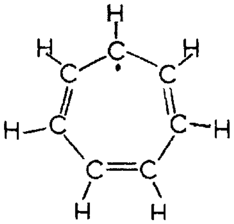
*Throughout Sections D-G, CHT will be assumed to have the symmetry of a regular heptagon.

density matrix in an atomic orbital representation will be required. These diagonal elements will be called the "spin densities". The SHMO spin densities are found from Equations 24, 37-39, to be

$$\rho_{nn} = (1/7)\left[1 + \cos(\,(8\pi n/7) + 2\theta_{om})\right] \qquad (40)$$

E. THE VALENCE BOND THEORY

The Valence Bond (VB) theory is the natural generalization of the chemist's classical picture of a molecule. Classically, a chemist would represent CHT by the following diagram:



The VB theory assigns to diagrams such as these a semi-precise mathematical meaning in the form of a simple many electron wavefunction. As with the SHMO theory, only the pi-electrons are considered explicitly. If the carbon atoms are numbered consecutively beginning with the odd electron, then the above diagram stands for the "bond eigenfunction"

$$\phi = 8^{-\frac{1}{2}}\, \hat{A}\; a_1\alpha\, a_2a_3(\alpha\beta-\beta\alpha)a_4a_5(\alpha\beta-\beta\alpha)a_6a_7(\alpha\beta-\beta\alpha) \quad (41)$$

The actual mechanics of the VB calculation for CHT are quite tedious (7), although the method is simple and described in standard texts (e.g., ref. (8)). The VB method is equivalent to the spin-state method, which in the case of CHT is somewhat simpler to apply. The VB wavefunction is nothing more than a linear combination of spin-states, each of which has the form

$$\phi = \hat{A}\; a_1\sigma_1 a_2\sigma_2 a_3\sigma_3 a_4\sigma_4 a_5\sigma_5 a_6\sigma_6 a_7\sigma_7 \quad (42)$$

where each σ_n is either α or β. There are $2^7 = 128$ such spin-states, of which only 35 have $S_z = \frac{1}{2}$, and from which only 14 independent doublets can be formed. The VB method starts by weeding out the states of unwanted multiplicity. It is in this step, however, that the complications associated with the VB theory are introduced. The simpler procedure in this case is to diagonalize the 35x35 matrix of H_e with respect to the states of mixed multiplicities using a digital computer. The states of different multiplicities are automatically separated (assuming that their energies differ) and one needs only to verify the spin of a state with a given energy. The spin-state matrix elements are much easier to calculate than the bond-eigenfunction matrix elements.

In calculating matrix elements, the following assumptions are made

$$(a_i a_j, \quad H_e \quad a_j a_i) = A < 0, \quad \text{if i and j are nearest neighbors, independent of i, j} \qquad (43)$$
$$= 0, \quad \text{otherwise}$$

$$(a_i, a_j) = \delta_{ij} \qquad (44)$$

The results of the VB and spin-state calculations for CHT are (a) the ground state is a doublet which is orbitally two-fold degenerate belonging to the E_2'' representation of D_{7h}; (b) the symmetry of the VB ground state is the same as for the SHMO ground state; (c) the energy of the ground state is 2.2104 A; (d) the spin densities are given by the formula

$$\rho_{nn} = (1/7)\left[1 + 3.2377 \cos((8\pi n/7) + 2\theta_{om})\right] \qquad (45)$$

F. THE UNRESTRICTED HARTREE-FOCK LCAO-MO THEORY

The unrestricted Hartree-Fock (UHF) LCAO-MO function is the single determinant LCAO-MO wavefunction which gives the lowest energy for a radical (9). It has the form

$$\phi = \hat{A}\, M_1 \alpha M_1{}'\beta\, M_2 \alpha M_2{}'\beta \ldots M_n \alpha M_n{}'\beta\, M_0 \alpha \qquad (46)$$

M_i may differ from M'_i. The UHF function is physically an improvement over the SHMO function in that it accounts for the average coulomb and exchange interactions of the electrons. As before, only the pi-electrons are considered explicitly.

In general, the UHF ϕ is not an eigenfunction of $\underset{\sim}{S}^2$. McLachlan (10) has shown, however, that in spite of this objection, the results obtained using a function of the type of Equation 46 are usually quite good, and when the UHF wavefunction is calculated from the SHMO wavefunction using first order perturbation theory, the results are essentially the same as those obtained from the SHMO theory by configuration interaction to first order perturbation theory.

A second objection is that the UHF ϕ will not in general transform according to an irreducible representation of the symmetry group of the molecule, if the molecule has high symmetry. However, when the UHF function and spin densities are calculated to first order from the SHMO function, the symmetry of the spin densities is not destroyed.

With these considerations in mind, we now proceed with an approximate UHF-LCAO-MO calculation. The UHF molecular orbitals (9) satisfy the equations

$$F^{\sigma} M_i^{\sigma} = e_i^{\sigma} M_i^{\sigma} \tag{47}$$

F^{σ} is the UHF Hamiltonian for electrons of spin σ. It is made up of the SHMO equivalent one-electron Hamiltonian, h, and the average coulomb and exchange interactions J, K^{σ}.

$$F^{\sigma} = h + J - K^{\sigma} \tag{48}$$

$$J = \sum_{\text{occupied orbitals}} (M_i, (e^2/r_{12}) M_i) \tag{49}$$

$$K^{\sigma} = \sum_{\substack{\text{occupied orbitals}\\ \text{of spin } \sigma}} |M_i) e^2/r_{12} (M_i| \tag{50}$$

In the spirit of perturbation theory, it is first assumed that $F^{\alpha}(0) = F^{\beta}(0)$, and that Equation 47 has been solved. Then one treats the difference $F^{\sigma} - F^{\sigma}(0)$ as a perturbation, F^{σ} being calculated from the "unperturbed" wavefunction.

For CHT, the arbitrary real SHMO wavefunction is given by Equations 38 and 39.

$$\phi = \hat{A}\, M_0 \alpha M_0 \beta M_1 \alpha M_1 \beta M_{-1} \alpha M_{-1} \beta M_{\theta_{om}} \alpha \tag{50.1}$$

(It should be noticed at this point that if $M_{(2)}$ in Equation 39 were taken to be $M_{\pm 2}$, then the SHMO molecular orbitals would already be solutions of Equation 47. Physically, this function has both uniform charge and spin density. That $\emptyset$, Equation 50.1, is not a solution of Equation 47, shows that the UHF procedure does not always lead to unique results.) The obvious definition for F(0) is (in Dirac notation)

$$F(0) = h + \sum_{i=-1}^{1} \left[2(M_i, (e^2/r_{12}) M_i) - |M_i) e^2/r_{12} (M_i| \right] \qquad (51)$$

F(0) is invariant under D_{7h}, as is h, and consequently, the SHMO orbitals are also eigenfunctions of F(0). The orbital energies, with the approximations and conventions of Equations 63-66, are

$$e_m = (M_m, F(0) M_m) \qquad (52)$$

$$= \alpha + 2\beta \cos(2\pi m/7) + 6K_{00} - \sum_{i=-1}^{1} K_{0\ m-i} \qquad (53)$$

where $$K_{0m} = (1/7)\ (G_{00} + \sum_{n=1}^{3} 2G_{0n} \cos(2\pi mn/7)\ ) \qquad (54)$$

The corrections to F(0) to obtain F^α and F^β are just the coulomb and exchange operators for the odd electron:

$$V^\alpha = V^\beta - |M_{\theta_{om}}) e^2/r_{12} (M_{\theta_{om}}| \qquad (55)$$

$$V^\beta = (M_{\theta_{om}}, (e^2/r_{12}) M_{\theta_{om}}) \qquad (56)$$

Note that $V^\alpha |M_{\theta_{om}}) = 0$ (57)

For the SHMO wavefunction, the unperturbed spin densities are (Equation 40)

$$\rho_{nn} = (1/7)\left[1 + \cos(\,(8\pi n/7) + 2\theta_{om})\right]$$

The first order changes in the spin densities are

$$\delta\rho_{nn} = 2\mathrm{Re} \sum_{i=-1}^{1} \sum_{|k|=2,3} (c_n^i)^* c_n^k \, (M_k,\ (V^\alpha - V^\beta)\ M_i)/(e_i - e_k) \qquad (58)$$

$$= (1/7)\ (T_x - 1)\ \cos(\,(8\pi n/7) + 2\theta_{om}) \qquad (59)$$

where T_x, the theory indexing parameter, is given by

$$T_x = 1 + 2K_{01}/(e_3 - e_1) + 2K_{02}/(e_3 - e_0) + 2K_{03}/(e_3 - e_1) \qquad (60)$$

Using the values of Section G for the G_{0n} and e_n,

$$\rho_{nn} = (1/7)\left[1 + 1.343\ \cos(\,(8\pi n/7) + 2\theta_{om})\right] \qquad (61)$$

G. THE RECIPE OF PARISER AND PARR

The Pariser-Parr theory (11) for treating pi-electron molecules introduces pi-electron correlation into the SHMO wavefunction by limited configuration interaction. The essential features of the recipe as it applies to CHT are

(i) pi-electrons only are treated (62)

(ii) $$H_e = \sum_i h(i) + \tfrac{1}{2} \sum_{i \neq j} e^2/r_{ij} \tag{63}$$

(iii) $$\begin{aligned}(a_i, ha_j) &= 0, \text{ if } i = j \\ &= \beta, \text{ if } i,\ j \text{ nearest neighbors, independent of } i,\ j. \\ &= 0, \text{ otherwise.}\end{aligned} \tag{64}$$

(iv) $$(a_i, a_j) = \delta_{ij} \tag{65}$$

(v) $$(a_i a_k, (e^2/r_{12})\, a_j a_l) = \delta_{ij}\, \delta_{kl}\, G_{ik} \tag{66}$$

(vi) the wavefunction is to be constructed from the SHMO ground and singly excited states (12) (67)

(vii) Empirical values are assigned to G_{00} and G_{01}. G_{0m}, $m \neq 0,1$, are given the values computed using Slater $2p_z$ orbitals with effective nuclear charge 3.18 electronic charges. (68)

The exact details of the Pariser-Parr recipe are not universally agreed upon, and as far as it concerns CHT, the values used for β, G_{00}, G_{01} have a certain arbitrariness. The exact numbers we use here are roughly those of Pariser (13). The values for G_{02}, and G_{03} were obtained for carbon-carbon distances of 2.52 and 3.15 Angstroms, from the table of Kotani et al. (32).

$\beta = -2.4$ e.v.

$G_{00}, G_{01}, G_{02}, G_{03} = 11.0, 7.0, 5.4, 4.4$ e.v.

In the SHMO theory, the ground state may be taken as

$$\phi_{\pm} = \hat{A}\, M_0 \alpha\, M_0 \beta\, M_1 \alpha\, M_1 \beta\, M_{-1} \alpha\, M_{-1} \beta\, M_{\pm 2} \alpha \tag{69}$$

Because of the high symmetry, ϕ_+ does not interact with any of its singly excited configurations. However, a linear combination of ϕ_+ and ϕ_- does interact with singly excited configurations. This is because ϕ_+ interacts with the singly excited configurations of ϕ_-. Thus ϕ_+ interacts with its pseudo-singly excited configurations.

By diagonalizing H_e over ϕ_+ and its pseudo-singly excited configurations, the energy lowering of the ground state is found to be 0.44 e.v., and the spin densities are given by the formula

$$\rho_{nn} = (1/7)\left[1 + 1.65 \cos\left((8\pi n/7) + 2\theta_{om}\right)\right] \tag{70}$$

H. THE STATIC JAHN-TELLER EFFECT

Until now, it has been assumed that CHT has D_{7h} symmetry. Both molecular orbital and VB theories predict that the ground state is orbitally two-fold degenerate with symmetry E_2''. An arbitrary linear combination of these states will not have in general a symmetric charge distribution. The forces the electrons exert on the nuclei can be computed directly from the charge distribution by Feynman's theorem (14); hence, the forces on the nuclei due to the electrons cannot be radial for each nucleus, and cannot balance the radial coulomb repulsion forces among the nuclei. The molecule ought to distort, and one has the Jahn-Teller effect (2).

The static Jahn-Teller distortion for CHT has been calculated by Hobey and McLachlan (15). They find changes in the bond lengths of the order of 0.02 Å, and a net gain in energy of 300 cm^{-1}. 300 cm^{-1} is less than the zero-point energy of any of the planar vibrations of CHT involving the carbon atoms. This fact casts serious doubt on the picture of a distorted CHT molecule.

That the forces on the nuclei do not vanish in the symmetrical configuration, and that the static distortion energy is less than a vibrational quantum, suggest that the nuclear and electronic motions might be strongly coupled. Indeed, the requirement for the uncoupling of the motions is just that the

Born-Oppenheimer (16) approximation be valid, which in turn requires that the forces on the nuclei in the equilibrium configuration vanish.

I. THE DYNAMIC JAHN-TELLER EFFECT

The solution of the Schrödinger equation when the motions of the electrons and nuclei are correlated is orders of magnitude more difficult than the usual uncoupled problem. The eigenfunction can be represented as a double, generalized Fourier series over a complete set of states for the nuclear motions $\{N_i\}$ and the electronic motions $\{M_j\}$:

$$\Phi = \Sigma c_{ij} N_i M_j \tag{71}$$

A crude approximation to Φ for CHT would be

$$\Phi = N_1 \phi_{+2} + N_2 \phi_{-2} \tag{72}$$

where $\phi_{\pm 2}$ are the electronic eigenfunctions for the symmetrical configuration. A calculation using a function of this type, based on the SHMO theory, was performed by McConnell and McLachlan (17) for the benzene negative ion. They found that only two E_{2g} vibrations coupled very strongly to the electronic motions, and that the vibronic ground state was still degenerate with E_{2u} symmetry.

A similar calculation was carried out for CHT. The frequencies of the normal modes of vibration of CHT were estimated by assuming the C-C stretching force constant and the C-C-C bending force constant appropriate for benzene (18). and treating the molecule as made up of only seven carbon atoms (no hydrogen). Only two E'_3 vibrations mixed strongly with the electron motions, and the ground state retains its symmetry and degeneracy.

Let R_7 denote the operator which rotates the molecule by $2\pi/7$. It is assumed that $\phi_{\pm 2}$ have been chosen to satisfy

$$R_7\phi_{\pm 2} = \exp(\pm 4\pi i/7)\ \phi_{\pm 2} \tag{73}$$

$$(\phi_{\pm 2})^* = \phi_{\mp 2} \tag{74}$$

Then the vibronic wavefunction has the form

$$\Phi_{+2} = N_0\phi_{+2} + N_4\phi_{-2} \tag{74.1}$$

$$\Phi_{-2} = N_0\phi_{-2} + N_4^*\phi_{+2} \tag{75}$$

The symmetry of the vibrational factors is given by

$$R_7N_0 = N_0 \tag{76}$$

$$N_0^* = N_0 \tag{77}$$

$$R_7N_4 = \exp(+8\pi i/7)\ N_4 \tag{78}$$

$$R_7N_4^* = \exp(-8\pi i/7)\ N_4^* \tag{79}$$

The effect of the vibronic coupling on matrix elements of electronic operators can be estimated by using Equations 74.1 and 75:

$$\begin{aligned}(\Phi_{\pm 2},\ \mathrm{Op}\ \Phi_{\pm 2}) &= (N_0,\ N_0)(\phi_{\pm 2},\ \mathrm{Op}\ \phi_{\pm 2}) \\ &\quad + (N_4,\ N_4)(\phi_{\mp 2},\ \mathrm{Op}\ \phi_{\mp 2})\end{aligned} \tag{80}$$

$$(\Phi_{\pm 2},\ \mathrm{Op}\ \Phi_{\mp 2}) = (N_0,\ N_0)(\phi_{\pm 2},\ \mathrm{Op}\ \phi_{\mp 2}) \qquad (81)$$

In particular, the expressions for the spin densities,

$$\rho_{nn} = (1/7)\left[1 + k\cos(\ (8\pi n/7) + 2\theta_{om})\right] \qquad (82)$$

become

$$\rho_{nn} = (1/7)\left[1 + (N_0,\ N_0)\ k\cos(\ (8\pi n/7) + 2\theta_{om})\right] \qquad (83)$$

where $(N_0,\ N_0)$ is probably of the order of 0.8.

J. OUT-OF-PLANE PUCKERING

Another type of distortion which would lower the symmetry of CHT, and therefore remove the ground state degeneracy, is ring puckering. If the effect of puckering is treated by perturbation theory, the puckering would select an orbital mixing parameter and produce a splitting precisely analogous to the crystal field effect (see Section K). It will be shown in Section P that the energy gained by puckering cannot be greater than 100 cm^{-1}. This is smaller than the theoretical energy gained from an in-plane distortion, so that a puckering of the ring is *a fortiori* not possible.

K. THE CRYSTAL FIELD SPLITTING

A weak crystalline electric field introduces terms into the Hamiltonian, H_e, which remove the degeneracy of the CHT ground state. The actual ground state will be real (neglecting spin-orbit coupling) and to zeroth order of perturbation theory, will be a linear combination of the two degenerate states. The spin densities will then be given by

$$\rho_{nn} = (1/7)\left[1 + T_x \cos\left((8\pi n/7) + 2\theta_{om}\right)\right] \tag{84}$$

The "theory indexing parameter", T_x, has the values 1, 1.343, 1.65, and 3.2377 for the SHMO, approximate UHF-LCAO-MO, Pariser-Parr, and VB theories, respectively. The orbital mixing parameter, θ_{om}, is determined by the crystal field, and specifies which linear combination of the two degenerate states is the actual ground state.

It is possible to estimate the order of magnitude of the crystal field splitting in organic crystals. If the crystal field is expanded in a power series about the center of the CHT molecule, then the lowest terms that can split the degeneracy are the third and fourth. In organic crystals, the source of the crystal field is most likely the dipole moment of the CH bonds. Depending somewhat upon what numbers are used for the relevant dipole moments and their distances from the CHT molecule, one estimates a splitting of the order of magnitude of 150 cm^{-1} for the third-order term, and about 30 cm^{-1} for the fourth-order term. In naphthalene, if the CHT replaces a naphthalene molecule substitutionally, then it is at a center of symmetry, and there is no third-order term.

L. ROTATION AND THE CRYSTAL FIELD

At high temperatures (see Section P) the CHT molecule undergoes "rotational reorientation" about its seven-fold axis. Modulation of the crystal field interaction by rotation has a dramatic effect on the nature of the CHT wavefunction. Suppose that the CHT molecule is rotated by $2\pi/7$. In the coordinate system of the crystal, the ground state eigenfunction of CHT will be identical before and after the rotation. In the reference frame of the molecule, the crystal field will have rotated by $-2\pi/7$, as will the ground state charge distribution. Hence, the "odd-electron" is frozen into the crystal. The rotation of CHT in a crystal field is analogous to that of a helicopter whose rotor is held fixed.

If CHT were to rotate freely about its seven-fold axis, its rotational frequency ω would be $\sqrt{2kT/I}$. The moment of inertia I is approximately $4\text{x}10^{-38}$ gm cm^2, so that for $T = 100^\circ$ K, $\omega = 10^{12}$ radians/second.

The existence of the low-temperature spectra in naphthalene indicates that rotation is not free, but restricted by a barrier V which might be high enough to trap at least one non-rotating bound state of energy around 15-20 cm^{-1}. In the absence of a contribution to this barrier from the crystalline electric field (see below), the potential energy of rotation will have (in naphthalene) a fourteen-fold periodicity, which may be approximated by

$$V_{rot} = \tfrac{1}{2} V \left(1 - \cos 14\theta \right) \tag{85}$$

$$\sim \tfrac{1}{4} \times 196 \times V \times \theta^{2} \tag{86}$$

If the zero-point energy, $\frac{1}{2}\hbar\sqrt{98V/I}$, were equal to 20 cm^{-1}, V would be about 120 cm^{-1}.

In order to understand the high-temperature behavior of CHT, it is important to realize that CHT cannot be described by a stationary state wavefunction. This unusual situation is a direct result of the degeneracy of the CHT ground state and the consequent strong coupling of the rotation of the molecule to the crystal field. We now examine this lattice-rotation coupling mathematically.

At high temperatures, when the molecule is rotating more or less freely, the electronic wavefunction is rather complicated. In order to simplify the mathematics, and yet retain the important physical aspects of this lattice-rotation coupling, we approximate the entire crystal field by the fourth-order terms only, and account for the rotation of the molecule by letting the crystal rotate about the stationary molecule with an angular frequency ω.

If the electronic wavefunctions $\phi_{\pm 2}$ for the unperturbed molecule are given the right phase, and if they satisfy Equations 73 and 74, then the matrix of the crystal field at time $t = 0$ is

$$H(0) = -\tfrac{1}{2}\Delta E \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{87}$$

After a time t, H will be

$$H(t) = -\tfrac{1}{2}\Delta E \begin{pmatrix} 0 & \exp(-4i\omega t) \\ \exp(+4i\omega t) & 0 \end{pmatrix} \qquad (88)$$

The rotation leaves the magnitude of the crystal field splitting unchanged and modulates the relative phases of $\phi_{\pm 2}$ in the wavefunction. (The higher order terms in the potential would produce a small modulation of the magnitude of the crystal field splitting.)

The instantaneous eigenfunctions of H(t) are

$$\psi_1 = 2^{-\frac{1}{2}} \left(\phi_{+2}\exp(2i\omega t) + \phi_{-2}\exp(-2i\omega t) \right) \qquad (89)$$

$$\psi_u = 2^{-\frac{1}{2}} \left(\phi_{+2}\exp(2i\omega t) - \phi_{-2}\exp(-2i\omega t) \right) \qquad (90)$$

Writing H(t) in Dirac notation,

$$H(t) = \tfrac{1}{2}\Delta E \left(|\psi_u)(\psi_u| - |\psi_1)(\psi_1| \right) \qquad (91)$$

Because the Hamiltonian H(t) is time-dependent, the Schrödinger equation, $H(t)\Psi = i\hbar\frac{\partial}{\partial t}\Psi$, has no stationary-state solutions. Two linearly independent, time-dependent solutions are

$$\Psi_L = (i\cos\Omega t - (\tfrac{1}{2}\Delta E/\hbar\Omega)\sin\Omega t)\,\psi_1 + (2\omega/\Omega)\sin\Omega t\;\psi_u \qquad (92)$$

$$\Psi_U = (2\omega/\Omega)\sin\Omega t\,\psi_1 + (i\cos\Omega t + (\tfrac{1}{2}\Delta E/\hbar\Omega)\sin\Omega t)\,\psi_u \qquad (93)$$

where $$\Omega = \sqrt{4\omega^2 + \tfrac{1}{4}(\Delta E/\hbar)^2} \qquad (94)$$

As one would expect intuitively, the major effect of the rotation is to average all the spin densities to 1/7. This partially explains the high temperature spectra. Another effect of the rotation-lattice coupling is to make the wavefunction complex. This will affect the spin-orbit interaction.

Throughout this entire section there has been an implicit swindle: that the rotation of the molecule is separable from the electronic motions. Indeed, the exact Hamiltonian describing CHT in a crystal field is not time-dependent and has stationary-state solutions. How is this reconciled with the above model? The answer can be found in a flurry of hand-waving. On general principles, the exact Schrödinger equation for CHT would have stationary state solutions, and from our above model, it may be inferred that this solution would be a complicated function of rotational, electronic, and vibrational coordinates. Rotation, however, is a semi-distinct property of a massive molecule, and separating rotation from the other motions should not be too bad an approximation. Hence, it is a reasonable hope that the time-dependence this separation introduces into the electronic wavefunction (which is definitely a property of the model) reflects the properties of a more exact treatment.

M. ON THE ANISOTROPIC AND ISOTROPIC HYPERFINE INTERACTIONS

An aim of theory is to predict experimental results accurately. We have examined the predictions of MO and VB theories of the spin densities of CHT, and have come to the point where the question of which theory predicts the spin densities for CHT correctly should be answered. The answer will occupy the next four sections of the thesis.

A theoretical computation of ESR spectra begins with the spin Hamiltonian, Equation 22. The important unknown quantities are the anisotropic traceless hyperfine tensors, Equation 21, and the isotropic hyperfine coupling constants, Equation 20. In evaluating the integrals of Equations 20 and 21, it is convenient to use the atomic orbital expansion, Equation 24, for the spin density. Thus, one may divide the labor into two parts; evaluating some integrals over a set of atomic orbitals and calculating the atomic orbital spin density matrix from theory.

One great deficiency of the MO and VB theories in practice is the small number of atomic orbitals on which the wavefunctions are based. This deficiency is partially compensated by giving the integrals involving the atomic orbitals empirical values. In practice, it is impossible to give all the integrals values from experiment and so some are given experimental values, others are given theoretical values, and most are neglected altogether.

Each of the tensors $(a_i, \underset{\approx}{h}_d(j)a_i)$ has three principal axes: one along the C_i-H_j direction (x), a second axis in the molecular plane perpendicular to the first (y), and a third parallel to the lobes of the p-orbitals (z). The largest of these tensors are the $(a_j, \underset{\approx}{h}_d(j)a_j)$ (whose principal values are independent of j). It would have been very difficult to evaluate this tensor from the present experiments; therefore the principal values for this tensor were arbitrarily adopted from the works of McConnell, Heller, Cole and Fessenden (19) and of Cole, Kushida and Heller (20) on the ESR of the malonic acid radical. The values are listed in Table 1.

The integrals, $(a_i, \underset{\approx}{h}_d(j)a_i)$ for $i \neq j$, were evaluated theoretically. Slater $2p_z$ orbitals with effective nuclear charges of 3.18 and 3.25, and Gaussian orbitals with scale factor $g = 0.0445$ and 0.0464 (Bohr radii)$^{-2}$ were used in this calculation. (When $g = 0.04396\ Z^2_{eff}/a_0{}^2$, the overlap between the Slater and Gaussian is maximal.) The integrals using the Slater orbitals were worked out by McConnell and Strathdee (21). The integrals using the Gaussians are given below. The values adopted are listed in Table 1; each represents a compromise of four calculated values.

$$\begin{aligned}
(a_i, h_d(j)_{xx}\, a_i) &= 8g^{3/2}\left[(-24/x^4 - 4/x^2)Q(x) + (12/x^5 - 2/x^3)P(x)\right] \\
(a_i, h_d(j)_{yy}\, a_i) &= 8g^{3/2}\left[(6/x^4)Q(x) + (-3/x^5 + 1/x^3)P(x)\right] \\
(a_i, h_d(j)_{zz}\, a_i) &= -\left[(a_i, h_d(j)_{xx}a_i) + (a_i, h_d(j)_{yy}a_i)\right] \qquad (96)
\end{aligned}$$

(These integrals are in units of $-g_e g_p |\beta| \beta_N$.)

where

$$
\begin{aligned}
a_i &= 2^{7/4} g^{5/4} \pi^{-3/4} z \exp(-g(\underset{\sim}{r}-\underset{\sim}{r}_i)^2) \\
\underset{\sim}{r}_i &= (R, 0, 0) \\
x &= 2\, g^{\frac{1}{2}} R \\
Q(x) &= (2\pi)^{-\frac{1}{2}} \exp(-\tfrac{1}{2}x^2) \\
P(x) &= \int_{-x}^{x} Q(r)\, dr
\end{aligned}
\qquad (97)
$$

The integrals $(a_i, \underset{\approx}{h}_d(j) a_k)$, $k \neq i$, were arbitrarily set equal to zero. It is argued elsewhere (25) that these integrals should be small. It might also be argued that they should be neglected to be consistent with the neglect of differential overlap in calculating the electronic wavefunction. Both these arguments are swindles. These integrals are neglected because we want to avoid the complication of keeping non-diagonal elements of the spin density matrix. This approximation might not be a very wise one.

In the pi-electron approximation, the spin density in the plane of the molecule is zero. The isotropic hyperfine coupling constants, Equation 20, would therefore appear to be zero, since the protons all lie in the molecular plane. Sigma-pi exchange interactions polarize the sigma electrons, however, and cause the spin density at each proton to be non-zero. The spin density at each proton is approximately proportional to the pi-electron spin density, ρ_{nn}, at the adjacent carbon atom, and hence the isotropic hyperfine coupling constant a_n is also proportional to ρ_{nn} (McConnell's relation (22)).

$$a_n = Q \rho_{nn} \tag{98}$$

Q is usually taken to be of the order of magnitude of -25 gauss. A more exact relation (23) expresses a_n as a linear combination of all the pi-electron atomic orbital spin density matrix elements ρ_{ij}. Although it is quite likely that a better approximation than Equation 98 is required to accurately predict the a_n for CHT, the McConnell relation is certainly the best first approximation. Unfortunately, it is impractical in CHT to try to go any further than Equation 98. $|Q|$ (see Section P) is found from the high temperature spectra of CHT in naphthalene to be 26.8 ± 1.0 gauss.

N. ON THE CALCULATION OF ENERGY LEVELS AND TRANSITION PROBABILITIES FROM THE SPIN HAMILTONIAN

The ESR spectra of CHT are determined by the 256x256 matrix of H_{sh}. If we let $\underset{\approx}{T}(ij)$ denote $(a_i, \underset{\approx}{h}_d(j) a_i)$, then from Equations 22, 98 and the considerations of Section M, H_{sh} is given by

$$H_{sh} = g|\beta| \underset{\sim}{S} \cdot \underset{\sim}{H} - \sum_j \left\{ g_p \beta_N \underset{\sim}{H} - \underset{\sim}{S} \cdot \sum_n \rho_{nn} \underset{\approx}{T}(nj) - Q\rho_{jj} \underset{\sim}{S} \right\} \cdot \underset{\sim}{I}_j \qquad (99)$$

With the exception of the g-factor, which may be taken as 2.003, and the exact value of Q, which is discussed in Section P, the numerical values of all the quantities appearing in Equation 99 have been discussed above. The procedure for obtaining the eigenvalues of H_{sh} will now be described. This procedure is essentially the method of McConnell, Heller, Cole and Fessenden (19).

Rather than find the eigenvalues of Equation 99 exactly, which would involve diagonalizing a 256x256 matrix, the eigenvalues and vectors are found to first order perturbation theory. The unperturbed Hamiltonian is just the electron Zeeman term, Equation 4, and its eigenvalues are $\pm \frac{1}{2} g|\beta| |\underset{\sim}{H}|$. The eigenfunctions all have the form ϕ ($S_H = \pm \frac{1}{2}$) multiplied by an arbitrary nuclear spin function. The zeroth order levels are both 128-fold degenerate. The hyperfine interaction removes this degeneracy, and in order to calculate the first order energies, one must diagonalize both 128x128 matrices of

$$H(\pm) = - \sum_j \left\{ g_p \beta_N \underset{\sim}{H} \mp \tfrac{1}{2} \underset{\sim}{e}_H \cdot \sum_n \rho_{nn} \underset{\approx}{T}(nj) \mp \tfrac{1}{2} \rho_{jj} Q \, \underset{\sim}{e}_H \right\} \cdot \underset{\sim}{I}_j \qquad (100)$$

where $$\underset{\sim}{e}_H = \underset{\sim}{H} / |\underset{\sim}{H}| \tag{101}$$

The eigenfunctions and eigenvalues of $H(\pm)$ may be written down by inspection, because $H(\pm)$ is the sum of one-proton terms,

$$H(\pm) = -\sum_j \underset{\sim}{h}(j,\pm) \cdot \underset{\sim}{I}_j$$

where $$\underset{\sim}{h}(j,\pm) = g_p \beta_N \underset{\sim}{H} \mp \tfrac{1}{2} \underset{\sim}{e}_H \cdot \sum_n \rho_{nn} \underset{\approx}{T}(nj) \mp \tfrac{1}{2} \rho_{jj} Q \, \underset{\sim}{e}_H \tag{102}$$

$\underset{\sim}{h}(j,\pm)$ is physically $g_p \beta_N$ times the effective magnetic field at proton j. Hence, the energy levels of the $S_H = \frac{1}{2}$ states are

$$E(+) = \sum_{j=1}^{7} (\pm) \left| \underset{\sim}{h}(j,+) \right| \tag{103}$$

and for the $S_H = -\frac{1}{2}$ states,

$$E(-) = \sum_{j=1}^{7} (\pm) \left| \underset{\sim}{h}(j,-) \right| \tag{104}$$

The hyperfine splittings are then

$$\Delta E = \sum_{j=1}^{7} (\pm) \left(\left| \underset{\sim}{h}(j,+) \right| \pm \left| \underset{\sim}{h}(j,-) \right| \right) \tag{105}$$

The wavefunctions are constructed from simple products of nuclear spin functions $\sigma_i(+)$ $(\sigma_i(-))$, which are eigenfunctions of the component of $\underset{\sim}{I}_i$ in the direction of $\underset{\sim}{h}(i,+)$ $(\underset{\sim}{h}(i,-))$, with eigenvalues $\pm\frac{1}{2}$.

$$\psi_\pm = \phi(\pm\tfrac{1}{2}) \sigma_1(\pm) \ldots\ldots \sigma_7(\pm) \tag{106}$$

The relative transition probability from a + to a - state is

$$\left| (\psi_+, S_+ \psi_-) \right|^2 = \prod_{i=1}^{7} \left| (\sigma_i(+), \sigma_i(-)) \right|^2 \tag{107}$$

If Θ is the angle between $\underset{\sim}{h}(i,+)$ and $\underset{\sim}{h}(i,-)$, and if $\sigma_i(+)$ and $\sigma_i(-)$ both have the same eigenvalues for the appropriate projections of $\underset{\sim}{I}_i$,

$$\left|(\sigma_i(+),\ \sigma_i(-))\right|^2 = \frac{1 + \cos\Theta}{2} \tag{108}$$

If their eigenvalues are opposite, then

$$\left|(\sigma_i(+),\ \sigma_i(-))\right|^2 = \frac{1 - \cos\Theta}{2} \tag{109}$$

O. CYCLOHEPTATRIENYL IN NAPHTHALENE

CHT was studied experimentally by Wood in several crystal hosts. In only one crystal host, however, could the orientation of the CHT molecule be regarded as even partially known. This host was naphthalene. Assuming that CHT replaces a naphthalene molecule substitutionally, the orientation of the CHT molecule is known, except for an angle Θ_{ro}, specifying the rotational orientation of the molecule about its seven-fold axis. An attempt was made to find the values of the experimental parameters Θ_{ro}, Θ_{om}, T_x, and Q for CHT in naphthalene.

The crystal structure of naphthalene was worked out by Abrahams, Robertson, and White (24). Naphthalene crystallizes according to the space group $P2_1/a$. The two molecules per unit cell are located at 000 and $\frac{1}{2}\frac{1}{2}0$, and are related by a two-fold screw axis. A diagram of the unit cell from (24) is reproduced in Figure 1.

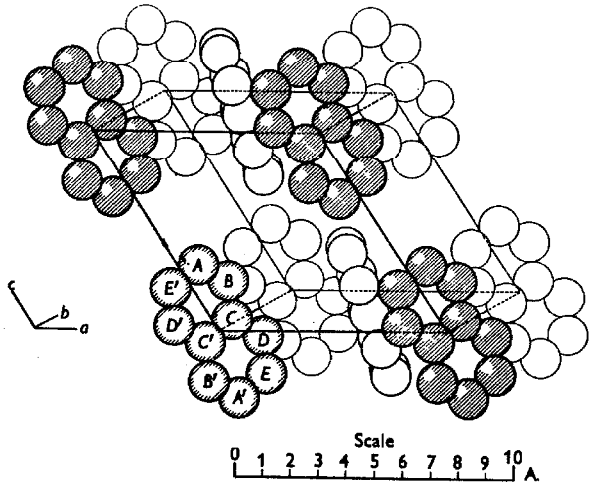


Figure 1: Molecular arrangement in the unit cell of naphthalene; taken from Robertson (24).

It is not difficult to see that the two molecules are magnetically equivalent when the magnetic field is in the AC-plane or parallel to the B-axis. Accordingly, low temperature spectra were taken with the magnetic field in the AC-plane so as to eliminate the complications of the g-factor anisotropy.

A Fortran-MAP program was written for an IBM 7090 computer to calculate derivative spectra for CHT in naphthalene. Both Gaussian and Lorentzian line shapes were tried, and the computed spectra were graphically represented by a Mosley-Plotter connected to the 7090 by a 7040 computer. For an overall picture of what values were assigned to the various theoretical and semi-theoretical parameters, see Table 1.

There are a number of reasons, both theoretical and experimental, why the calculations should fail to give exact agreement with experiment:

Theoretical Achilles' Heels:

Malonic acid radical values for the CHT anisotropic tensor may be very poor because the CHT carbon are not sp^2.

The theoretically estimated hyperfine tensor values might not be close enough to the experimental values, and the neglect of the overlap contributions might be bad.

The simple relation $a_n = Q \rho_{nn}$ may be too simple.

TABLE 1. NUMEROLOGY

Quantity	Value	Comment
$(a_j, \underset{\approx}{h}_d(i) a_j)$ $j = i$	11.0 gauss -11.8 gauss 0.8 gauss	x-principal value Cole (20) y-principal value z-principal value
$j = i+1$	4.7 gauss - 2.7 gauss - 2.0 gauss	These values are in x-y-z order. x refers to the C_j-H_i direction, z to the direction of the lobes of the p-orbitals, and y the mutually perpendicular direction. Values are the average of integrations of Slaters (3.18, 3.25) and Gaussians (0.445, 0.464 Bohr radii^{-2}). They are independent of i.
$j = i+2$	1.27 gauss - 0.66 gauss - 0.61 gauss	
$j = i+3$	0.712 gauss -0.366 gauss -0.346 gauss	
C-C C-H	1.40 Å 1.09 Å	Aromatic carbon-carbon distance and carbon-hydrogen distance; Pauling (33).
Q Δ (max. to min. line width)	-26.8 gauss 1.7 gauss 2.4 gauss	Best fit for high temperature spectra in naphthalene. Rough fit for low temperature spectra.
$\dfrac{g_p \beta_N \lvert\underset{\sim}{H}\rvert}{g_e \lvert\beta\rvert}$	5.23 gauss	Experimental electron Larmor frequency was 9.6 kmc/s.
(N_o, N_o)	$\sim$0.8	Nuclear vibration matrix element, estimated by method of McConnell and McLachlan (17).
θ_{om} θ_{ro}		Orbital mixing and rotational orientation parameters to be determined from low temperature experiments.
T_x		Theory indexing parameter, to be determined from experiment.
$T_x/(N_o, N_o)$	1.0 1.343 1.65 3.2377	Theoretical predictions: SHMO; approximate UHF-LCAO-MO; Pariser-Parr; VB.

The derivative spectra, being a complicated superposition of 128 (or a multiple of 128) overlapping lines, might be a fairly sensitive function of the line shape function assigned to the individual lines.

Experimental Uncertainties:

The low temperature spectra are slightly saturated, which tends to destroy the structure in the center of the spectra.

The crystal may be misoriented by as much as 5 degrees.

The CHT might not replace the naphthalene in a strictly coplanar fashion.

The crystal might be disordered or distorted by the presence of the CHT.

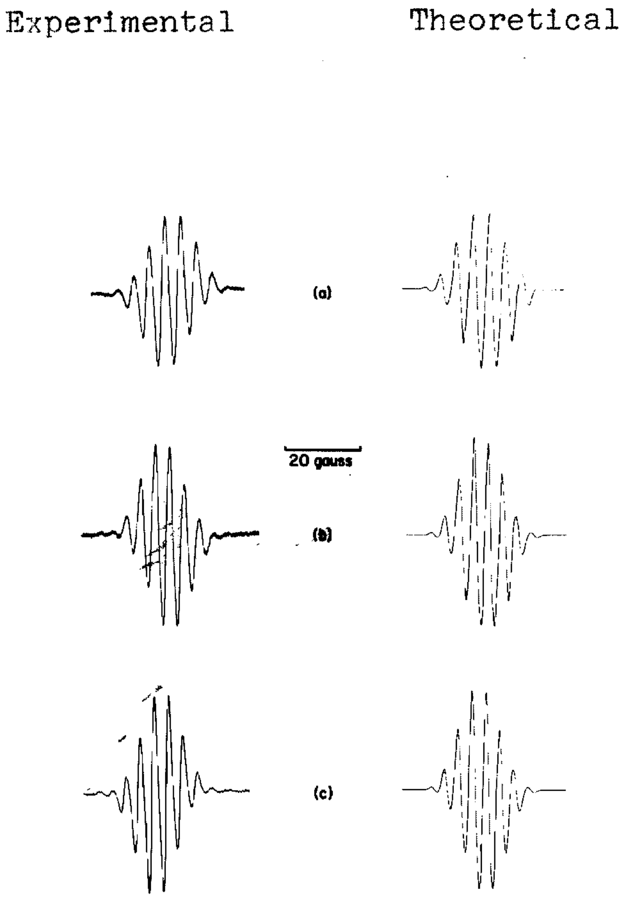
The unit cell dimensions might change appreciably at the very low temperatures of the experiments.

P. HIGH TEMPERATURE SPECTRA IN NAPHTHALENE

The high temperature CHT ESR spectra observed by Wood were briefly described in Section A. The similarity of the eight-line spectra to the solution spectra of CHT (26) suggests that rotation may play a part in averaging out the anisotropic hyperfine interaction. Since the average value of the in-plane principal values of the malonic acid radical anisotropic hyperfine tensor is -0.4 gauss (20), rotation evidently need take place only about the seven-fold axis. In Section L, it was shown that this type of rotation also averaged the spin densities to 1/7. More carefully, one must average the product of the spin densities and the anisotropic hyperfine interaction. Within the framework of the model of Section L (concerning the form of the crystal field), the average of the product is the product of the averages.

The values used for the various interaction constants in computing the high temperature spectra are listed in Table 1, except that the values for the x- and y-components of the hyperfine tensors were replaced by their averages. The spin densities were all taken as 1/7. Q and the linewidth were varied, and both Gaussian and Lorentzian lineshapes were tried. Since the best experimental measurements can be made on the center four lines, only the center four lines were used in comparison of experimental and theoretical spectra. The best results were obtained with Q = -26.8 gauss, distance between points of maximum and minimum slopes = 1.7 gauss, Gaussian line shape. The experimental and theoretical spectra for the magnetic field along the A, B and C* axes of naphthalene are compared in Figure 2 and Table 2. All measurements of experimental and theoretical spectra were made on maxima and minima of the derivative spectra.

High temperature in naphthalene means over 20° K. At 20° K, the drastic change in the ESR spectra is interpreted to mean that the molecule no longer rotates with a frequency greater than 10^7 radians/sec. The temperature of transition from high to low temperature spectra is taken as a measure of the rotational barrier (Section L). The crystal field splitting cannot be obtained from the transition temperature, but a bound on the magnitude of the variation of the crystal field splitting as a function of θ_{ro} can. Furthermore, the transition temperature places an experimental bound on the energy of a Jahn-Teller or out-of-plane distortion, because such a distortion, (even if smaller than the crystal field splitting) would have to be overcome for the molecule to rotate. On the basis of the naphthalene experiments alone, this bound is about 100 cm^{-1} (Sections A and L). The cycloheptatriene and argon experiments suggest that this bound might be an order of magnitude smaller, but in any event, to claim a static distortion of even 100 cm^{-1} would indicate a gross misunderstanding of the Jahn-Teller effect and the Born-Oppenheimer approximation.



Experimental Theoretical

Figure 2. High temperature CHT ESR spectra in naphthalene.

a) Magnetic field along A-axis;

b) B-axis;

c) C*-axis.

TABLE 2

Comparison of experimental and theoretical high temperature CHT ESR spectra in naphthalene

For theoretical spectra, Q =-26.8 gauss, Δ = 1.7 gauss, and the line shape is Gaussian.

	Hyperfine Splitting (Gauss)	
Orientation of magnetic field	Experimental	Theoretical
A-axis	4.1	4.2
B-axis	3.7+	3.7
C*-axis	3.7-	3.6

Q. LOW TEMPERATURE SPECTRA IN NAPHTHALENE

The agreement of theory with experiment for the high temperature spectra in naphthalene is quite good. At low temperatures, both the experimental and theoretical spectra are more complicated. The experimental spectra display a large anisotropy and much poorer resolution. The cessation of rotation restores the dependence of the spin Hamiltonian on Θ_{om}, Θ_{ro}, and T_x.

Theoretical spectra were computed, varying these three parameters and using the values for the other parameters listed in Table 1. Gaussian line shape and $\acute{Q}$ of -26.8 were taken from the high temperature analysis. The following statements summarize the results of the attempt to match the low temperature spectra by a judicious choice of values for Θ_{om}, Θ_{ro} and T_x.

(a) In general, given any orientation of the magnetic field (in the AC-plane), a triple of values could be found for which the calculated spectra agreed quite well with the experimental spectra. Three examples are displayed in Figure 3.

(b) In general, the triple of values associated with one direction of the magnetic field was different from that associated with another direction.

(c) The average spread of the low temperature spectra is 28-29 gauss (3). This indicates that T_x should be in the range 1.25 to 1.55.

(d) In Figure 3, three computed spectra for a compromise set of values are displayed.

In view of the experimental and theoretical shortcomings listed in Section 0, the results are as good as could be hoped for. Θ_{om} and Θ_{ro} could not be evaluated in a way that would give agreement for all orientations of H, but that any given spectrum could be matched by a pair of values for these parameters merely indicates that some of the errors listed in Section 0 could be compensated for by adjusting these parameters. In this respect, it is important to note that the general trend of the spectra could be accounted for by a single set of values (see Figure 3). Furthermore, the limits on the values of T_x indicate that both the UHF and Pariser-Parr theories (with vibronic coupling) give the best predictions of the spin densities. This is in accord with the qualitative idea that the SHMO theory underestimates electron correlation, that the VB theory overestimates correlation, and that the UHF and Pariser-Parr theories lie in between. T_x is properly, of course, a measure of spin- (or exchange-) correlation (10), not of the *entire coulomb correlation.*

There are three relations between Θ_{om} and Θ_{ro} which slightly simplify the calculations. The spectra are invariant to

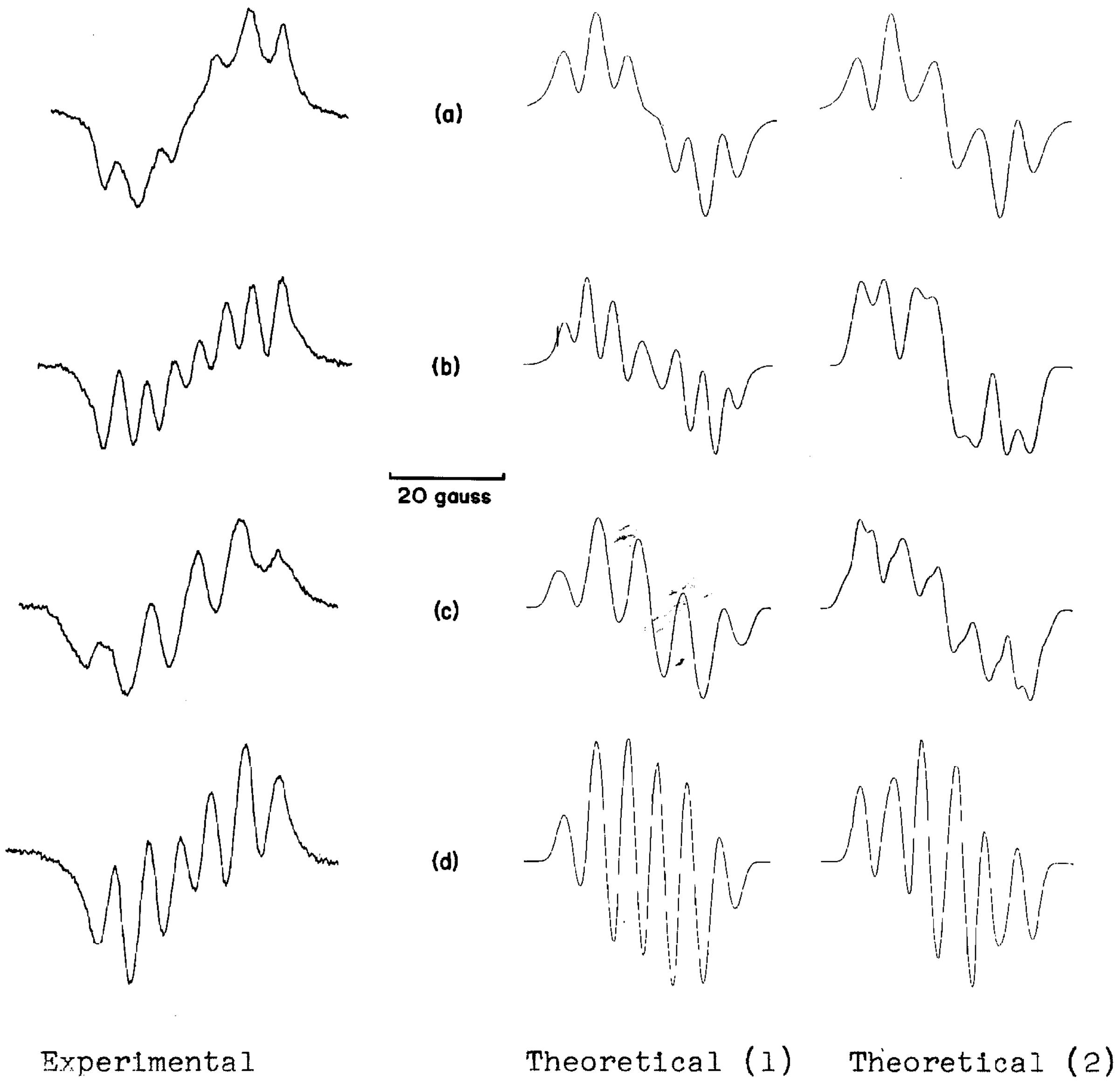


Figure 3. Low Temperature CHT ESR spectra in napthalene. Magnetic field is (a) parallel to A-axis; (b) 70° from A, -20° from C*; (c) 108° from A, 18° from C*; (d) 160° from A, 70° from C*. Theoretical (1): (θ_{om}, θ_{ro}, T_x) =

(a) (0.2244, 0.75, 1.35) (1.122, 2.767, 1.35)
(b) (0.045, 0.67, 1.30) or (1.301, 0.377, 1.30)
(c) (0.26, 2.15, 1.35) (1.086, 2.72 , 1.35)
(d) (0.60, 0.94, 1.30) (0.746, 1.79, 1.30)

Theoretical (2): (0.21, 0.34, 1.4)

Line shape: (a) Lorentzian, (b)-(d) Gaussian

$$\begin{aligned} \theta_{om}, \theta_{ro} \longrightarrow\ & \theta_{om} && , \theta_{ro} + \pi \\ & \theta_{om} + \pi/7 && , \theta_{ro} + 4\pi/7 \\ & -\theta_{om} && , 2\theta_{ro}(0) - \theta_{ro} \end{aligned}$$

θ_{ro} (0) is the angle the long-axis of the naphthalene molecule makes with the projection of the magnetic field onto the molecular plane. In particular, one can restrict the ranges of θ_{om} and θ_{ro} to $0 \leq \theta_{om} < \pi/7$, $0 \leq \theta_{ro} < \pi$.

R. THE SPIN-ORBIT COUPLING AND THE G-TENSOR

In most pi-electron, hydrocarbon radicals, the g-tensor is very nearly isotropic, with the average principal value close to the free electron value 2.0023. In general the principal value of the g-tensor for the direction perpendicular to the ring, g_{zz}, is closest to the free electron value, while the other two principal values are somewhat larger (27). The deviations are caused by the spin-orbit interaction through virtual sigma-pi and pi-sigma* excitations (27, 28). Pi-pi* excitations, which affect g_{zz} only, are usually unimportant because of the small value of the pi-electron spin-orbit matrix element (29).

The low lying, excited pi state of CHT changes the above considerations, because the smallness of the excitation energy compensates for the smallness of the spin-orbit matrix element. The contribution to g_{zz} will be estimated using SHMO theory.

The SHMO wavefunction is given by Equations 38 and 39. Denote the orbital of the odd electron, $M_{\theta_{om}}$, by ϕ_1, and the entire wavefunction by Φ_1. The lowest excited state, Φ_u is obtained from Φ_1 by replacing ϕ_1 with ϕ_u.

$$\phi_u = -i\, 2^{-\frac{1}{2}} \left(M_2 \exp(+i\theta_{om}) - M_{-2} \exp(-i\theta_{om}) \right) \qquad (110)$$

The energy separation, $e_u - e_1 = \Delta E$, is the crystal field splitting.

The spin orbit interaction is given by (4)

$$H_{so} = (2\beta^2/e)\, \underset{\sim}{\xi}_i \times \underset{\sim}{p}_i \cdot \underset{\sim}{s}_i \qquad (111)$$

where $\underset{\sim}{\xi}_i$ is the total electric field acting on electron i. For simplicity, $\underset{\sim}{\xi}_i$ can be approximated (29) by

$$\underset{\sim}{\xi}_i = \sum_{\text{carbon nuclei } k} Z_k e\, \underset{\sim}{r}_{ik}/r_{ik}^3 \qquad (112)$$

The effective nuclear charge Z_k is given a value between 6 (no screening) and 1 (complete screening).

The contribution to the g-tensor of the spin-orbit interaction is easily derivable from the appropriate term in the second order perturbation theory correction to the energy, $\frac{-2}{\Delta E} (\phi_1, H_{so}\phi_u)\, (\phi_u, \underset{\sim}{L} \cdot \underset{\sim}{H}\phi_1)$. Combined with Equation 112, the contribution to g_{zz} is

$$\Delta g_{zz} = (-2/\Delta E)(\phi_1, 2\beta^2 \sum_k Z_k [(\underset{\sim}{r}_{ik}/r_{ik}^3) \times \underset{\sim}{p}_i]_z \phi_u) \cdot (\phi_u, l_z\, \phi_1) \qquad (113)$$

The second matrix element can be worked out using Slater $2p_z$ orbitals, and has the approximate value 1. The first matrix element can be evaluated approximately, and is about 1 cm^{-1}.

It is well known, however, that the Hückel theory overestimates l_z matrix elements. The equivalent VB calculation, with the neglect of overlap, gives zero. It is therefore reasonable that the l_z matrix element might be an order of magnitude smaller, say 0.1.

The spin-orbit matrix element has been estimated by at least one author (30) to be as high as 5 cm^{-1}. It is certainly in the range 0.5 - 5 cm^{-1}.

Apart from the uncertainties in estimating the above matrix elements, the above discussion must be modified to include the effects of vibronic coupling (Section I). According to Equations 80 and 81, the above matrix elements should be reduced by the factor $(N_0, N_0) - (N_4, N_4)$, (0.2 to 0.6), and the crystal field splitting by (N_0, N_0) (~0.8). Hence the conservative theoretical estimate for Δg_{zz} is

$$-5/\Delta E \leq \Delta g_{zz} \leq 0.005/\Delta E(cm^{-1}) \qquad (114)$$

A quantitative, purely theoretical estimate of g_{zz} appears to be impossible. Qualitatively, it has been shown that the pi-pi contribution to g_{zz} is negative, inversely proportional to the crystal field splitting, and that vibronic coupling tends to reduce the contribution. Since ΔE is estimated to be of the order of 30 cm^{-1} or less for appropriate crystals (Section K), even the most pessimistic value in Equation 114 is measurable. Even more important, since the crystal field can be easily varied, changes in the value of g_{zz} are a measure of the strength of the crystal field.

Experimentally, measurement of the g-tensor at low temperatures is very difficult. Wood (3) was able to obtain measurements for polycrystalline samples of CHT in thiourea and in cycloheptatriene that are of interest here. The polycrystalline g-values represent an average of the x, y and z values, and were 2.0023 ± 0.0002 for thiourea, and 1.9985 ± 0.0015 for cycloheptatriene. Only g_{zz} is expected to be less than 2.0023.

These average values indicate that g_{zz} is less than 2.0023 for CHT in thiourea, and considerably less than 2.0023 for CHT in cycloheptatriene. This indicates that the crystal field splitting in thiourea is greater than in cycloheptatriene, which is in accord with the more polar nature of thiourea. It is also compatible with the higher transition temperature, 40° K, in thiourea, vs. 13° K in cycloheptatriene.

If the crystal field splitting in cycloheptatriene is as low as 10 cm^{-1}, then the product of the spin orbit and angular momentum matrix elements would be $> 10^{-2}$ cm^{-1}. If it is as large as 100 cm^{-1}, the product would be $> 10^{-1}$ cm^{-1}.

S. SPIN-LATTICE RELAXATION IN THE HIGH TEMPERATURE FORM OF CHT

Wood and McConnell (3) have noticed that the ESR spectra of the high temperature form of CHT are more difficult to saturate than the ESR spectra of ordinary aromatic hydrocarbon radicals. This enhanced spin-lattice relaxation has also been observed in other presumably degenerate systems (31). McConnell has suggested that the short spin-lattice relaxation time T_1 in solutions is caused by a magnetic pulse - effect of the spin-orbit interaction when the molecule, because of fluctuations in its environment, passes through a degenerate state. McConnell and McLachlan (17) also investigated the possibility of relaxation occurring through the hyperfine interaction and the sloshing around of the spin densities, but they found that the hyperfine interaction was too weak to account for the short T_1.

In Section L a model was developed for the rotational interaction of the lattice and the CHT molecule. This model will now be used to derive the spin-orbit induced spin-lattice relaxation in CHT.

The spin-orbit interaction, Equations 111, 112, may be treated as a perturbation on the Hamiltonian of Equation 91. If at time t = 0, the wavefunction Ψ is equal to $\Psi_L \alpha$ where the spin function α is an eigenfunction of S_x, then at time t the coefficients of $\Psi_L \beta$ and $\Psi_U \beta$ are approximated by

$$(i\Lambda\omega / 4\Omega^2) \cos 2\Omega t \qquad (115)$$

$$(-i\Lambda / 4\Omega) (\sin 2\Omega t - (\Delta E/\hbar\Omega)\cos 2\Omega t) \qquad (116)$$

Both coefficients are sinusoidal with angular frequency 2Ω. The average probability of finding the spin flipped is of the order of $\frac{1}{4}\Lambda^2/\Omega^2$, where Λ is essentially the spin-orbit matrix element. Suppose after a time T the CHT molecule is subjected to a process in which the phases of the different instantaneous eigenfunctions of the Hamiltonian are destroyed. Such a process might be a "collision" with the lattice, in which either the crystal field or the rotation were suddenly changed and might be viewed as a measurement by the crystal lattice of the state of the molecule. The probability of finding the molecule in a state with its spin flipped is of the order of $1/4\,\Lambda^2/\Omega^2$ and would lead to a T_1 of the order of $\sim (4\Omega^2/\Lambda^2)\,T$.

If one uses the values $T_1 = 10^{-7}$ sec, $\Lambda = .5$ cm^{-1}, $\Omega = 30$ cm^{-1} then $T \sim 10^{-11}$ sec, which is not an unreasonable value. Since there is no simple way of estimating T, the most that can be said is that (once again) the spin-orbit interaction <u>can</u> be responsible for the enhanced spin-lattice relaxation.

A way to test experimentally the hypothesis that the spin-orbit interaction is responsible for the spin-lattice relaxation, is to measure the anisotropy of the relaxation time. When the magnetic field is perpendicular to the plane of the molecule, the vanishing of the pi-electron spin-orbit matrix elements eliminates the special mechanism for relaxation.

SUMMARY AND CONCLUSIONS

The ESR spectra of CHT provide overwhelming evidence that the ground state of CHT in the absence of a crystal field would be orbitally degenerate. This degeneracy is required for the quantitative interpretation of the high temperature spectra, and for the magnitude and direction of the variations in the low temperature g-factors. Degeneracy is required to explain why the crystal lattice has a large effect on the nature of the low temperature hyperfine structure, and it is an implicit feature of the approximate UHF-LCAO-MO and Pariser-Parr theories which provide a semi-quantitative explanation of the low temperature spectra in naphthalene.

Degeneracy in turn requires that the molecule have the symmetry of a regular heptagon.

The static Jahn-Teller effect in CHT is shown not to exist, and the theoretical modifications required by the breakdown of the Born-Oppenheimer approximation are shown to affect primarily the values of the matrix elements of the spin-orbit coupling and the angular momentum.

Degeneracy also plays an implicit role in the spin-orbit induced spin-lattice relaxation mechanism.

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PROPOSITION I

THE ELECTRON SPIN-SPIN INTERACTION IN EXCITED STATES OF MOLECULES AND THE SPIN-HAMILTONIAN

Abstract

It is shown that the spin-Hamiltonian $D(S_z^2 - \frac{1}{3}\mathbf{S}^2) + E(S_x^2 - S_y^2)$ can be used to represent the electron spin-spin interaction within the $2S + 1$ - dimensional space of an arbitrary spin multiplet of spin S.

. . . .

The electron spin-spin interaction (H_d) is given by

$$H_d = \sum_{i<j} g^2 \beta^2 r_{ij}^{-5} \left(\mathbf{s}_i \cdot \mathbf{s}_j \, r_{ij}^2 - 3(\mathbf{s}_i \cdot \mathbf{r}_{ij})(\mathbf{s}_j \cdot \mathbf{r}_{ij}) \right) \qquad (1)$$

where

$\hbar \mathbf{s}_i$ = spin angular momentum operator for electron i.

$\mathbf{r}_i$ = position vector of electron i.

$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$

$r_{ij} = |\mathbf{r}_{ij}|$

g = free-electron g-factor

β = Bohr magneton

The spin-spin interaction was first studied in molecules by Hutchison and Mangum (1) in 1958 in their classic experiment on the electron spin resonance of the lowest triplet state naphthalene. Since 1958, various other triplet systems have been investigated by ESR (2). For triplet states it is easy to show (3) that H_d can be replaced by the "spin-Hamiltonian" (H)

$$H = D(S_z^2 - \frac{1}{3}\underset{\sim}{S}^2) + E(S_x^2 - S_y^2); \qquad (2)$$

that is, for a special choice of coordinate axes xyz, and for appropriately chosen constants D, E, the 3x3 matrices of H_d and H are identical. The simple form of Equation 2 greatly simplifies the interpretation of experiments, and D and E can often be measured quite accurately.

Recently the cycloheptatrienyl radical (4) and various substituted carbenes (5) and nitrenes (5) have been prepared in crystals and glasses. The ground state of cycloheptatrienyl is a Kramers doublet and the ground states of the carbenes and nitrenes are triplets. It is quite likely that the lowest quartet and quintet states of these systems will soon be studied by ESR. The question then arises, "can a spin-Hamiltonian of the form (2) be used to represent H_d for multiplets with spin greater than one?" The answer is usually affirmative* and will be considered in detail below.

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*In a recent paper, A.D. McLachlan, Mol. Phys. 6, 441 (1963) has derived the D, E Hamiltonian by using the Wigner-Eckart theorem. The present derivation was first discovered when the author was a first-year graduate student and, at the risk of being redundant, is repeated here for its pedagogical value.

Formulation of the Problem

The $2S + 1$ states of a multiplet having total spin S will be denoted by $|SM)$, $M = S, S-1, \ldots, -S$. $\underset{\sim}{S}, S_z, S_{\pm} = S_x \pm iS_y$ denote the usual total electron spin operators; e.g., $S_x = \sum_{i=1}^{N} s_{ix}$, where the total number of electrons is N.

The $|SM)$ satisfy

$$
\begin{aligned}
\underset{\sim}{S}^2 \; |SM) &\pm S(S+1) \; |SM) \\
S_z \; |SM) &= M \; |SM) \qquad\qquad (3) \\
S_+ \; |SM) &= \sqrt{S(S+1)-M(M+1)} \; |S\, M+1)
\end{aligned}
$$

Define

$$D = 3\,(2S^2 - S)^{-1}\,(SS|\,H_d\,|SS) \qquad (4)$$

$$E = [S(2S-1)]^{-1}\,(SS|\,H_d\,|S\,S-2) \qquad (5)$$

We assert that we can choose the coordinate axes xyz so that the $(2S+1) \times (2S+1)$ matrices of H_d and

$$H = D\,(S_z^2 - \tfrac{1}{3}\underset{\sim}{S}^2) + E\,(S_x^2 - S_y^2)$$

are identical. H_d and $(S_x^2 - S_y^2)$ are Hermitian, but according to Equation (5) E is not _a priori_ real. It will also be shown that in this coordinate system E is real.

Proof of the Assertion

The assertion is proved by taking advantage of relations among the spin operators, and of the relations (3) among the $|SM)$. The important relations among the spin operators are

$$\begin{aligned}
&[\underset{\sim}{s}_i, \underset{\sim}{s}_j] = 0 \\
&[s_{iz}, s_{i\pm}] = \pm s_{i\pm} \\
&[s_{i+}, s_{i-}] = 2s_{iz} \qquad\qquad (6) \\
&s_{iz}s_{i\pm} + s_{i\pm}s_{iz} = 0 \\
&P^{\sigma}_{ij} = \text{operator which permutes spin coordinates of electrons } i,j \\
&\underset{\sim}{s}_i \cdot \underset{\sim}{s}_j = \tfrac{1}{2}P^{\sigma}_{ij} - \tfrac{1}{4}
\end{aligned}$$

It will be convenient to define

$$x_{ij\pm} = x_{ij} \pm i\, y_{ij} \qquad (7)$$

Using (1), (6) and (7), H_d can be decomposed into the following sum:

$$H_d = H_{2+} + H_{2-} + H_{1+} + H_{1-} + H_0 \qquad (8)$$

$$H_{2\pm} = -(3/8)\, g^2\beta^2 \sum_{i<j} r_{ij}^{-5}\, x_{ij\mp}^2\, (s_{i\pm} + s_{j\pm})^2 \qquad (8_2)$$

$$H_{1\pm} = -(3/4)\, g^2\beta^2 \sum_{i<j} r_{ij}^{-5} z_{ij} x_{ij\mp} \{(s_{iz}+s_{jz})(s_{i\pm}+s_{j\pm}) + (s_{i\pm}+s_{j\pm})(s_{iz}+s_{jz})\} \qquad (8_1)$$

$$H_0 = (3/4)\, g^2\beta^2 \sum_{i<j} r_{ij}^{-5}(r_{ij}^2-3z_{ij}^2)\{(s_{iz}+s_{jz})^2 - (1/3)(\underset{\sim}{s}_i+\underset{\sim}{s}_j)^2\} \qquad (8_0)$$

The decomposition (8) simplifies the computation of the matrix of H_d:

$$\begin{aligned}
(SM|\, H_d \,|SM') &= 0, & |M-M'| &> 2 \\
&= (SM|\, H_{2\pm} \,|SM'), & |M-M'| &= 2 \\
&= (SM|\, H_{1\pm} \,|SM'), & |M-M'| &= 1 \qquad (9) \\
&= (SM|\, H_0 \,|SM'), & M-M' &= 0
\end{aligned}$$

(a) $\triangle M = 2$ elements

$$
\begin{aligned}
&(SM + 2 \,|\, H_{2+} \,|\, SM) \\
&\quad = (S\ M{+}2 \,|\, H_{2+}\, S_{+} \,|\, S\ M{-}1)/(S(S+1)-(M-1)M)^{\frac{1}{2}} \\
&\quad = (S\ M{+}2 \,|\, S_{+}\, H_{2+} \,|\, S\ M{-}1)/(S(S+1)-(M-1)M)^{\frac{1}{2}} \\
&\quad = \sqrt{\frac{S(S+1)-(M+1)(M+2)}{S(S+1)-(M-1)M}}\ (S\ M{+}1 \,|\, H_{2+} \,|\, S\ M{-}1)
\end{aligned}
\tag{10}
$$

since $[H_{2+}, S_{+}] = 0$. But

$$
(S\ M{+}2 \,|\, S_{+}^{2} \,|\, S\ M) = \sqrt{\frac{S(S+1)-(M+1)(M+2)}{S(S+1)-(M-1)M}}\ (S\ M{+}1 \,|\, S_{+}^{2} \,|\, S\ M{-}1) \tag{11}
$$

From (10) and (11),

$$
H_{2+} = \tfrac{1}{2}[S(2S-1)]^{-\frac{1}{2}}\ (SS \,|\, H_{d} \,|\, SS{-}2)\ S_{+}^{2} \tag{12}
$$

The Hermitian conjugate of H_{2+}, $H_{2+}^{\dagger} = H_{2-}$. Hence,

$$
H_{2+} + H_{2-} = [4S(2S-1)]^{-\frac{1}{2}}\ (SS|H_{d}|SS{-}2)S_{+}^{2} + (SS{-}2|H_{d}|SS)S_{-}^{2} \tag{13}
$$

(b) $\triangle M = 1$ elements.

First we shall show that

$$
(SM \,|\, H_{d} \,|\, S\ M{-}1) = \frac{2M-1}{2S-1}\sqrt{\frac{S(S+1)-(M-1)M}{2S}}\ (SS \,|\, H_{d} \,|\, S\ S{-}1) \tag{14}
$$

This is trivially so for $M = S$. We assume (14) holds for $M = m + 1$ and establish its truth for $M = m$.

$$
\begin{aligned}
(Sm \,|\, H_{1+} \,|\, S\ m{-}1) &= [S(S+1)-m(m+1)]^{-\frac{1}{2}}\ (Sm{+}1 \,|\, S_{+}\, H_{1+} \,|\, S\ m{-}1) \\
&= \sqrt{\frac{S(S+1)-(m-1)m}{S(S+1)-m(m+1)}}\ (S\ m{+}1 \,|\, H_{1+} \,|\, S\ m) \\
&\quad + (S(S+1)-m(m+1))^{-\frac{1}{2}}(3/4)g^{2}\beta^{2}\sum_{i<j}(S\ m{+}1 \,| \\
&\quad\ r_{ij}^{-5} z_{ij} x_{ij-}{}^{2}(s_{i+}+s_{j+})^{2} \,|\, S\ m{-}1)
\end{aligned}
$$

In the second term (8_1) has been substituted for H_{1+} and the commutator with S_+ taken. Substituting (14) into the first term, noting that $\left[(s_{i+} + s_{j+}), S_+\right] = 0$, and using (3) repeatedly, the above expression becomes

$$(Sm|\, H_{1+} \,|S\ m-1)$$

$$= \frac{2m+1}{2S-1}\sqrt{\frac{S(S+1)-(m-1)m}{2S}}\ (SS\,|\,H_d\,|\,S\ S-1)$$

$$+\frac{\sqrt{S(S+1)-(m-1)m}\quad (3/4)g^2\beta^2 \sum_{i<j}}{\sqrt{S(S+1)-(S-1)S}\sqrt{S(S+1)-(S-2)(S-1)}}\,(SS|\,r_{ij}^{-5} z_{ij}\, x_{ij} - 2\,(s_{i+}+s_{j+})^2\,|SS-2)$$

Using $|S\ S-2) = (4S-2)^{-\frac{1}{2}}\ S_-|S\ S-1)$, $(SS|\,S_- = 0$ and $\left[(s_{i+}+s_{j+})^2, S_-\right] = 2\left\{(s_{i+}+s_{j+})(s_{iz}+s_{jz})+(s_{iz}+s_{jz})(s_{i+}+s_{j+})\right\}$, we find that

$$(Sm\,|\,H_{1+}\,|\,S\ m-1) = \frac{2m-1}{2S-1}\sqrt{\frac{S(S+1)-(m-1)m}{2S}}\ (SS\,|\,H_d|S\ S-1)$$

which establishes (14). Moreover,

$$(SM\,|\,(S_+S_z + S_zS_+)\,|S\ M-1) = (2M-1)\sqrt{S(S+1)-(M-1)M}$$

which taken with (14) gives

$$H_{1+} = \frac{(SS\,|\,H_d\,|\,S\ S-1)}{(2S-1)\sqrt{2S}}\,(S_zS_+ + S_+S_z)$$

and

$$H_{1+} + H_{1-} = \left[(2S-1)\sqrt{2S}\right]^{-1}\left\{(SS|\,H_d|SS-1)(S_zS_++S_+S_z) + (SS-1\,|H_d|\,SS)(S_zS_-+S_-S_z)\right\} \qquad (15)$$

(c) $\Delta M = 0$ elements.

We shall show that

$$(SM|H_d|SM) = 3(2S^2-S)^{-1}\ (SS|H_d|SS)(M^2 - S(S+1)/3) \qquad (16)$$

This is trivially true for $M = S$. Assuming (16) is true for $M = m + 1$, we consider $M = m$:

$$(Sm|H_d|Sm) = (S\ m+1|\,H_d\,|Sm+1)+\left\{S(S+1)-m(m+1)\right\}^{-\frac{1}{2}}(Sm+1\,|\left[S_+, H_0\right]|\,Sm)$$

Substituting (8_0) for H_o and evaluating the commutator,

$$(Sm|H_d|\,Sm) = (Sm+1|\,H_d\,|Sm+1) + \left\{S(S+1)-m(m+1)\right\}^{-\frac{1}{2}}(-3/4)g^2\beta^2 \sum_{i<j}$$

$$(Sm+1\,|\,r_{ij}^{-5}(r_{ij}^{2}-3z_{ij}^{2})\left\{(s_{i+}+s_{j+})(s_{iz}+s_{jz})+(s_{iz}+s_{jz})(s_{i+}+s_{j+})\right\}|\,Sm)$$

By the proof of Equation (14), we can simplify the second term above:

$$(Sm|H_d|Sm) = (Sm{+}1|H_d|Sm{+}1) - (3/4)g^2\beta^2 \frac{2M+1}{2S-1}\frac{1}{\sqrt{2S}} \sum_{i<j}$$

$$(SS|r_{ij}^{-5}(r_{ij}^2-3z_{ij}^2)\{(s_{i+}+s_{j+})(s_{iz}+s_{jz})+(s_{iz}+s_{jz})(s_{i+}+s_{j+})\}|SS-1)$$

Using

$S_-|SS) = \sqrt{2S}|SS-1)$, $(SS\ |S_- = 0$, $[(s_{i+}+s_{j+})(s_{iz}+s_{jz})+(s_{iz}+s_{jz})(s_{i+}+s_{j+}),\ S_-] = 6\{(s_{iz}+s_{jz})^2-(\underset{\sim}{s}_i+\underset{\sim}{s}_j)^2/3\}$, and substituting Equation 16 into the first term, $(Sm|H_d|Sm) =$

$$3\,(2S^2-S)^{-1}(SS|H_d|SS)\{m^2-S(S+1)/3\}$$

establishing (16).

Clearly $H_0 = 3\,(2S^2-S)^{-1}\,(SS|H_d|SS)\,(S_z^2 - \underset{\sim}{S}^2/3)$ (17)

(d) From Equations (8), (13), (15), and (17)

$$H_d = aS_x^2+bS_y^2+cS_z^2+d(S_xS_y+S_yS_x)+e(S_xS_z+S_zS_x)+f(S_yS_z+S_zS_y)+g$$

where a, b, c, d, e, f, g, are real numbers. H_d is a symmetric quadratic form in the total spin operators. $\underset{\sim}{S}$ transforms as a vector under rotations. By elementary algebra, there is a rotated coordinate system XYZ in which the coefficients of the cross terms vanish, and H_d has the form

$$H_d = A\,S_x^2 + B\,S_y^2 + C\,S_z^2 + g$$

Now let us suppose that the $|SM)$ are the states quantized along the Z-axis in the special coordinate system. No XZ or YZ terms occur $\Rightarrow$

$$H_{1+} + H_{1-} = 0$$

No $S_xS_y + S_yS_x$ term $\Rightarrow$

$(SS|H_d|SS-2)$ is real ,

Consequently, in this coordinate system,

$$H = 3\,(2S^2 - S)^{-1}\,(SS|H_d|SS)\,(S_z^2 - \underset{\sim}{S}^2/3) + (2S^2 - S)^{-\frac{1}{2}}\,(SS|H_d|SS-2)\,(S_x^2 - S_y^2)$$

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PROPOSITION II

A NOTE ON THE CALCULATION OF MATRIX ELEMENTS OF THE TWO-ELECTRON SPIN-ORBIT TERMS OF THE HAMILTONIAN

Abstract

It is shown that calculated two-electron spin-orbit matrix elements are more reliable than the wavefunctions used in the calculations. The antisymmetry of the wavefunction and of part of the interaction compensates for the poor correlation properties of the wavefunction.

. . . .

The two-electron spin-orbit terms of the Hamiltonian are very large when the two electrons are close together. To try to calculate their matrix elements with approximate wavefunctions would seem pointless, because (the usual) approximate wavefunctions are poorest when two electrons are close together. It will be shown, however, that each matrix element has at least two factors which are antisymmetric (1) with respect to exchange of electronic spatial coordinates, mitigating the lack of correlation of the wavefunctions.

We wish to calculate $(\emptyset, H\Psi)$. H is given (2) by

$$H = \sum_{i,j} H_{ij}$$

$$H_{ij} = 2\beta^2\left\{-(\underset{\sim}{r}_{ij}/r_{ij}^3) \times \underset{\sim}{p}_i + 2(\underset{\sim}{r}_{ij}/r_{ij}^3) \times \underset{\sim}{p}_j\right\}\cdot\underset{\sim}{s}_i$$

$H_{ij} + H_{ji}$ can be written

$$H_{ij} + H_{ji} = \beta^2\Big\{-3(\underset{\sim}{r}_{ij}/r_{ij}^3) \times (\underset{\sim}{p}_i - \underset{\sim}{p}_j)\cdot(\underset{\sim}{s}_i + \underset{\sim}{s}_j)$$

$$+ (\underset{\sim}{r}_{ij}/r_{ij}^3) \times (\underset{\sim}{p}_i + \underset{\sim}{p}_j)\cdot(\underset{\sim}{s}_i - \underset{\sim}{s}_j)\Big\}$$

The two-electron density matrix of the n-electron wavefunctions ϕ and Ψ is defined by

$$\rho(\underset{\sim}{r}_1{}', \sigma_1{}', \underset{\sim}{r}_2{}', \sigma_2{}'; \underset{\sim}{r}_1, \sigma_1, \underset{\sim}{r}_2, \sigma_2)$$

$$= \frac{n(n-1)}{2} \int d\tau_1\, d\tau_2 \ldots d\tau_n\, \phi^*(\underset{\sim}{r}_1{}', \sigma_1{}', \underset{\sim}{r}_2{}', \sigma_2{}', \underset{\sim}{r}_3, \sigma_3, \ldots \underset{\sim}{r}_n, \sigma_n)$$

$$X\, \Psi(\underset{\sim}{r}_1, \sigma_1, \underset{\sim}{r}_2, \sigma_2, \underset{\sim}{r}_3, \sigma_3 \ldots \underset{\sim}{r}_n, \sigma_n)$$

where $d\tau_m$ is the space-spin volume element for electron m. In terms of ρ, $(\phi, H\Psi) = \int (H_{12}+H_{21}) \rho \Big|_{\underset{\sim}{r}_1{}'=\underset{\sim}{r}_1; \underset{\sim}{r}_2{}'=\underset{\sim}{r}_2} d\tau_1\, d\tau_2$.

ρ can be written as

$$\rho = \sum_{l,m} \rho_{lm}{}'$$

$$\rho_{lm}{}' = \rho_{lm}(\underset{\sim}{r}_1{}', \underset{\sim}{r}_2{}'; \underset{\sim}{r}_1, \underset{\sim}{r}_2)\, f^*_l(1'2')\, f_m(12)$$

$$f_1 = 2^{-\frac{1}{2}} (\alpha\beta - \beta\alpha).$$

$$f_2 = \alpha\alpha$$

$$f_3 = \beta\beta$$

$$f_4 = 2^{-\frac{1}{2}} (\alpha\beta + \beta\alpha)$$

The ρ_{lm} depend on <u>only</u> <u>spatial</u> coordinates. The ρ_{lm} are symmetric with respect to exchange of 1' and 2' when l = 1, antisymmetric when l > 1, and symmetric with respect to exchange of 1 and 2 when m = 1, antisymmetric when m > 1.

The integral $(\phi, H\Psi)$ breaks up into two terms: one proportional to $\underset{\sim}{s}_1 + \underset{\sim}{s}_2$, and one proportional to $\underset{\sim}{s}_1 - \underset{\sim}{s}_2$. Since $(\underset{\sim}{s}_1 + \underset{\sim}{s}_2)\, f_1 = 0$, only ρ_{lm} with both l and m greater than 1, contribute to the first term. But each of these ρ_{lm} is antisymmetric with respect to both exchange of the spatial coordinates of electrons 1 and 2 and 1' and 2'.

Similarly, the term proportional to $\underset{\sim}{s}_1 - \underset{\sim}{s}_2$ contains contributions from the ρ_{lm} for which either l or m, but not both, = 1. Each of these ρ_{lm} is antisymmetric with respect to exchange of electrons 1 and 2 *or* 1' and 2'. Also, the coefficient of $\underset{\sim}{s}_1 - \underset{\sim}{s}_2$ in $H_{12} + H_{21}$ is antisymmetric with respect to exchange of spatial coordinates.

Hence, each matrix element of the two-electron spin-orbit interaction has at least two factors which are antisymmetric with respect to exchange of the spatial coordinates of the two electrons.

References

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PROPOSITION III

CALCULATION OF EIGENVALUES USING AN OPERATOR TECHNIQUE

Abstract

It is proposed that $e^{-k(H-E)}$ be used to calculate energy eigenvalues through the behavior of $e^{-k(H-E)}\, f$ (for some function f) at large k as a function of E.

. . . .

Suppose H is a Hermitian operator whose lowest eigenvalue, E_{min}, is finite, with eigenfunction ϕ. Let f be any function such that $(\phi, f) \neq 0.$,

Then
$$\lim_{k\to\infty} e^{-k(H-E)}f \begin{aligned} &= 0, \quad \text{if } E < E_{min}, \\ &= \phi(\phi, f), \text{ if } E = E_{min}, \\ &= \infty, \quad \text{if } E > E_{min}. \end{aligned}$$

It is proposed that these relations be the basis of a new method for finding eigenvalues of H.

This method consists in choosing a convenient function f, a large value for k, and computing $e^{-k(H-E)}\, f$ as a function of E at a convenient point in the n-electron space of H. When E passes through E_{min}, the value of the expression should increase suddenly.

The main difficulty in using this exponential operator method is in the evaluation of the exponential. Because, in practice, only a finite number of terms of the exponential power series can be used, convergence problems may occur. In particular, the number of terms kept restricts the size of k. Also, careful attention must be paid to the choice of f, since f expressed in terms of the eigenfunctions of H, will almost certainly have terms whose eigenvalues (times k) lie outside the range for which the finite series is accurate.

With these considerations in mind, a careful study of this method and of its application to some simple problems is being planned.

PROPOSITION IV

THE ROLE OF SPIN CORRELATION IN THE CALCULATION OF THE ZERO-FIELD SPLITTING PARAMETERS, D AND E

Abstract

It is shown that the calculated values of the zero-field splitting parameters, D and E, are changed greatly when the SHMO wavefunction is modified to account for spin correlation.

. . . .

Active theoretical interest in calculating the zero-field splitting (See Proposition I) parameters D and E for the lowest triplet state of a molecule dates from the classic experiment of Hutchison and Mangum (1) on naphthalene. Several theoretical calculations have been reported. In particular, those of Boorstein and Gouterman (2), who in <u>some</u> cases were able to obtain agreement with experimental results with a <u>two</u>-configuration wavefunction, indicate that the lowest triplet (single configuration) SHMO wavefunction does not correctly give D and E. We propose to show, by example, that the deficiency of the SHMO wavefunction, insofar as D and E are concerned, is its lack of spin correlation.

There are essentially two physical faults with the SHMO triplet wavefunction: coulomb and spin-correlation. (Spin correlation is properly a part of the coulomb correlation.) The possible influence of spin correlation on calculations of D and E was pointed out by McLachlan (3). That the average coulomb correlation should be relatively unimportant was suggested qualitatively by McConnell (4).

D and E may be calculated from the triplet $S_z = 1$ wavefunction ϕ.

$$D = (3/4)\ g^2\beta^2 \int dV_1 dV_2\ S(1,2)\ r_{12}^{-5}\ (r_{12}^2 - 3\ z_{12}^2) \tag{1}$$

$$E = (3/4)\ g^2\beta^2 \int dV_1 dV_2\ S(1,2)\ r_{12}^{-5}\ (y_{12}^2 - x_{12}^2) \tag{2}$$

$$S(1,2) = (\phi,\ \sum_{i \neq j}\ \delta(\underset{\sim}{r}_i - \underset{\sim}{r}_1)\,\delta(\underset{\sim}{r}_j - \underset{\sim}{r}_2)\,(3 s_{iz} s_{jz} - \underset{\sim}{s}_i \cdot \underset{\sim}{s}_j)\ \phi) \tag{3}$$

In the simple Hückel theory, ϕ has the form

$$\phi = \hat{A}\ M_1\alpha\ M_1\beta\ \ldots M_m\alpha\ M_m\beta\ M_{m+1}\alpha\ M_{m+2}\ \alpha \tag{4}$$

One may calculate the <u>average</u> effects of correlation by using UHF-LCAO-MO orbitals. From Equation 4, the SHMO S(1,2) is simply

$$S(1,2) = \tfrac{1}{2}\left|\ M_{m+1}M_{m+2} - M_{m+2}M_{m+1}\ \right|^2 \tag{5}$$

When the UHF functions are calculated to first order from Equation 4, the corrections to Equation 5 consist in a term which is largely the average coulomb correlation and a term which is explicitly the average spin correlation effect.

$$\delta \underset{\text{coul}}{S(1,2)} = \sum_{k,\ k \neq m+1,\ m+2} (M_{m+1}M_{m+2} - M_{m+2}M_{m+1}) \left\{ (M_{m+1}M_k - M_k M_{m+1}) \frac{V^{\alpha}_{k\ m+2}}{e_{m+2} - e_k} + (M_k M_{m+2} - M_{m+2} M_k) \frac{V^{\alpha}_{k\ m+1}}{e_{m+1} - e_k} \right\} \tag{6}$$

$$\delta S(1,2)_{\text{sp.cor.}} = \sum_{i=1}^{m} \sum_{j=m+1}^{m+2} \sum_{\substack{k\neq m,j \\ k>m}} (M_i M_j - M_j M_i)(M_k M_j - M_j M_k)(V^{\alpha}_{ki} - V^{\beta}_{ki})/(e_i - e_k) \quad (7)$$

e_n represents the one electron SHMO energies.

$$V_{ij} = (M_i, V M_j) \quad (8)$$

$$V^{\alpha} = V^{\beta} + \sum_{j=m+1}^{m+2} (M_j, e^2/r_{12}\, M_j) - |M_j)\, e^2/r_{12}\, (M_j| \quad (9)$$

$$V^{\beta} = \sum_{i=1}^{m} 2(M_i, e^2/r_{12}\, M_i) - |M_i)\, e^2/r_{12}\, (M_i| \quad (10)$$

The corrections to D and E were calculated with the assumptions made by McLachlan (5) in his successful treatment of spin-correlation in radicals: only the one-center coulomb terms in the V_{ij} matrix elements are kept, and the SHMO theory β is replaced by $\beta - \frac{1}{2}(P_{rs})_{av}\, G_{01}$, where G_{01} is the nearest neighbor two-center coulomb integral, and $(P_{rs})_{av}$ is the average nearest neighbor total bond order.

All the integrals of equations 1 and 2 were done exactly using Gaussian atomic orbitals (6). The results were that the SHMO value for D was reduced by about 1/3 and the SHMO value for E changed sign from negative to positive. The contribution of the spin correlation terms of Equation 7 was found to be an order of magnitude larger than that of Equation 6. The exact numbers are not important because this effect on D and E, in contrast to the effect on the spin densities, is clearly too large to be computed by perturbation theory. Nonetheless, that the size of the correction was so large, shows that it is lack of spin correlation which makes the SHMO wavefunction so poor for calculating D and E.

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6. Calculations were performed for the lowest SHMO triplet state of naphthalene.

PROPOSITION V

THEORETICAL SPIN DENSITIES FOR CYCLOPENTADIENYL

Abstract

The spin densities for planar pentagonal cyclopentadienyl radical, C_5H_5, are calculated according to a) the SHMO, b) approximate UHF-LCAO-MO, c) Pariser-Parr, and d) VB theories.

. . . .

The cyclopentadienyl radical C_5H_5 (CPD) is currently being studied by electron spin resonance over a wide range of temperatures in this laboratory (1). The theory of the ESR spectra of CPD is very similar to that of CHT, and in this proposition calculations of the spin densities of CPD by the a) SHMO, b) approximate UHF-LCAO-MO, c) Pariser-Parr, and d) VB theories are presented.

Each of these theories was described in the thesis and will not be described again here. The ground state of planar pentagonal CPD is predicted to be orbitally degenerate by both the MO and VB theories, with symmetry E''_1. The spin densities for an arbitrary real eigenfunction can be described by

$$\rho_{nn} = (1/5)\left[1 + T_x \cos(4\pi n/5 + 2\theta_{om})\right]$$

where the orbital mixing parameter, θ_{om}, and the theory indexing parameter, T_x, play the same roles as for CHT.

a) As with CHT, the SHMO value of T_x is 1.

b) The approximate UHF-LCAO-MO method leads to the expression

$$T = 1 + 2\left[\frac{-K_{01}}{e_0 - e_1} + \frac{-K_{02}}{e_1 - e_2}\right]$$

where

$$e_m = 2\beta\cos(2\pi m/7) - K_{0m}$$

$$K_{0m} = (1/5)(G_{00} + 2\cos(2\pi m/5)\,G_{01} + 2\cos(4\pi m/5)G_{02})$$

β, G_{00}, G_{01}, as before, were adopted from Pariser (2). G_{02} was calculated for a C-C distance of 2.27 Å, nuclear charge 3.18. The values used were

β, G_{00}, G_{01}, G_{02} = -2.4, 11.0, 7.0, 6.0 electron volts. T_x is calculated to be 1.467.

c) The discussion of the Pariser-Parr method can be carried over almost without change. Diagonalizing the matrix of H over the ground state of CPD and its pseudo-singly excited configurations, the energy lowering is found to be 0.44 e.v., and the computed T_x is 1.286. The values used for the integrals were the same as for the UHF calculation.

d) The VB method for CPD is simple to apply because the wavefunction is determined by symmetry (3). The VB prediction of T_x is 2.667.

In summary, the spin densities for CPD are given theoretically by the formula

$$\rho_{nn} = (1/5)\left[1 + T_x \cos((4\pi n/5) + 2\,\theta_{om})\right]$$

The orbital mixing parameter, θ_{om}, is determined by the environment of the molecule. The theory indexing parameter, T_x , is given the values 1, 1.467, 1.286, and 2.667 by the SHMO, approximate UHF-LCAO-MO, Pariser-Parr, and VB theories, respectively.

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