SOME FACTORS WHICH AFFECT THE SPIN DENSITIES OF PROTONS, WITH PARTICULAR EMPHASIS ON THE β-PROTONS OF CYCLOBUTENYL

Thesis by

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DEDICATION

To my late father

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ABSTRACT

Both first-order and variational valence bond calculations were made to estimate the ESR hyperfine splittings of the β-protons of cyclobutenyl. The ESR spectrum of the radical has not been obtained; but on the basis of these calculations, it is anticipated that the β -proton splittings will be large and in the range 42g to 101g. The first-order results indicate considerably larger splittings than the variational calculation; this situation was shown to be in marked contrast with another valence bond calculation on a free radical containing β-protons. Possible inequality in the β-proton splittings of cyclobutenyl at low temperatures was also discussed.

The dependence of the spin densities of β-protons on π-electron excitation energies (in appropriate free radicals) was discovered and was shown to reduce the size of the β-proton hyperfine splittings. The agreement with experiment was satisfactory.

The transformation between the vector-coupling states for an eight electron system and its canonical states was obtained. The canonical states were found to be especially amenable to computer computations, involving the non-overlap, empirical valence bond theory.

The reasons for the suitability of the use of vector-coupling functions in configuration interaction in the valence bond theory were discussed. A case was presented in which it appeared desirable to distribute the antisymmetrical spatial components of the ground-state

wave function somewhat differently in space than that of the symmetrical spatial components.

An anomaly in the ESR spectra of irradiated benzene was deduced from theoretical considerations.

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INTRODUCTION

The problems of this work were to predict the ESR spectrum of a free radical, cyclobutenyl, using the valence bond theory and to improve that theory for such work. The fact that the β-proton hyperfine splitting constants in an aromatic free radical such as cyclobutenyl (CB) are dependent on the excited states of the π-electrons was discovered and is also discussed.

In line with the goal of improving the theory, a further extension of the extended valence bond theory is proposed; and some indication of the effects which might be observed using it are given in a first-order calculation on the C-H fragment model.

The need for reconsideration of the source of an ESR spectrum, originally attributed to phenyl, was deduced from theoretical considerations, which are presented here.

I. THE HAMILTONIAN AND THE EFFECTS WHICH ARE OBSERVABLE IN ESR EXPERIMENTS

The total Hamiltonian for the system of cyclobutenyl (CB) in a magnetic field is:

$$\mathcal{H} = \mathcal{H}_0 + g_e\beta_e \vec{S}\cdot\vec{H} - \sum_j \left(g_p\beta_N \vec{H} - \vec{S}\cdot \underset{\approx}{T}_j - a_j\vec{S}\right)\cdot\vec{I}_j + \mathcal{H}_{\substack{\text{interaction from}\\ \text{neighbor molecules}}} \quad \text{(eq. 1)}$$

The sum over j is over all protons of the molecule; $\beta_N = \frac{e\hbar}{2m_pc}$; $\beta_e = \frac{e\hbar}{2m_ec}$. This Hamiltonian is suitable for hydrocarbon free radicals in a doublet spin ground state and which have no molecular axis about which electron orbital angular momentum is conserved (1), (6). For magnetic fields used in ESR experiments, the term $\sum_j g_p\beta_N \vec{H}\cdot\vec{I}_j$ is negligible since $g_p \sim g_e\left(\frac{1}{1840}\right)$. Other than the use of g_e (instead of the free electron g value 2.0023), spin-orbit effects have also been neglected. g_e is the rotational average of the g tensor, or (1/3) (tr $\underset{\approx}{g}$), which differs from g because of the second-order interaction of orbital Zeeman and spin-orbit effects (3). g_e further implies that $\vec{\mu}_S$, the magnetic moment of the electron, is only approximately equal to $\gamma_S\vec{S}$, where γ_S is a multiplicative constant. Hence the dipolar interaction (discussed below) between $\vec{\mu}_S$ and the nuclear magnetic moment due to the spin angular momentum of the nucleus does not exactly average to zero with rotational tumbling (4).

The terms $\sum_j \vec{S}\cdot\underset{\approx}{T}_j\cdot\vec{I}_j$ and $\sum_j a_j\vec{S}\cdot\vec{I}_j$ both arise from the interaction of the unpaired electron spin of the free radical with the magnetic field whose vector potential is:

$$\vec{A}_I = -\vec{\mu}_I \times \left(\vec{\nabla}\left(\tfrac{1}{r}\right)\right) \quad \text{, where} \quad \vec{\mu}_I = \gamma_I\vec{I} = \frac{Ze\hbar}{Mc}\vec{I}.$$

The derivation, reported in (3), of these terms involving the anisotropic dipolar interaction and the Fermi contact interaction, is given below:

$$\vec{H}_I = \vec{\nabla} \times \vec{A}_I = -\vec{\nabla} \times \{\vec{\mu}_I \times \vec{\nabla}(\tfrac{1}{r})\}$$

$$-\vec{H}_I = \gamma_I \{\vec{I}\,\Delta(\tfrac{1}{r}) - \vec{I}\cdot\vec{\nabla}(\vec{\nabla}(\tfrac{1}{r}))\}$$

$$\mathcal{H}_{int} = -\vec{\mu}_s \cdot \vec{H}_I = \gamma_I \gamma_s \{ (\vec{I}\cdot\vec{S})(\Delta(\tfrac{1}{r})) - \vec{I}\cdot\vec{\nabla}(\vec{S}\cdot\vec{\nabla})(\tfrac{1}{r})\},$$

$$\text{where } \vec{\mu}_s = \gamma_s \vec{S},\ \gamma_s = \frac{-ge\hbar}{2mc}.$$

$$E_{I,S} = \langle \psi | \mathcal{H}_{int} | \psi \rangle = \gamma_I \gamma_S [-4\pi(\vec{I}\cdot\vec{S})|\psi(0)|^2$$
$$- \langle \psi(\vec{r}) | (\vec{I}\cdot\vec{\nabla})(\vec{S}\cdot\vec{\nabla})(\tfrac{1}{r}) | \psi(\vec{r}) \rangle], \text{ using } \Delta(\tfrac{1}{r}) = -4\pi\delta(r).$$

For the spherically symmetric case,

$$\langle \psi(\vec{r}) | (\vec{I}\cdot\vec{\nabla})(\vec{S}\cdot\vec{\nabla})(\tfrac{1}{r}) | \psi(\vec{r}) \rangle = \tfrac{1}{3}(\vec{I}\cdot\vec{S}) \langle \psi(\vec{r}) | \Delta(\tfrac{1}{r}) | \psi(\vec{r}) \rangle$$

Then $E_{I,S} = -\frac{8\pi\gamma_I\gamma_S}{3}(\vec{I}\cdot\vec{S})|\psi(0)|^2$

For non-spherical symmetry,

$$E_{I,S} = -\frac{8\pi\gamma_I\gamma_S}{3}(\vec{I}\cdot\vec{S})|\psi(0)|^2 + \gamma_I\gamma_S \left\langle \psi(\vec{r}) \left| \frac{(\vec{I}\cdot\vec{S})r^2 - 3(\vec{I}\cdot\vec{r})(\vec{S}\cdot\vec{r})}{r^5} \right| \psi(\vec{r}) \right\rangle$$

$$\mathcal{H}_{int} = -\frac{8\pi\gamma_I\gamma_S}{3}(\vec{I}\cdot\vec{S})\delta(\vec{r}) + \gamma_I\gamma_S \frac{(\vec{I}\cdot\vec{S})r^2 - 3(\vec{I}\cdot\vec{r})(\vec{S}\cdot\vec{r})}{r^5} \quad (eq. 2).$$

This expression gives a_j and $\underset{\approx}{T}_j$ immediately for the case of one electron interacting with one proton.

Generalizing eq. 2 to the case of many electrons involved in interaction with a nucleus N, it is found that

$$\mathcal{H}_{int} \text{ (Fermi contact)} = \left(\frac{8\pi}{3}\right)\frac{ge\hbar}{2mc}\frac{\mu_I}{I}\sum_k \delta(\vec{r}_k - \vec{r}_N)\vec{S}_k\cdot\vec{I}_N$$

The Fermi contact term is thus proportional to the quantity $\rho(r_N) \equiv \langle \psi | \Sigma_k \delta(\vec{r}_k - \vec{r}_N)\underset{\sim}{\sigma}_k | \psi \rangle$, where $\underset{\sim}{\sigma}_k$ is the Pauli spin matrix operating on the spin states of electron k. $\rho(r_N)$ is the spin density at the nucleus N. By the indistinguishability of electrons,

$$\langle \psi | \Sigma_k \delta(\vec{r}_k - \vec{r}_N)\underset{\sim}{\sigma}_k | \psi \rangle = N \langle \psi | \delta(\vec{r}_1 - \vec{r}_N)\underset{\sim}{\sigma}_1 | \psi \rangle$$

Thus a_N of eq. 1 is:

$$a_N = \left(\frac{8\pi}{3}\right) \frac{g e \hbar}{2mc} \frac{\mu_I}{I} \rho(r_N) \qquad (17)$$

Similarly, it can be shown that the dipolar interaction portion of is given by

$$\mathcal{H}_{int} \text{ (dipolar)} = -g|\beta|\hbar\gamma_I \vec{S} \cdot \left(\text{Trace} \left(\rho \underset{\approx}{T} \right)\right) \cdot \vec{I},$$

where $\underset{\approx}{T} = \frac{1}{r^3}\left(\underset{\approx}{U} - \frac{3\vec{r}\vec{r}}{r^2}\right)$ (1), (6). Since the anisotropic coupling tensor $\underset{\approx}{T}$ is traceless, there is no contribution to $E_{I,S}$ from $\mathcal{H}_{int}$ (dipolar) for a rapidly rotating molecule. The effect of rapid rotation may be simulated by averaging the results of many ESR spectra obtained for a reasonable distribution of orientations of the crystal relative to the magnetic field.

The interplay of $\mathcal{H}_0$ and $\mathcal{H}_{int}$ from neighbor molecules $\equiv (\mathcal{H}_n)$ in the crystal of a free radical containing β-protons such as CB can be studied only approximately theoretically. The experimental data must be fitted in order to determine $\mathcal{H}_n$ qualitatively and/or the apparent temperature dependence of $\mathcal{H}_0$. This fitting often involves using theoretical results calculated for isotropic splittings of the β-protons to a single spectrum, since the ESR spectra for other orientations are smeared. In such cases, simulated rotational averaging cannot be used to eliminate the effects of anisotropic coupling in the crystal. Fortunately, the anisotropic effects are rather small, as has been shown in cases in which the spectrum can be resolved for a large number of orientations, examples being the radical $COOH\dot{C}HCH_2COOH$, derived from the parent compounds β-succinic acid (7) and dl-aspartic acid (8). The variation about the isotropic value for the hyperfine splittings of β -protons is about 6 Mc (2.80 Mc = 1g). Hence it is still worthwhile to compare the calculated isotropic splittings of the β-protons of CB for various possible distortions of the methylene unit with future experimental data, despite the fact that the ESR spectrum of only one orientation of the crystal may be resolvable.

Because of the strong dependence, as predicted by electron structure theory (Section III), of the β-proton hyperfine splittings on distortions occurring at the methylene carbon (in appropriate free radicals), it is possible to determine whether the methylene unit undergoes a rocking distortion and/or a spread in the angle between the hybrids extending from the methylene carbon to the β-protons. The inequalities, which accompany such distortions, in the hyperfine splittings of the β-protons are definitely outside the range of anisotropic effects. This fact has been amply demonstrated in the two cases of the $COOH\dot{C}HCH_2COOH$ radical mentioned above.

The remaining problems in this analysis of the order of magnitude of the terms appearing in $\mathcal{H}$ are to determine the size of $\mathcal{H}_n$ and to consider the character of ψ_0, where $\mathcal{H}_0\psi_0 = E_0\psi_0$, at low temperatures. There is the possibility that even without the presence of $\mathcal{H}_n$, the potential energy surface which determines the positions of the β-protons has a dual minimum at the methylene carbon, located symmetrically on either side of the molecular plane. The barrier to rotation between two such wells, hypothesized to exist at the methylene carbon adjacent to an allyl section in a long-chain polymer (hereafter called MCAALCP), has been estimated to be .104 kcal/mole (9). This barrier is very low compared to those in ethane (3 kcal/mole) (10) and in ethylene (40 kcal/mole) (11). The idea that dual wells exist in MCAALCP is based on the fact that there is a continuous increase starting from zero in the difference between the ESR splittings of the β-protons of MCAALCP as the temperature is increased.

Possibly, in the case of MCAALCP, the unequal β-proton splittings detected at low temperatures are independent of $\mathcal{H}_n$; but experiments studying $COOHCH_2\dot{C}HCOOH$ (I′), for instance, show that $\mathcal{H}_n$ may severely perturb ψ_0 in other radicals. Radical (I′), produced from the different parent species dl-aspartic acid and β-succinic acid, gave the unequal splittings of 115 and 18 Mc and of 80 and 100 Mc, respectively. The author has suggested that it would be of interest to obtain the ESR spectrum of radical (I′) within the crystalline structure of α-succinic acid (18) as well.

A third class of radicals, in this classification of the relative strengths of $\mathcal{H}_0$ and $\mathcal{H}_{int}$ in determining the molecular electronic structure at low temperatures, are those which have equal proton splittings at any temperature. An example is cyclohexadienyl, which has equal β -proton splittings of 50g at low temperatures (12). The two β -protons are evidently not tunnelling between two asymmetrical positions at high temperatures, though $\mathcal{H}_n$ may also contribute to the low temperature symmetry of the wave function at the methylene carbon. Another indication that CB will be found to belong to this third class is the fact that the barrier to rotation of the β-protons in cyclobutyl is very high, as indicated by their high temperature ESR spectrum and theoretical considerations (13).

An approximation of proven utility in the analysis of ESR spectra is McConnell's relation $a_h = \rho Q$, where ρ is the spin density on a π -orbital, which is adjacent to a σ-proton, in an aromatic radical. Q is the hyperfine coupling constant from which the splitting a_h of the

σ -proton may be deduced. This relation allows one to relate the theory of the π -electron wave functions to the experimental proton splittings without considering the total free Hamiltonian $\mathcal{H}_0$. The discussion of the means of calculating Q and fluctuations in it is of considerable theoretical importance. Various aspects of the problem of determining different Q's will be discussed in Section IV in the course of calculations involving first-order perturbation theory in the general framework of the valence bond (VB) theory. The scheme is to perform a calculation of spin densities for fragmental portions of molecules, such as the C-H (14), π -methyl (15), and π -methylene (16) fragments in order to obtain a value for Q from which the hyperfine splittings of the protons of such a fragment, appearing in an aromatic free radical, can be estimated from a knowledge of only the spin densities of the π -electrons. The Q's of special interest in this work are:

for β -protons,

1) Q = 29.15g (15), theoretical;
2) Q = 24.68g (13), experimental, β-protons on rapidly rotating methylene group;
3) Q = 38g (13), experimental, β -protons in cyclobutyl at high temperatures experiencing hindered rotation; Q $\cong$(3/4 = $\cos^2 30^\circ$) x2 x24.68g;
4) Q = 35.16g, (13), experimental, β-protons on cyclopentyl;

for σ -protons,

1) Q = -63 Mc = -22.5g, experimental (4);
2) Q = $\pm$21.20g, experimental, σ -proton in cyclobutyl (13);
3) Q = $\pm$21.48g, experimental, σ -proton in cyclopentyl (13);

4) Q = -25.67g, experimental, σ -proton in cycloctatetraene anion[1] (44).

In addition, the author has obtained Q for the allyl - β -proton fragment, which will be demonstrated in Section IV to be different from that of the $\pi - \beta$ -proton fragment. This Q is defined by the equation:

$a_h = Q \rho$, where ρ is the total spin density in the allyl section of the fragment.

Q = 21.3g, experimentally, and 22g, theoretically, for the splittings at high temperature of the β-protons of MCAALCP. The experimental value is given in (9). Q = 66.2g, theoretically, for the β-protons of CB, if their motion is restrained because of rotational hindrance. Q = 44.1g, theoretically, for the CB β-protons if they experience free rotation. Both of these Q's are taken from first-order calculations, as are the other theoretical Q's given above.

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[1] This value for Q in the cyclooctatetraene negative anion may be compared with that of the other planar aromatic radicals since ^{13}C splittings in this anion indicate the radical is planar (19). The dependence of these splittings on the out-of-plane angle $\chi = \frac{\pi}{2} - \theta$ is very large (19) as can be seen by the following equation:

$$a^{C}_{2s} = 1191\ Mc\,[\,(1-\cot^2\theta)\,\Gamma(\sigma_{CH}) + 2\cot^2\theta\,\Gamma(\pi)],$$

where $\Gamma(\pi)$ is the π-orbital spin density of the C atom and $\Gamma(\sigma_{CH}) \simeq .05\,\Gamma(\pi)$ (17).

II. THE VALENCE BOND THEORY, ITS COMPUTATIONAL UTILITY, AND IDENTITIES USEFUL IN RELATING IT TO VECTOR-COUPLING THEORY

The problem of calculating the ESR spectrum of CB has been reduced to solving the equation $\mathcal{H}_0 \Psi_0 = E_0 \Psi_0$ for various arbitarily chosen nuclear positions and then using the ground-state Ψ_0 to calculate the a_N's.

The choice of the valence bond (VB) theory to use in calculating Ψ_0 was made because it had been used extensively in the past to study β -proton splittings (14-16, 20). The evaluation of σ-π interaction parameters is a considerable obstacle to the application of MO theory in such cases (21).

Inspection of the perfect-pairing state, the well-known ground-state of VB theory, with the view of calculating spin densities on β -protons, reveals the need for the introduction of configuration interaction, or perturbation of the ground state wave function by various excited states. Otherwise, the theory would not predict the occurrence of any unpaired spin density on these protons (or on σ -protons) of a hydrocarbon free radical, which is contrary to experiment. There are two alternatives for introducing configurational interaction: the variational method and first-order perturbation theory.

The variational method further subdivides into the linear and non-linear variation techniques. In both cases, the object is to improve the accuracy of the ground-state wave function Ψ_0 by finding a Ψ such that $\langle \Psi | \mathcal{H}_0 | \Psi \rangle$ is a minimum. The nonlinear variation process, which formerly involved hybridizing the perfect-pairing wave function(s) so as to attain a minimum in the energy, has evolved to manipulating the spatial components of orthogonal bond orbitals, with the spin portion of the wave function still that of the perfect-pairing function. This technique introduces ionic components in the wave function. This theory is called the extended VB theory (22). However, it fails to give any unpaired spin density on protons in aromatic free radicals.

The linear variation form assumes that Ψ, the exact wave function is of the form: $\Psi = \sum_i c_i \phi_i$ where the c_i are the variational parameters of the known set ϕ_i. If Ψ is the ground-state wave function, then, by the variational theorem, $\langle \Psi | \mathcal{H}_0 | \Psi \rangle \leq \langle \sum c_i \phi_i | \mathcal{H}_0 | \sum_i c_i \phi_i \rangle$; so $\Psi' = \sum c_i \phi_i$ is a no-less accurate approximation to Ψ than any of the ϕ_i. The linear variational method is to differentiate the equation

$$\langle \textstyle\sum_i c_i \phi_i | \mathcal{H}_0 | \sum_i c_i \phi_i \rangle = \langle \sum_i c_i \phi_i | E | \sum_i c_i \phi_i \rangle .$$

with respect to each of the variational parameters c_i (one at a time) and to solve the resulting set of equations for the eigenvalues and eigenvectors. The equations to be solved, written in matrix notation, are:

$\underset{\approx}{\mathcal{H}} \underset{\sim}{x} = E \underset{\approx}{O} \underset{\sim}{x}$, where $\underset{\sim}{x}$ is an eigenvector. $\underset{\approx}{\mathcal{H}}_{ij} = \langle \phi_i | \mathcal{H}_0 | \phi_j \rangle$,
$\underset{\approx}{O}_{ij} = \langle \phi_i | 1 | \phi_j \rangle \neq \delta_{ij}$.

The ϕ_i chosen in the conventional VB theory of singlet states are known as canonical states. The "singlet" states with one phantom orbital are a set of linearly independent doublet states, as are needed in studying free radicals of spin $\frac{1}{2}$. More physically complete function sets can be composed by using ionic functions and non-electron pairing functions. The latter are a means of introducing additional atomic states of the carbon atoms involved into the variational procedure. Only the canonical states are used in calculations in this thesis.

The predominance of the canonical states in chemical theory can be attributed to the following facts:

(1) Chemical intuition once supported the model that singlet pairings between electrons are as applicable in excited states of a molecule as in the perfect-pairing state. Though the perfect-pairing state is capable of giving reasonably accurate ground-state energies in hydrocarbons (23), the excited states are usually physically inaccurate (24). A notable exception appears to be the excited states of ethylene (25).

(2) The canonical states are clearly eigenfunctions of $S^2 = 0$, or $S^2 = 3/4$ (if one of the orbitals is treated as a phantom).

(3) The restriction to only singlet pariings throughout the canonical states (CS's) leads to considerable mathematical convenience. The CS's can be represented by Rumer diagrams , each of which is a collection of lines drawn between points equally spaced on a circle, such that only one line touches each point. The fourteen CS's of an eight electron system are given in Fig. 1 below. The points represent orbitals, the lines are bonds between any two orbitals such that the spin function of the electrons involved in the bond is a singlet. Further, since any singlet state is a linear combination of canonical states (assuming the same total basis set considered is that of the CS's), any singlet

state can be expressed as a linear combination of these diagrams. The diagram representation then allows one to calculate the $\underset{\approx}{\mathcal{H}}$ and $\underset{\approx}{\mathcal{O}}$ matrices for any eigenfunction of $S^2 = 0$ (or 3/4) by the especially simple rules given in fact (4) below.

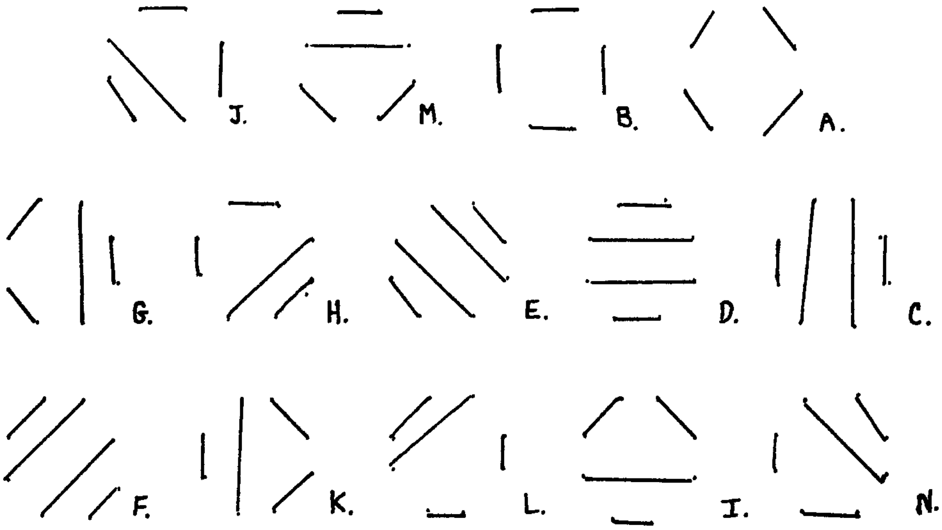


Fig. 1

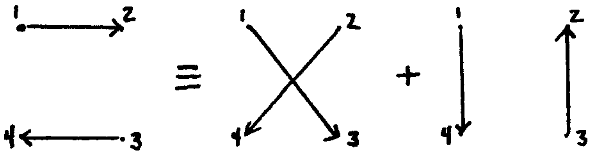
Two useful identities which are helpful in expressing spin functions which are not CS's in terms of the Rumer diagrams (or CS's) are:

$$(s_1-s_2)(s_3-s_4) \equiv (s_1-s_3)(s_2-s_4) + (s_1-s_4)(s_3-s_2) \quad \text{(Identity 1).}$$

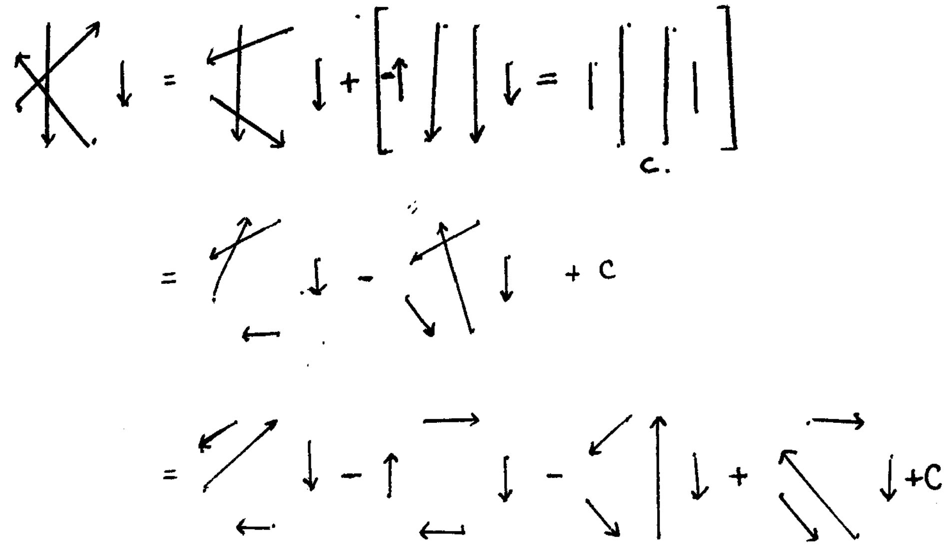
$$\frac{1}{\sqrt{3}}\left(s_1 s_2 - \frac{1}{2}(s_1+s_2)(s_3+s_4) + s_3 s_4\right) = \frac{1}{\sqrt{3}}\left[\frac{1}{2}(s_1-s_2)(s_3-s_4) - (s_1-s_4)(s_3-s_2)\right] \quad \text{(Identity 2).}$$

(s_i corresponds to α-spin for electron i, 1 to β-spin.)

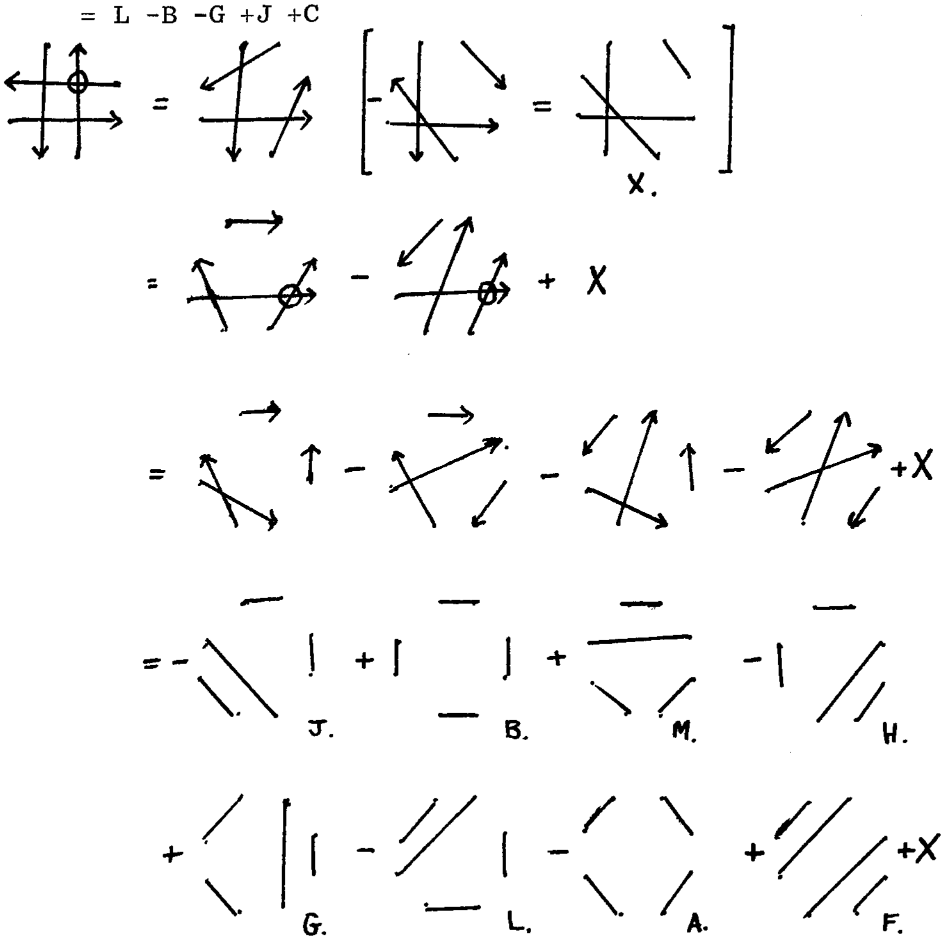
In terms of vectors, whose "direction" is significant, identity (1) may also be written in the well-known form (25):



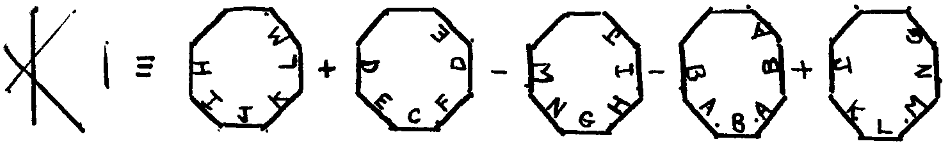
Applying identity (1) to more complex vector decoupling problems, as will appear in Section IV, the author derived the following:



= L -B -G +J +C

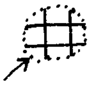


To evaluate X, one rotates identity (3) since identity (3) is valid for all rotations and inversions of the Rumer diagrams. The following version of identity (3) is useful:



(Identity 3)

Then X = I + K + E − (N + A).

So  = −(J+N+H+ 2A +L) + (B + M + G + F + K + I + E) (identity 4).

Similarly, identity (4) is valid for all rotations and/or inversions of the Rumer diagrams involved. Rotating it so that it rests on the side to which the arrow is drawn, one finds:

 = −(I + G + M + 2B + K) + (A + L + N + C + J + H + D)

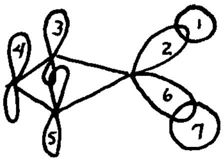
(4) The most useful quality of these canonical structures is the ease with which one can compute the matrix elements $\phi_j \mathcal{H} \phi_i$, $\phi_j \phi_i$. The rules for computing them can be formulated in terms of Pauling's "islands" (26) or the Eyring-Walter-Kimball "cycles" (25). In terms of the latter, they are:

$H_{12} = \langle 1|\mathcal{H}|2\rangle = 2^{x-n}\{Q + \frac{3}{2}[\sum$(single exchange integrals between orbitals in the same cycle with opposite spins) $-\sum$(single exchange integrals between orbitals in the same cycle with the same spin)] $-\frac{1}{2}\sum$(all single exchange integrals)$\}$ where $\mathcal{H}$ is the total molecular Hamiltonian, n − x = total number of cycles possible minus the number appearing in the cycle diagram for canonical structures 1 and 2. (The factor

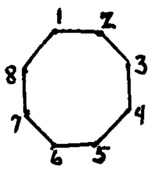
$(-1)^{\nu}$, which appears in reference (25), is of no consequence provided every factor of the various canonical structures is of the form $(S_{2m+1}-S_{2n+2})$, where m and n are integers.)

Also, the overlap matrix, assuming orthogonality of all space orbitals, is formed by using the coefficients of the Coulomb integral Q. Rule (1)

This formula for the matrix elements, because of its simplicity, proves to be amenable to computer computation. The computer program, which the author wrote to handle the entire problem of calculating the spin densities for an eight orbital problem, is given and discussed in Appendix I. The program treats only the non-overlap, empirical VB theory. This program was checked, using $\underset{\approx}{\mathcal{H}}$ and $\underset{\approx}{\mathcal{O}}$ matrices, which the author had constructed by hand for the seven functions of A symmetry of the rotation group C_2 for CB. (If one labels the orbitals of principal interest in CB as follows:



and numbers the orbitals of each of the Rumer diagrams of Fig. 1 in the following fashion



then one can construct the table:

operation of C_2 rotation group	canonical states
E	J A G I C K D
C_2	M B H N F L E

One then takes the positive sum of each pair of functions to form the (unnormalized) functions of A symmetry.)) The $\underset{\approx}{\mathcal{H}}$ and $\underset{\approx}{\mathcal{O}}$ matrices, in turn, had been checked by substituting suitable eigenvalues of the equation $\underset{\approx}{\mathcal{H}}\underset{\sim}{x} = E\underset{\approx}{\mathcal{O}}\underset{\sim}{x}$ into $\underset{\approx}{\mathcal{H}}$ and determining left and right multipliers, $\underset{\approx}{T}_l$ and $\underset{\approx}{T}_r$, such that $\underset{\approx}{T}_l(\underset{\approx}{H} - E\underset{\approx}{O})\underset{\approx}{T}_r = \underset{\approx}{A}$, where $\underset{\approx}{A}$ has at least one row or column of zeroes. These eigenvalues were linear combinations of the π-exchange integrals (called $J(p_3p_4)$ and $J(p_4p_5)$ in Section III) and the exchange integrals of the C-H bonds ($J(h_7\sigma_6)$, $J(h_1\sigma_2)$). Though it is necessary to use vector-coupling functions (Section IV) to be certain the eigenvalues, guessed by a semi-vector-coupling approach, are appropriate to functions of A symmetry, the rule that the sign and value of an exchange integral in a triplet bond is minus that of the same integral for a singlet bond leads eventually to the following table:

Energy ($A = J(\sigma_k h_\ell)$, $B = J(p_ip_j)$)	Spin function as direct product of spin functions in the allyl and methylene regions*
(1) 2A + B (A symmetry)	DS
(2) 2A - B (B symmetry)	D_qS
(3) B	DT
(4) -B	DT
(5) -2B	QT
(6) -2A + B	DS_q, DT_q
(7) -2A - B	D_qS_q, D_qT_q
(8) -2A - 2B	QT_q, QQ

---

*Notation:
D = doublet
T = triplet
S = singlet
Q = quartet (allyl), quintet (methylene)
D_q= doublet arising from the appropriate coupling of spin ½ to spin 1
S_q= singlet arising from the appropriate coupling of spin 1 to spin 1
T_q= triplet arising from the appropriate coupling of spin ½ to spin 1

Energies (3) through (8) were found to belong to functions of A and B symmetry, as evidenced by the fact that each of them appeared twice (in terms of a distinctive numerical value) in the computer calculation on the fourteen orbital system, using only the characteristic parameters of the table above. The eigenfunctions calculated by the computer differed from those calculated by hand by an orthogonal transformation.

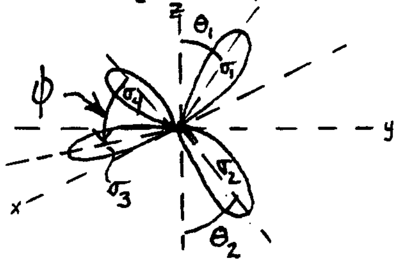
The accuracy of the computer program was further confirmed by the fact that the results obtained with it for the spin densities of the benzyl radical, using fourteen canonical structures and one parameter, were in exact agreement with those of a hand calculation of the spin densities on the same number of states and parameters (27).

III. A VALENCE BOND CALCULATION OF THE SPIN DENSITIES OF THE β-PROTONS OF CYCLOBUTENYL AND COMPARISON WITH RELATED THEORETICAL CALCULATIONS

Calculations with the program of Appendix I, which uses the conventional variational VB theory, were made on the eight orbital model (Section II) of CB. The following hybridizations of the methylene carbon were considered:

(1) tetrahedral hybrids ($\theta_1 = \theta_2 = 30^{\circ}$);
(2) hybrids such that $\phi = 104^{\circ}\ 29'$, $\theta_1 = 28^{\circ}$, $\theta_2 = 37^{\circ}$;
(3) hybrids such that $\phi = 104^{\circ}\ 29'$, $\theta_1 = 9.6^{\circ}$, $\theta_2 = 65.7^{\circ}$.

The angles θ_1, θ_2 and ϕ are given in the following diagram:



, ϕ is the in-plane hybrid angle.

The relations between the 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals of the methylene carbon and its hybrids are given by: (28):

$$\begin{pmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\end{pmatrix} = \begin{pmatrix} b & 0 & \frac{\sqrt{2}\,a\,b}{\sqrt{1-2a^2}} & \frac{\sqrt{1-2a^2-b^2}}{\sqrt{1-2a^2}}\\ \sqrt{1-2a^2-b^2} & 0 & \frac{\sqrt{2}\,a\sqrt{1-2a^2-b^2}}{\sqrt{1-2a^2}} & \frac{-b}{\sqrt{1-2a^2}}\\ a & \frac{1}{\sqrt{2}} & -\sqrt{\frac{1-2a^2}{2}} & 0\\ a & -\frac{1}{\sqrt{2}} & -\sqrt{\frac{1-2a^2}{2}} & 0 \end{pmatrix}\begin{pmatrix}2s\\ 2p_x\\ 2p_y\\ 2p_z\end{pmatrix}$$

where $\phi = \cos^{-1}(a^2)(a^2-1)^{-1}$
$\tan\theta_1 = ab\left(\sqrt{1-2a^2-b^2}\ \sqrt{1-b^2}\right)^{-1}$
$\tan\theta_2 = a\sqrt{1-2a^2-b^2}\left(b\sqrt{1-a^2}\right)^{-1}$
$\tan\theta_1\ \tan\theta_2 = a^2(1-a^2)^{-1}$.

The values of the parameters a and b corresponding to the hybridizations (1) through (3) are:

(1) $a = b = \frac{1}{2}$;
(2) $a = \frac{1}{5}$, $b = \frac{1}{5}$;
(3) $a = \frac{1}{5}$, $b = \frac{\sqrt{14}}{5}$.

In view of the very approximate dependence upon hybridization of the exchange integrals of the empirical VB theory, the possibility that the methylene carbon is tilted out of the plane of the other three carbons was disregarded. The assumption that CB is planar at high temperatures is probably correct since cyclobutyl is planar (13). Further, electron diffraction studies have shown that gaseous cyclobutene is planar (29). The possibility that a skew hybridization exists at the methylene carbon can be shown to be negligible by the fact that such a hybridization is impossible for normal electron-pairing type hybrids.[2]

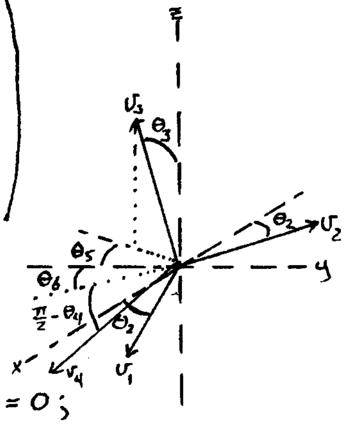
---

[2] Proof that the normal hybrids of a carbon atom lie in two perpendicular planes: The vectors of hybridization must be orthogonal both row- and column-wise when aligned as a four-dimensional array since otherwise (the column orthogonality not holding), the determinant of the coefficients would vanish. This, however, implies that the rows are also linearly dependent. A general hybrid matrix is:

$$\begin{pmatrix} v_1 \\ v_2 \\ v_3 \\ v_4 \end{pmatrix} = \begin{pmatrix} a_1 & \cos\theta_1 \, a_1^* & \sin\theta_1 \, a_1^* & 0 \\ a_x & -\cos\theta_1 \, a_x^* & \sin\theta_1 \, a_x^* & 0 \\ a_y & -\sin\theta_3 \sin\theta_5 \, a_y^* & -\sin\theta_3 \cos\theta_5 \, a_y^* & a_y^* \cos\theta_3 \\ x & \sin\theta_4 \sin\theta_6 \, x^* & -\sin\theta_4 \cos\theta_6 \, x^* & -x^* \cos\theta_4 \end{pmatrix} \begin{pmatrix} s \\ p_x \\ p_y \\ p_z \end{pmatrix}$$

$$a_1^* = \sqrt{1-a_1^2}\,, \quad a_x^* = \sqrt{1-a_x^2}\,, \quad a_y^* = \sqrt{1-a_y^2}\,,$$

$$x = \sqrt{1-(a_1^2+a_x^2+a_y^2)}\,, \quad x^* = \sqrt{1-x^2}\,.$$



Then $-[(a_y^*)^2 \cos\theta_3 \sin\theta_3 \sin\theta_5 + (x^*)^2 \cos\theta_4 \sin\theta_4 \sin\theta_6] = 0$;

$$-[(a_y^*)^2 \cos\theta_3 \sin\theta_3 \cos\theta_5 + (x^*)^2 \cos\theta_4 \sin\theta_4 \cos\theta_6] = 0.$$

If $\theta_3, \theta_4 \neq 0$, $\tan\theta_5 = -\tan\theta_6$. $\theta_5 = \theta_6 = 0$, or $\theta_5 = -\theta_6$. That is, the vectors v_3 and v_4 lie in the same plane, perpendicular to the x-y plane (author's proof).

Only the seven orbital system for CB was considered because of computing limitations. A revision of the program of Appendix I could handle a twelve orbital system. Then the effects of the in-plane orbitals could be included. However, it has been found empirically (see Section V) that the in-plane hybridization is of less importance in determining at least σ-proton spin densities. Such a result means that the Q values given in Section I are most likely applicable to CB. The value -22.5g will be used to estimate, by application of McConnell's relation, the hyperfine splittings of the σ-protons in CB.

Six sets of exchange integrals were considered in calculating the spin densities in the seven orbital CB system. They were (giving only one of a kind, if sufficient):

Trial	$J(h_1\sigma_2)$	$J(h_7\sigma_6)$	$J(p_3p_4)$	$J(\sigma_2 p_3)$	$J(\sigma_6 p_3)$	$J(\sigma_2\sigma_6)$	$J(h_1h_7)$	$J(h_1\sigma_6)$	$J(h_7\sigma_2)$	$J(h_1p_3)$
(1a)	-3.8	-3.8	-1.9	-.62	-.62	0	0	0	0	0
(1b)	"	"	"	"	"	0	-1.	0	0	0
(1c)	"	"	"	"	"	-1.	"	0	0	0
(1d)	"	"	"	"	"	"	"	.233	.233	0
(2)	-3.8	-3.94	"	-.722	-.518	0	0	0	0	0
(3)	-3.	-3.94	"	-1.16	-.08	-1.	-1.	.745	0	-.5(est.)

All the exchange integrals given in the above table and throughout this thesis are in units of electron volts. The trial numbers (1) through (3) correspond to the three hybridizations of this section.

The exchange integrals between two orbitals χ_i, χ_j of the VB theory are defined as $\langle \chi_i(1)\chi_j(2)|\mathcal{H}|\chi_i(2)\chi_j(1)\rangle$. $\mathcal{H}$ is the total Hamiltonian for the isolated molecule. The choices and means of determining the $J(\chi_i\chi_j)$ were:

$$(1) \quad J(p_i p_j) = \begin{cases} -1.24 & (1.54\ \text{Å})\ (28) \\ -1.9 & (1.395\ \text{Å})\ (26) \\ -2.27 & (1.34\ \text{Å})\ (30) \\ (-2.46) & \quad '' \qquad\quad '' \end{cases}$$

$J(p_i p_j) = -1.9$ was used for the allyl section.

(2) The perpendicular distance between the π-orbitals, p_3 and p_5, and an axis in the z-direction through the methylene carbon was taken to be 1.54 Å. Using only the p_z component of the hybrids σ_2 and σ_6, one finds that

$$J(p_3\sigma_2) = J(p_5\sigma_2) = J(p_i p_j)(1 - 2a^2 - b^2)(1 - 2a^2)^{-1}$$

$$J(p_3\sigma_6) = J(p_5\sigma_6) = J(p_i p_j)(b^2)(1 - 2a^2)^{-1}$$

where $J(p_i p_j) = -1.24$.

The other components of $J(p_3\sigma_2)$, etc., are very small (15), (28). It has been assumed in estimating these integrals that the methylene protons in CB experience hindered rotation as they do in cyclobutyl. The latter fact has been verified by the extraordinarily large splittings of the β-protons found in cyclobutyl. Their hyperfine splittings are 38g as compared to the value of 25g for a radical in which the methylene group is freely rotating (Section I).

(3) $J(h_1 h_7) = -1.$ (31). This is 85% of the dissociation energy of H_2 (32). The distance between the two β-protons does not vary sufficiently to require a significant change in this estimate between trials (1) and (3).

(4) $J(h_1\sigma_6) = J(h_7\sigma_2) = +.233$, for tetrahedral hybridization (31),

$J(h_1\sigma_6) = +.745$, as the exchange integral between a π-orbital and a σ-proton.

$J(h_7\sigma_2)$ in trial (3) is only a rough approximation.

(5) $$J(\sigma_2\sigma_6) = \begin{cases} -1., & \text{for tetrahedral hybridization (31), (33);} \\ .88, & \text{for } sp^3 \text{ hybridization (34);} \\ 1.707, & \text{'' '' '' (30).} \end{cases}$$

Use of $J(\sigma_2\sigma_6)$ = .88 in trial (3) would most likely give an even more negative spin density on the nearly in-plane β-proton. This idea is based on the fact that a positive value of $J(\sigma_2\sigma_6)$ leads to negative spin densities on the σ-proton of the C-H fragment in a first-order calculation (14).

$$(6)\quad J(h_1\sigma_2) = b^2N_{ss} + b(1-b^2)^{\frac{1}{2}}(2N_{s\sigma}) + (1-b^2)N_{\sigma\sigma}$$

$$J(h_7\sigma_6) = (1-2a^2-b^2)N_{ss} + (1-2a^2-b^2)^{\frac{1}{2}}(2a^2+b^2)^{\frac{1}{2}}(2N_{s\sigma}) + (2a^2+b^2)N_{\sigma\sigma}$$

N_{ss} = -2.
$N_{s\sigma}$ = -1.82
$N_{\pi\pi}$ = .60
$N_{\sigma\sigma}$ = -2.30

The expressions are Van Vleck's formula for J(ch) in terms of the hybridization coefficients of σ_2 and of σ_6 (35), (28). Corresponding to the trials above, the following electron spin densities were calculated. (The rules used to calculate the isotropic hyperfine splittings were:

a_h = (507.6g)·(spin density on the proton) (20);
a_h = (22.5g)·(" " in " π-orbital of the same carbon atom).)

Trial No.	Spin density (splitting of appropriate proton in gauss)				
	Methylene proton	Methylene carbon hybrid	π-orbitals (allyl)		
1a	.122 (62)	-.110	.653	(14.7),	-.333 (7.5)
1b	.106 (54)	-.095	.65	(14.6),	"
1c	.088 (45)	-.080	.66	"	"
1d	.082 (42)	-.075	"	"	"
(2)	.145 (74); .096(49)	-.128; -.088	.65	"	"
(3)	.199 (100); -.06(3)	-.174; .072	.645	(14.5)	"

A better estimate of the isotropic hyperfine splittings of the σ-protons is probably that obtained using the SCF theory spin densities of .622 and -.231 for the π-orbitals (9). Then the splittings due to the σ-protons would be 14g (ortho protons) and 5.2g.

In view of the fact that an overcorrelation (relative to "experimental" spin densities) is nearly always observed in VB calculations employing the full set of CS's (28, 27), the first-order result should be considered, too. The first order result is obtainable in this case from eq. 4 on p. 30. The spin density on each of the β-protons for the case of hindered rotation is found to be .130, corresponding to a hyperfine splitting of 66.2g. Without rotational hindrance, this spin density is .087; the splitting 44.2g. The same integrals were used to obtain this result as in trial (1a). If the first-order results and the variational results differed significantly, one would be inclined to choose the former since it has been found empirically (15, 16, 20, 27) that the use of the minimum set of exchange integrals in a first-order calculation gives good agreement with experiment.

That agreement between the two types of calculations does not prevail in all studies of β-proton spin densities is well illustrated by the VB variational calculation on the β-proton spin densities in MCAALCP (28). There the π-β-proton fragment results (obtained by the variational VB) were multiplied by the SCF estimate of the spin density on a terminal π-orbital in the allyl radical (.622) in order to estimate the β-proton spin densities of MCAALCP. This approach has two major drawbacks: (1) the β-proton spin densities of MCAALCP are dependent on the π-electron excitation energies and the Q of the π-β-proton fragment is consequently larger than the true Q, and (2) the Q which was obtained for the π-β-proton fragment itself is much too large. One may deduce from the results in (28) that $Q_{\pi\text{-}\beta\text{-proton}} \approx 41.1g$, whereas the actual $Q_{\pi\text{-}\beta\text{-proton}} \approx 24.7g$ (13). The first-order estimate obtained in Section IV for $Q_{\pi\text{-}\beta\text{-proton}}$ is 25g.

A sketch of the ESR spectrum of CB, as a line spectrum, using the values $a_{h_\beta} = 42g$, $a_{h_\sigma\text{-ortho}} = 14g$, $a_{h_\sigma\text{-non-ortho}} = 5.2g$ is given below (Fig. 2). The results of the variational calculation on CB are graphed on the next page (Fig. 3).

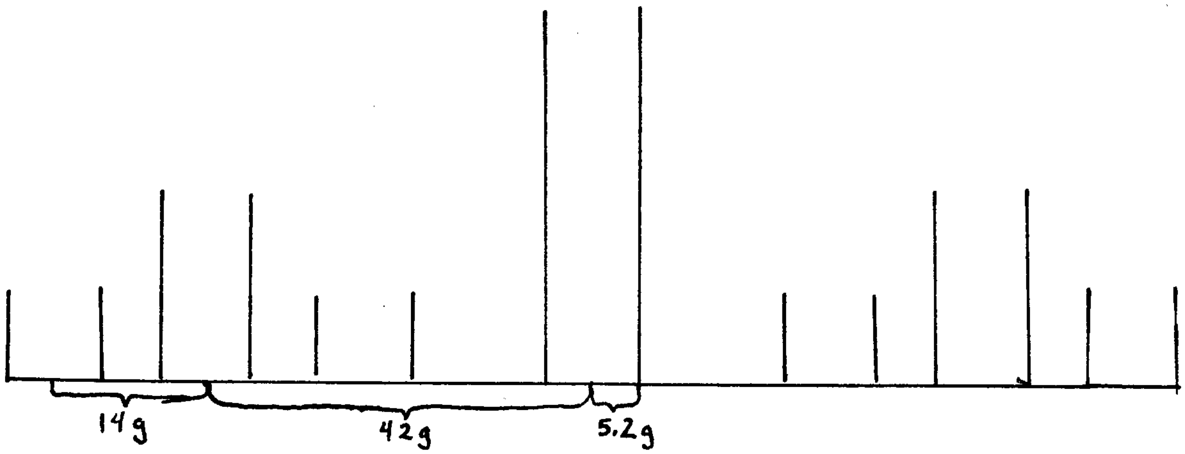


Fig. 2

Should isotropic inequalities appear in the ESR hyperfine splittings of the β-protons in CB, the nature of the contortion occurring at the methylene carbon could be estimated from this graph, as was done in the case of MCAALCP.

Other information available from the variational calculation on CB is:

(1) Inclusion of an increased number of exchange integrals tends to lower the spin density on the β-protons.

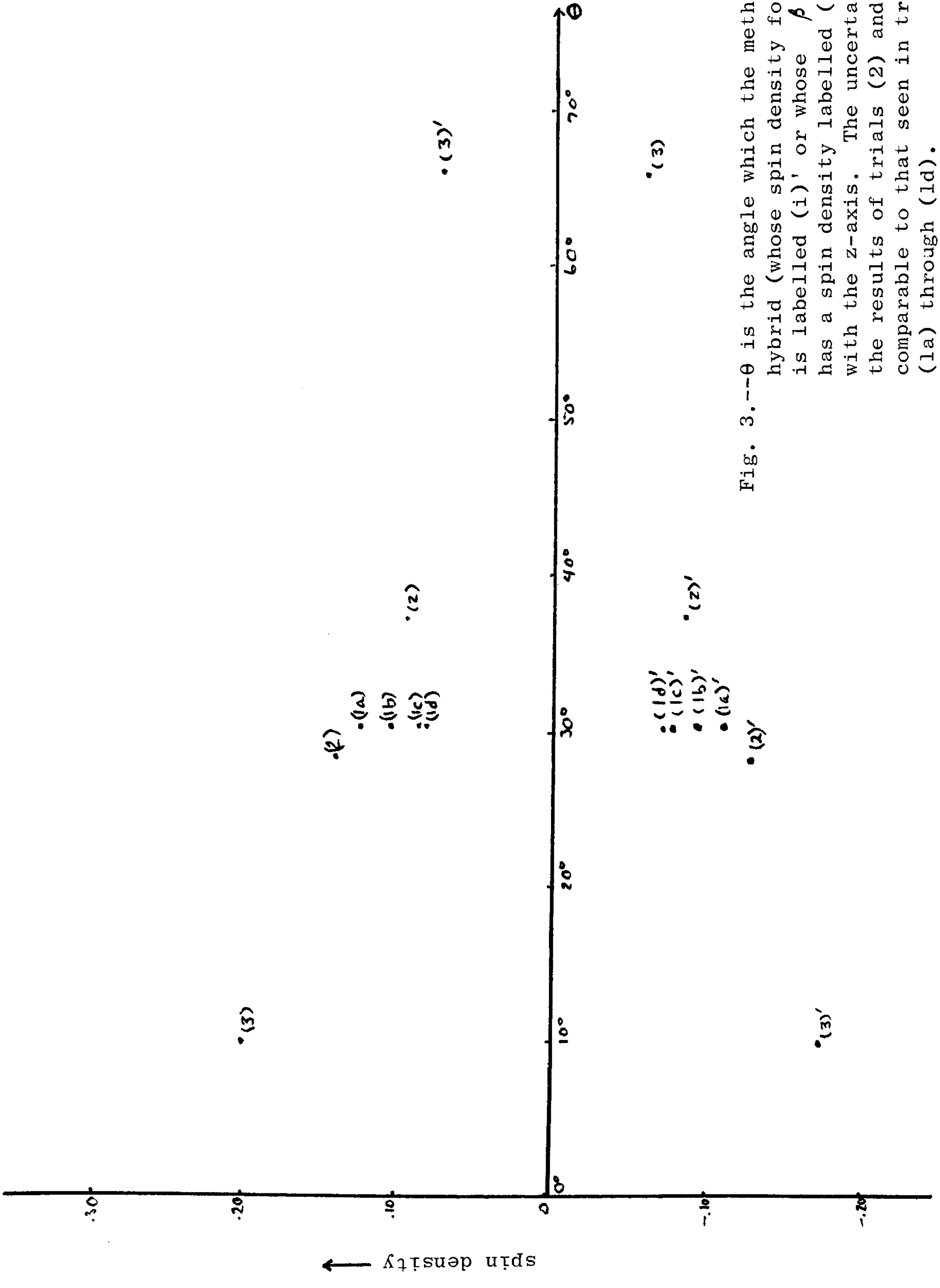


Fig. 3.--θ is the angle which the methylene hybrid (whose spin density for trial i is labelled (i)' or whose β-proton has a spin density labelled (i)) makes with the z-axis. The uncertainty in the results of trials (2) and (3) is comparable to that seen in trials (1a) through (1d).

(2) The methylene carbon σ-orbital spin densities show a decrease in magnitude relative to that of the proton spin densities. This effect may be important in ^{13}C splittings, though polarization of the 1s electrons seems to be an adequate explanation of the reduction in spin density on the ^{13}C nucleus, as long as there is a π-orbital at the same carbon (20). But otherwise, large discrepancies appear (36).

(3) A negative spin density of the same order of magnitude as that appearing on the in-plane σ-proton of the C-H "fragment" may appear on an in-plane β-proton.

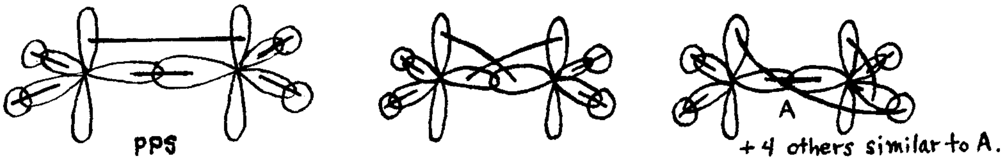
(4) There is a considerable increase in β-proton spin density when one assumes a small attractive exchange integral between the π-orbitals and a β-proton (trial (3)).

This last effect, though mentioned (37, 12) as a primary contributor to β-proton spin densities appears not to have been calculated before. This effect is a direct rather than an indirect coupling of the π-orbital electron spin to that of the β-proton. However the need for the existence of this phenomenon, originally cited to explain a discrepancy between theory and experiment in the case of the β-proton splittings of cyclohexadienyl (38), has been removed (28b).

A shortening of the methylene carbon-ortho-carbon distances (from 1.54 A) would enhance the magnitude of the spin density appearing on the β-protons of CB. If the distance is only 1.395 A (and J(PP) = -1.9), then the first-order result for the β-proton splittings in CB is 101g (hindered rotation).

IV. REQUIREMENTS ON THE WAVE FUNCTIONS USED IN FIRST-ORDER PERTURBATION THEORY CALCULATIONS OF THE SPIN DENSITIES OF THE β-PROTONS ; A CALCULATION ON THE CYCLOBUTENYL RADICAL DEMONSTRATING THE DEPENDENCE OF THE SPIN DENSITIES OF ITS β-PROTONS ON THE π-ELECTRON EXCITATION ENERGIES

Certain functions belonging to an incomplete set of canonical states give more accurate results in predicting various Q's using first-order perturbation theory than if a complete set of functions had been used. These functions are linear combinations of the perfect-pairing state (PPS) and the singly broken-bond states of conventional VB theory. Such functions, together with the PPS, had proven to be an adequate set for the calculation of energy levels of aromatic hydrocarbons, prior to their use in computing the spin densities on σ- or β-protons of aromatic free radicals. One of the best known VB calculations (of reasonable accuracy) on the energy levels of an aromatic molecule is that of Altman on ethylene (30). The PPS and five singly broken-bond structures, employed in Altman's variational calculation on ethylene, were:



The complete set of CS's for such a twelve orbital system is 132, as given by Rumer's rule (discussed later in this section). Similar reductions in the size of the basis set, as used in first-order calculations of the spin densities of σ- or β-protons in aromatic free radicals were subsequently shown to give close agreement with experiment. Two classic examples were the π-methyl (15) and the C-H fragment (14) calculations. The π-methyl study involved only five canonical CS's out of the 42 possible CS's for a ten orbital system.

The particular linear combination of PPS and the broken-bond states to be used as excited states of a first-order perturbation expansion should satisfy the following criteria:

(1) They must be diagonal in the energies (expressed as exchange integrals) which involve orbitals of the bonds of the PPS. (Bonds are distinguished by the fact that the spins of the two electrons in a bond are coupled to form a singlet state of themselves.) Such integrals in aromatic free radicals are J(ch) and $J(\pi\pi)$.

(2) The functions of an <u>incomplete</u> set must be orthonormal; otherwise, the spin densities calculated by first-order perturbation expansion theory are not invariant upon a unitary transformation of the basis functions. The CS's are nonorthogonal and hence are not suitable for the use in first-order perturbation theory on an incomplete set.

Requirements (1) and (2) are both satisfied if the excited state, which is a linear combination of the PPS and a particular singly broken-bond state, has a triplet pairing of the spins of the electrons at the site of the broken-bond. The signed exchange integral of a bond with a triplet pairing is simply minus that of the bond with a singlet pairing. Orthogonality of the states is guaranteed by the fact that two spin states, orthogonal in at least one bond factor of an overall spin function, are orthogonal. Using identity (2) of Section II, one finds that the linear combination ex_{bb} ($\frac{1}{2}$PPS - singly broken-bond state) is an eigenfunction of $S^2_{\text{broken-bond}} = 2$. (The total spin of both the PPS and of the singly broken-bond state is still 0 (or $\frac{1}{2}$, if one orbital is a phantom).) The Pauling island overlap coefficients (given in Appendix II) for the CS's are useful in checking the orthogonality of CS expansions of the ex_{bb}'s.

The first-order calculation on CB utilized the same seven orbital model as the variational treatment (Section III). Tetrahedral hybridization of the methylene carbon was assumed and the same set of exchange integrals as in trial (1a) employed. The perturbation expansion used linear combinations of the PPS and the singly broken-bond states, satisfying requirements (1) and (2) above. The use of these particular functions allows one to describe the origin of spin density on the methylene protons as due to an excited triplet in a particular C-H bond (15, 17). (The same reasoning is also applicable to the σ-proton of the C-H fragment (17).) This dependence is evident in the following results on the π-methyl radical.

$$\psi = \psi_0 + \frac{J(c_1 p)}{2J(c_1 t_4)}\left[\psi_4 - \tfrac{1}{2}\psi_0\right] + \sum_{r=1,2,3} \frac{J(t_r p)}{2J(t_r h_r)}\left[\psi_r - \tfrac{1}{2}\psi_0\right],$$

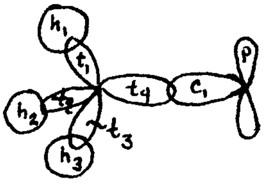
where $\psi_0 = (t_1 h_1)(t_2 h_2)(t_3 h_3)(t_4 c_1)p$

$\psi_1 = (t_1 p)(\;"\;)(\;"\;)(\;"\;)h_1$

$\psi_2 = (t_1 h_1)(t_2 p)(\;"\;)(\;"\;)h_2$

$\psi_3 = (\;"\;)(t_2 h_2)(t_3 p)(\;"\;)h_3$

$\psi_4 = (\;"\;)(\;"\;)(t_3 h_3)(c_1 p)h_4.$



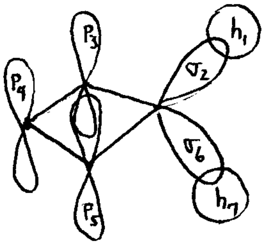
$\rho_{h_i} = -\rho_{t_i} = \frac{J(t_i p)\rho_p}{2J(t_i h_i)} = 25g/\ 507.6g$ (free rotations assumed, so $J(t_1 p) = \frac{1}{2}(-1.24)$; $J(t_1 h_1) = -3.75$) (eq. 3)
$(i \neq 4)$

$\rho_{c_1} = -\rho_{t_4} = \pm\frac{J(c_1 p)\rho_p}{2J(c_1 t_4)}$ (eq. 3a)

Comparable results for CB, obtained by the vector-coupling approach and assuming again that the major contribution to the methylene proton spin densities will arise from single triplets in the C-H bonds were:

$$\psi = \frac{1}{\sqrt{3}}(J+M) + \frac{(-I_{32}+I_{13}-I_{25}+I_{15})}{(A^S_{12}+A^T_{12}+B)}\left(\frac{\sqrt{2}}{3}\right)(J-(E+G))$$
$$+ \frac{(-I_{36}+I_{37}-I_{56}+I_{57})}{(A^S_{76}+A^T_{76}+B)}\left(\frac{\sqrt{2}}{3}\right)(M-(H+D)),$$

where
$$\begin{aligned} J &= (h_1\sigma_2)(h_7\sigma_6)(p_3p_4)p_5 \\ E &= (h_1p_4)(\;''\;)(p_3\sigma_2)p_5 \\ G &= (p_5\sigma_2)(\;''\;)(p_3p_4)h_1 \\ M &= (h_1\sigma_2)(\;''\;)(p_5p_4)p_3 \\ H &= (\;''\;)(p_3\sigma_6)(\;''\;)h_7 \\ D &= (\;''\;)(p_5\sigma_6)(h_7p_4)p_3, \end{aligned}$$



$$\rho_j = -\rho_i = \frac{2}{3}\left[\frac{-I_{3j}+I_{3i}-I_{5j}+I_{5i}}{A^t_{7j}+A^S_{7j}+B}\right],\ i,j=7,6;\ 1,2\ ;\ \rho_j = \begin{cases} .083 \text{ (unhindered rotation)} & \text{(eq. 4).} \\ .130 \text{ (hindered ")} \end{cases}$$

where I_{ij} = the exchange integral between orbitals i, j; $I_{23} = \begin{cases} -.62 \text{ (freely moving)} \\ -.93 \text{ (hindered).} \end{cases}$

A^S_{ij} = " " " for a C-H bond (singlet) = -3.80;

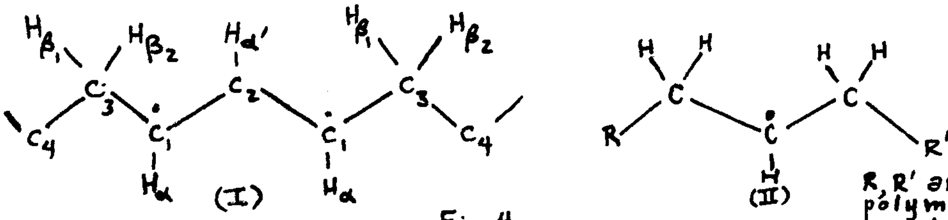
A^t_{ij} = " " " " " " " (triplet) = -3.80.

B = " " " between p_3 and p_4, or p_5 and p_4 = -1.9.

Diagrams for the functions J, C, G, M, N, D were given in Section II.

It is evident that the contribution of the π-electron excitation energy tends to lower the magnitude of the coupling constant Q between the spin of a π-orbital and the hyperfine splittings of its β-protons in CB as compared to the π-methyl radical. This is a factor of the right magnitude to explain the decrease of 3g between the high temperature splittings of the β-protons of MCAALCP (Fig. 4, I) (9) and one with a single π-orbital (Fig. 4, II) (13). The two splittings are 21.3g and 24.6g, respectively, and are estimated from first-order calculations (using the same exchange integrals and the free rotation character of long-chain polymers) to be 22g and 25g. The calculation appropriate to radical

(II) has been given in eq. 3.



(I)

(II)

Fig. 4

R, R' are polymer continuations.

For radical I, eq. 2 becomes:

$$\rho_1 = \rho_7 = -\rho_6 = -\rho_2 = -\frac{2}{3}\,\frac{[-I_{36} + I_{37}]}{A^t_{76} + A^s_{76} + B} = \frac{2}{3}\,\frac{[-.62]}{-9.5} = .0428$$

a_{h_β} = 22.1g (a_h for a single electron in the 1s orbital of hydrogen is 507.6g (20)).

B = -1.9
A^s_{76} = A^t_{76} = -3.80
I_{36} = $\frac{1}{2}$ (-1.24) (I_{36} is the average of J(pp) (1.54 Å) over "free rotation".)

(The symmetry appropriate to cyclobutenyl was explicitly expressed in eq. 4, but one needs merely to omit the terms I_{15}, I_{25}, I_{65}, I_{75}, say, to obtain the equation applicable to radical (I). There is difficulty in assessing the proper value of I_{36} because the long-chain polymer radical (II) has a lower a_{h_β} than does a similar molecule, $C_2H_5\dot{C}HC_2H_5$, which presumably has freer motion in its β-protons (24.8g as compared to 28.8g (13)). However, the relative values of a_{h_β} for (I) and (II) do show an effect, which may be attributed to the presence of allyl in (I).

The results of eq. 4, which indicate a dependence of the β -proton hyperfine splittings on the π -electron-excitation energies (in the appearance of the B exchange integrals in the energy denominators) extend previous theoretical conclusions (17). The most direct means of proving that the π -electron-excitation energies do contribute is to use vector-coupling functions. Vector-coupling functions may be defined as the spin functions of two or more electrons, which are constructed by coupling the spins of every two electrons to form "particles" of spin 1 or 0, repeating the spin coupling process on the spins of these "particles", and then continuing this procedure until there is only one uncoupled spin angular momentum vector. In this section, the vector-coupling functions are all spin doublet states. As an example of these functions, the PPS and one $ex_{bb'}$ such as discussed above, constitute the two possible vector-coupling singlet states for a four electron system.

The simplest case in which the effect of π-electron-excitation energies appear is that of a system of three " π " electrons and two " σ ". electrons, the latter in a C-H bond. There are two ways to couple the spins of the three electrons so as to get a doublet spin state (the notation is $\left|{S \atop M_S}\right\rangle$):

$$\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{I} = \frac{1}{\sqrt{2}}\left[\alpha\beta\alpha - \beta\alpha\alpha\right]$$

$$\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{II} = \frac{1}{\sqrt{3}}\left[\frac{\alpha\beta\alpha + \beta\alpha\alpha}{\sqrt{2}} - \sqrt{2}\,\alpha\alpha\beta\right] = \frac{1}{\sqrt{6}}\left[\alpha\beta\alpha + \beta\alpha\alpha - 2\alpha\alpha\beta\right]$$

$\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{II}$ is a doublet state which is orthogonal to $\left|{\frac{3}{2} \atop \frac{1}{2}}\right\rangle$, obtained by application of the spin lowering operators to $\left|{\frac{3}{2} \atop \frac{3}{2}}\right\rangle = \alpha\alpha\alpha$. In terms of the spin of a composite "particle" whose spin is either 1 (triplet) or 0 (singlet), these spin states and the relations between them are:

$$\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{I} = \left|{0 \atop 0}\right\rangle\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle,$$

$$\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{II} = \frac{1}{\sqrt{3}}\left[\left|{1 \atop 0}\right\rangle\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle - \sqrt{2}\left|{1 \atop 1}\right\rangle\left|{\frac{1}{2} \atop -\frac{1}{2}}\right\rangle\right]$$

$$\text{obtained from } \left|{\frac{3}{2} \atop \frac{3}{2}}\right\rangle = \left|{1 \atop 1}\right\rangle\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle,$$

$$\left|{\frac{3}{2} \atop \frac{1}{2}}\right\rangle = \frac{1}{\sqrt{3}}\left[\sqrt{2}\left|{1 \atop 0}\right\rangle\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle + \left|{1 \atop 1}\right\rangle\left|{\frac{1}{2} \atop -\frac{1}{2}}\right\rangle\right].$$

To achieve an unpaired spin density on the σ-protons of a C-H fragment (a model system consisting of the p_z and σ orbitals of a carbon atom in an aromatic hydrocarbon radical), it is necessary to mix the "ground-state" wave function, which has the spin function $\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{I}$, with the "excited state" having the spin function $\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{\mathrm{II}}$. The energies of these two states, in first order, are J(ch) (ground-state) and -J(ch) (excited state). (J(ch) is negative.) The perturbation is due to σ-π interaction, the matrix element of which is proportional to $(-J(p_z\sigma) + J(p_z h))$. If $\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{\mathrm{II}}$ is neglected as a possible doublet spin function for the three "π"-electrons, then the excited states of the "σ"-electrons are the only ones affecting the σ-proton spin density. But this truncation of the first-order perturbation expansion is too severe.

The π-electron excitation energies are expected to appear in the more complete expansion because the energies of π-electron wave functions with spin functions $\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{\mathrm{I}}$ and $\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{\mathrm{II}}$ are not the same even in first order. Let ψ_{I} correspond to $\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{\mathrm{I}}$, ψ_{II} to $\left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{\mathrm{II}}$. Then

$$\langle\psi_{\mathrm{I}}|\mathcal{H}|\psi_{\mathrm{I}}\rangle = \left\langle \left\| \pi_1\pi_2\pi_3 \left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{\mathrm{I}} \right\| \middle| \mathcal{H} \middle| \left\| \pi_1\pi_2\pi_3 \left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{\mathrm{I}} \right\| \right\rangle \qquad \text{(eq. 5)}$$

$$= \tfrac{1}{2}(\uparrow\downarrow\uparrow - \downarrow\uparrow\uparrow) * (\uparrow\downarrow\uparrow - \downarrow\uparrow\uparrow)$$

$$= \tfrac{1}{2}[J(pp) + J(pp) - J(pp)] = \frac{J(pp)}{2} \qquad \text{(eq. 6)}$$

$\uparrow\uparrow\downarrow$ represents a Slater determinant in which the spin-orbital of column one has spin $\frac{1}{2}$; that of column two, spin $\frac{1}{2}$; and that of column three, spin $-\frac{1}{2}$. The results of the operation * on the various products of three arrows is given in Table I below. The result in eq. 6 may be calculated by direct manipulation of eq. 5, as well.

Similarly, for ψ_{II},

$$\langle\psi_{\mathrm{II}}|\mathcal{H}|\psi_{\mathrm{II}}\rangle = \left\langle \left\| \pi_1\pi_2\pi_3 \left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{\mathrm{II}} \right\| \middle| \mathcal{H} \middle| \left\| \pi_1\pi_2\pi_3 \left|{\frac{1}{2} \atop \frac{1}{2}}\right\rangle_{\mathrm{II}} \right\| \right\rangle$$

$$= \tfrac{1}{3}\left[\frac{\uparrow\downarrow\uparrow + \downarrow\uparrow\uparrow}{\sqrt{2}} - \sqrt{2}\,\uparrow\uparrow\downarrow\right] * \left[\frac{\uparrow\downarrow\uparrow + \downarrow\uparrow\uparrow}{\sqrt{2}} - \sqrt{2}\,\uparrow\uparrow\downarrow\right]$$

$$= \tfrac{1}{3}\left[\frac{\uparrow\downarrow\uparrow * \uparrow\downarrow\uparrow + 2\,\downarrow\uparrow\uparrow * \uparrow\downarrow\uparrow + \downarrow\uparrow\uparrow * \downarrow\uparrow\uparrow}{2} + 2(\uparrow\uparrow\downarrow * \uparrow\uparrow\downarrow)\right.$$

$$\left. - 2(\uparrow\uparrow\downarrow * \uparrow\downarrow\uparrow + \uparrow\uparrow\downarrow * \downarrow\uparrow\uparrow)\right]$$

$$= \tfrac{1}{3}\left[-J(pp) - \frac{J(pp)}{2} - 2J(pp) + 2J(pp)\right] = -J(pp).$$

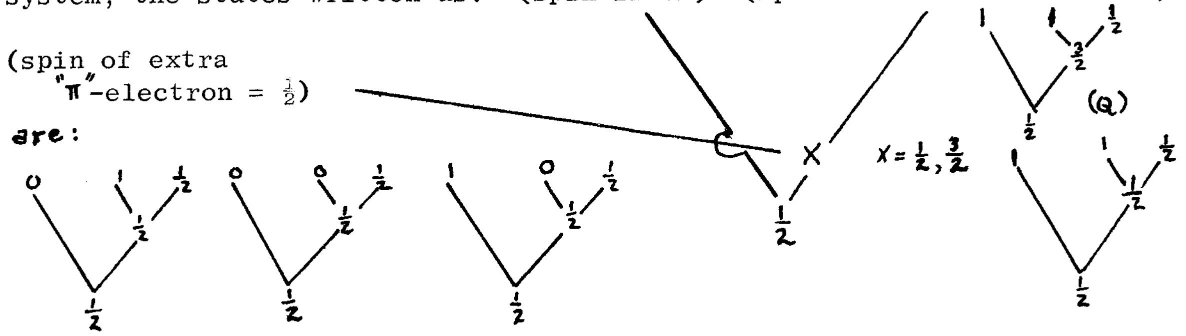
Let the order of the arrows, from left to right, in the above symbolic notation for Slater determinants correspond to the ordering p_3 p_4 p_5 ($p \equiv \pi$) of the space portions of the spin-orbitals. Considering only exchange integrals between p_3 and p_4, and between p_4 and p_5, one will get contributions to $\langle \mathcal{H} \rangle$ from the exchange integrals $J(p_3 p_4)$ and $J(p_4 p_5)$ in accordance with the table:

TABLE 1

*	↑↑↑	↑↑↓	↑↓↑	↓↑↑	↑↓↓	↓↑↓	↓↓↑	↓↓↓
↑↑↑	$-B_{34}-\frac{B_{45}}{2}$							
↑↑↓		$-B_{34}$	$-B_{45}$					
↑↓↑				$-B_{34}$				
↓↑↑				$-B_{45}$				
↑↓↓					$-B_{45}$	$-B_{34}$		
↓↑↓							$-B_{45}$	
↓↓↑							$-B_{34}$	
↓↓↓								$-B_{34}-B_{45}$

Since the table is symmetric, only non-zero elements above the diagonal are given.

Finally, the vector-coupling diagrams describing this system of three "π"-electrons and two "σ"-electrons clarify the answers to the questions as to how many doublet states are possible and which have been considered. There are a total of five doublet states to a five electron system; the states written as: (spin in CH) (spin of two "π"-electrons)



The coupling diagram labelled (Q) has a quartet spin state in the "π"-electrons and can be excluded because of its high energy ($-J(ch) - 2J(pp)$) as compared to that of the ground state ($J(ch) + \frac{1}{2}J(pp)$).

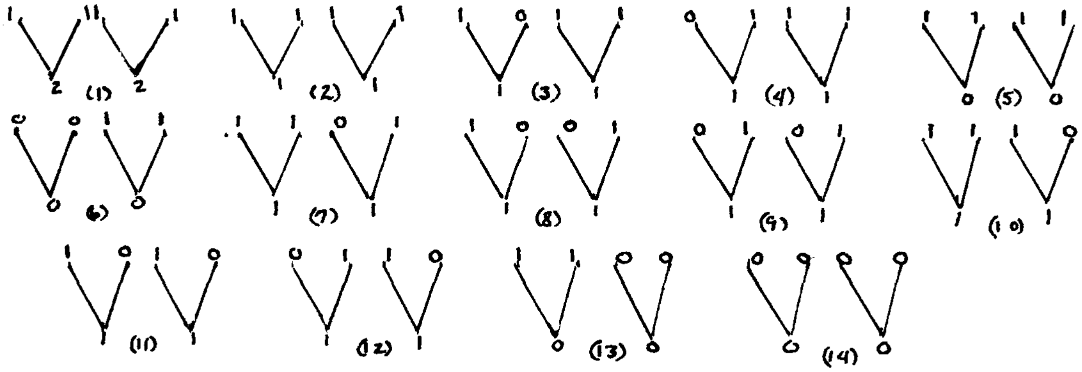
The essential point is that even in this simplest case, the spin densities of the β-protons depend on the excitation energies of the "π"-electrons as long as appropriate matrix elements of the spin density operator do not vanish. That these matrix elements do not vanish can be deduced from eq. 4, p 30 . The entire calculation of the spin densities of the β-protons of radical (II) and of CB will now be given.

The calculation begins with the formation of the fourteen possible singlet states for an eight electron system; in the VB theory, this total number is given by Rumer's rule (or directly by permutation group theory):

total number of VB singlets $= \frac{n!}{(\frac{n}{2})!\,((\frac{n}{2}+1))!}$, where n is the number of orbitals (26).

The singlet states, which are linear combinations of the VB CS's, are chosen to be eigenfunctions of S^2, $S^2_{``\sigma"}$ , and $S^2_{``\pi"}$. $S^2_{``\sigma"}$ and $S^2_{``\pi"}$ are the total spin angular momentum of the electrons in the methylene and π -orbitals subregions, respectively. One composes the various spin angular momentum states which result from the coupling of two particles of spin 1, or one particle of spin 1 and one of spin 0, or both of spin 0 (each of these having been obtained from the coupling of two particles of spin $\frac{1}{2}$). These form eigenfunctions of $S^2_{``\sigma"}$ and of $S^2_{``\pi"}$. The coupling is repeated to form functions of $S^2 = 0$.

This procedure is indicated schematically below (42).



The Clebsch-Gordan coefficients useful in expressing these states explicitly in terms of spin states of particles of spin $\frac{1}{2}$ are evident in the following equations (see also Appendix III):

$$|{2 \atop 2}\rangle = |{1 \atop 1}\rangle |{1 \atop 1}\rangle$$

$$|{2 \atop 1}\rangle = \frac{1}{\sqrt{2}}\left[|{1 \atop 1}\rangle |{1 \atop 0}\rangle + |{1 \atop 0}\rangle |{1 \atop 1}\rangle \right]$$

$$|{2 \atop 0}\rangle = \sqrt{\frac{2}{3}}\, |{1 \atop 0}\rangle |{1 \atop 0}\rangle + \frac{1}{\sqrt{6}} |{1 \atop 1}\rangle |{1 \atop -1}\rangle + \frac{1}{\sqrt{6}} |{1 \atop -1}\rangle |{1 \atop 1}\rangle$$

$$|{1 \atop 1}\rangle = \frac{1}{\sqrt{2}}\left[|{1 \atop 1}\rangle |{1 \atop 0}\rangle - |{1 \atop 0}\rangle |{1 \atop 1}\rangle \right]$$

$$|{1 \atop 0}\rangle = \frac{1}{\sqrt{2}}\left[|{1 \atop 1}\rangle |{1 \atop -1}\rangle - |{1 \atop -1}\rangle |{1 \atop 1}\rangle \right]$$

$$|{0 \atop 0}\rangle = \frac{1}{\sqrt{3}}\left[|{1 \atop 1}\rangle |{1 \atop -1}\rangle - |{1 \atop 0}\rangle |{1 \atop 0}\rangle + |{1 \atop -1}\rangle |{1 \atop 1}\rangle \right]$$

Once proper eigenfunctions were constructed, they were resolved, for calculation convenience, into linear combinations of the CS's. This problem is discussed in Section V for all fourteen states. The results of interest for this first-order perturbation calculation, in which no excited states with two triplet pairings in the methylene region were included, are:

TABLE 2

eigenfunction	eigenvalue energy
$(14) = J$	$A^{S}_{12} + A^{S}_{67} + B_{34} - \frac{1}{2}B_{45}$
$(13) = \frac{1}{\sqrt{3}}(J - 2M)$	$A^{S}_{76} + A^{S}_{12} - B_{34} + \frac{1}{2}B_{45}$
$(12) = \frac{1}{\sqrt{3}}(J - 2G)$	$A^{S}_{76} - A^{T}_{12} + B_{34} - \frac{1}{2}B_{45}$
$(11) = \frac{1}{\sqrt{3}}(J - 2E)$	$A^{S}_{76} - A^{T}_{12} - B_{34} - \frac{1}{2}B_{45}$
$(10) = \sqrt{\frac{2}{3}}[(J + 2A) - (G + E + M)]$	$A^{S}_{76} - A^{T}_{12} - B_{34}$
$(9) = \frac{1}{\sqrt{3}}(J - 2B)$	$A^{S}_{12} - A^{T}_{76} + B_{34} - \frac{1}{2}B_{45}$
$(8) = \frac{1}{\sqrt{3}}(2(M + B - D - H) - J)$	$A^{S}_{12} - A^{T}_{76} - B_{34} - \frac{1}{2}B_{45}$
$(7) = \sqrt{\frac{2}{3}}(H - D)$	$A^{S}_{12} - A^{T}_{76} - B_{34}$

The energies were calculated using Rule 1 of Section III. One way to verify that the eigenvalues given in Table 2 are indeed correct is to calculate directly the eigenvalues of the doublet states to which the states (10) through (14) correspond. The energies of states of (7), (8), and (9) are then readily deducible from those of (10), (11), and (12), respectively. Only the B-type integrals will be considered since the correct coefficients of the A's (either plus or minus one) can be determined by inspection. Using earlier notation and results in this section, we have:

$$(14)*(14) = \tfrac{1}{2}\left[(\uparrow\downarrow - \downarrow\uparrow)\uparrow\right] * \left[(\uparrow\downarrow - \downarrow\uparrow)\uparrow\right] = B_{34} - \frac{B_{45}}{2}$$

$$(13)*(13) = \tfrac{1}{3}\left[|{}^{1}_{0}\rangle\uparrow - \sqrt{2}\,|{}^{1}_{1}\rangle\downarrow\right] * \left[|{}^{1}_{0}\rangle\uparrow - \sqrt{2}\,|{}^{1}_{1}\rangle\downarrow\right]$$

$$= \tfrac{1}{3}\left[\frac{\uparrow\downarrow\uparrow*\uparrow\downarrow\uparrow + 2\downarrow\uparrow\uparrow*\uparrow\downarrow\uparrow + \downarrow\uparrow\uparrow*\downarrow\uparrow\uparrow}{2} + 2(\uparrow\uparrow\downarrow*\uparrow\uparrow\downarrow) - 2(\uparrow\uparrow\downarrow*\uparrow\downarrow\uparrow + \uparrow\uparrow\downarrow*\downarrow\uparrow\uparrow)\right]$$

$$= \tfrac{1}{3}\left[-B_{34} - \frac{B_{45}}{2} - 2B_{34} + 2B_{45}\right] = -B_{34} + \frac{B_{45}}{2} = (13)*(13).$$

(10), (11), and (12) are linear combinations of doublet functions, two of which arise from a quartet state of the allyl section ((10) and (11)), one from a doublet state of the allyl section (12).

$$(12) = \frac{1}{\sqrt{3}}\left[\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_A \left|\begin{smallmatrix}1\\ 0\end{smallmatrix}\right\rangle_M - \sqrt{2}\left|\begin{smallmatrix}\frac{1}{2}\\ -\frac{1}{2}\end{smallmatrix}\right\rangle_A \left|\begin{smallmatrix}1\\ 1\end{smallmatrix}\right\rangle_M\right] .$$

A labels the spin function appropriate to the electrons of the allyl section, M that of the methylene section.

In this case $\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_A = \frac{(s_3 - s_4)s_5}{\sqrt{2}}$, so (12) has the same coefficients of B_{34} and B_{45} as does (14). (10) and (11) are linear combinations of the two doublet states, one of which arises from $\left|\begin{smallmatrix}\frac{5}{2}\\ \frac{5}{2}\end{smallmatrix}\right\rangle = \left|\begin{smallmatrix}\frac{3}{2}\\ \frac{3}{2}\end{smallmatrix}\right\rangle_A \left|\begin{smallmatrix}1\\ 1\end{smallmatrix}\right\rangle_M$, the other from

$$\left|\begin{smallmatrix}\frac{3}{2}\\ \frac{3}{2}\end{smallmatrix}\right\rangle = \left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_A \left|\begin{smallmatrix}1\\ 1\end{smallmatrix}\right\rangle_M .$$

The doublet state arising from the latter state, $\left|\begin{smallmatrix}\frac{3}{2}\\ \frac{3}{2}\end{smallmatrix}\right\rangle$, is:

$$\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_I = \frac{1}{\sqrt{3}}\left[\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_A \left|\begin{smallmatrix}1\\ 0\end{smallmatrix}\right\rangle_M - \sqrt{2}\left|\begin{smallmatrix}\frac{1}{2}\\ -\frac{1}{2}\end{smallmatrix}\right\rangle_A \left|\begin{smallmatrix}1\\ 1\end{smallmatrix}\right\rangle_M\right] .$$

$\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_A$ is not the same function here as that used in (12). This fact may be deduced by inspection of the vector-coupling diagrams above. The doublet state obtained from $\left|\begin{smallmatrix}\frac{5}{2}\\ \frac{5}{2}\end{smallmatrix}\right\rangle$ is:

$$\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{II} = \sqrt{\frac{1}{2}}\left[\left|\begin{smallmatrix}\frac{3}{2}\\ \frac{3}{2}\end{smallmatrix}\right\rangle_A \left|\begin{smallmatrix}1\\ -1\end{smallmatrix}\right\rangle_M - \sqrt{\frac{2}{3}}\left|\begin{smallmatrix}\frac{3}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_A \left|\begin{smallmatrix}1\\ 0\end{smallmatrix}\right\rangle_M + \frac{1}{\sqrt{3}}\left|\begin{smallmatrix}\frac{3}{2}\\ -\frac{1}{2}\end{smallmatrix}\right\rangle_A \left|\begin{smallmatrix}1\\ 1\end{smallmatrix}\right\rangle_M\right]$$

$\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_A$, $\left|\begin{smallmatrix}\frac{3}{2}\\ \frac{3}{2}\end{smallmatrix}\right\rangle_A$, and $\left|\begin{smallmatrix}\frac{3}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_A$, etc., are given by the following relations:

$$\left|\begin{smallmatrix}\frac{3}{2}\\ \frac{3}{2}\end{smallmatrix}\right\rangle = \left|\begin{smallmatrix}1\\ 1\end{smallmatrix}\right\rangle \left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle$$

$$\left|\begin{smallmatrix}\frac{3}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle = \frac{1}{\sqrt{3}}\left[\sqrt{2}\left|\begin{smallmatrix}1\\ 0\end{smallmatrix}\right\rangle \left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle + \left|\begin{smallmatrix}1\\ 1\end{smallmatrix}\right\rangle \left|\begin{smallmatrix}\frac{1}{2}\\ -\frac{1}{2}\end{smallmatrix}\right\rangle\right] \qquad \text{(eq. 7a)}$$

$$\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle = \frac{1}{\sqrt{3}}\left[\left|\begin{smallmatrix}1\\ 0\end{smallmatrix}\right\rangle \left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle - \sqrt{2}\left|\begin{smallmatrix}1\\ 1\end{smallmatrix}\right\rangle \left|\begin{smallmatrix}\frac{1}{2}\\ -\frac{1}{2}\end{smallmatrix}\right\rangle\right] \qquad \text{(eq. 7b)}$$

Hence,

$$\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_I = \frac{1}{3}\left[\cancel{\frac{s_{135} + s_{145} + s_{235} + s_{245}}{2}} - (s_{134} + s_{234}) + (s_{123} + s_{124}) - 2s_{125}\right]\frac{(s_7 - s_6)}{\sqrt{2}},$$

where $s_{ijk} \equiv s_i\, s_j\, s_k$.

$$\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{II} = \frac{1}{\sqrt{2}}\Big[s_{345} - \frac{1}{3}\big(s_{135} + s_{145} + s_{134} + s_{235} + s_{245} + s_{234}$$
$$- s_{125} - s_{123} - s_{124}\big)\Big]\frac{(s_7 - s_6)}{\sqrt{2}} .$$

After some expansion and cancellation, one finds that

$$(10) = \frac{1}{\sqrt{6}}\left[s_{124}-s_{125}-s_{134}+s_{123}+s_{345}-s_{234}\right]\frac{(s_7-s_6)}{\sqrt{2}}$$

$$(11) = \frac{1}{2\sqrt{3}}\left[-s_{135}-s_{245}-s_{235}-s_{145}+2(s_{345}+s_{125})\right]\frac{(s_7-s_6)}{\sqrt{2}}$$

$$\text{so}\quad (10) = \sqrt{\tfrac{2}{3}}\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{I}} + \sqrt{\tfrac{1}{3}}\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{II}}$$

$$(11) = -\sqrt{\tfrac{1}{3}}\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{I}} + \sqrt{\tfrac{2}{3}}\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{II}}$$

Now let the total wave functions of which $\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{I}}$, $\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{II}}$ are the spin functions be represented by $\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{I}}$, $\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{II}}$. Then considering only the coefficients of B_{34} and B_{45}, we have:

$$\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{II}} * \left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{II}} = \frac{1}{2}\left[\uparrow\uparrow\uparrow * \uparrow\uparrow\uparrow + \frac{1}{3}(\uparrow\downarrow\uparrow + \downarrow\uparrow\uparrow + \uparrow\uparrow\downarrow) * (\uparrow\downarrow\uparrow + \downarrow\uparrow\uparrow + \uparrow\uparrow\downarrow)\right]$$

$$= \frac{1}{2}\Big[-B_{34}-B_{45}+\frac{1}{3}\big((\uparrow\downarrow\uparrow * \uparrow\downarrow\uparrow + 2\uparrow\downarrow\uparrow \times \downarrow\uparrow\uparrow$$

$$+ 2\uparrow\downarrow\uparrow * \uparrow\uparrow\downarrow) + (\downarrow\uparrow\uparrow * \uparrow\downarrow\uparrow + \downarrow\uparrow\uparrow * \downarrow\uparrow\uparrow + 2\downarrow\uparrow\uparrow * \uparrow\uparrow\downarrow)$$

$$+ \uparrow\uparrow\downarrow * \uparrow\downarrow\uparrow + \uparrow\uparrow\downarrow * \downarrow\uparrow\uparrow + \uparrow\uparrow\downarrow * \uparrow\uparrow\downarrow\big)\Big]$$

$$= \frac{1}{2}\left\{\left[-1-\frac{2}{3}-\frac{1}{3}\right]B_{34}+\left[-1-\frac{2}{3}-\frac{1}{3}\right]B_{45}\right\} = -(B_{34}+B_{45})$$

$$\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{I}} * \left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{I}} = \frac{1}{3}\left[\frac{\uparrow\downarrow\uparrow + \downarrow\uparrow\uparrow}{\sqrt{2}} - \sqrt{2}\uparrow\uparrow\downarrow\right] * \left[\frac{\uparrow\downarrow\uparrow + \downarrow\uparrow\uparrow}{\sqrt{2}} - \sqrt{2}\uparrow\uparrow\downarrow\right]$$

$$= \frac{1}{3}\left[-B_{34}-\frac{B_{45}}{2}-2(\uparrow\uparrow\downarrow * \uparrow\downarrow\uparrow + \uparrow\uparrow\downarrow * \downarrow\uparrow\uparrow) + 2\uparrow\uparrow\downarrow * \uparrow\uparrow\downarrow\right]$$

$$= \frac{1}{3}\left[-B_{34}-\frac{B_{45}}{2}-2(-B_{45})+2(-B_{34})\right] = -B_{34}+\frac{B_{45}}{2}.$$

$$(11)*(11) = \frac{2}{3}\left[\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{II}} * \left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{II}}\right] + \frac{1}{3}\left[\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{I}} * \left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{I}}\right]$$

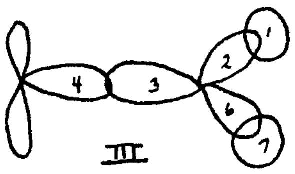
$$= -\frac{2}{3}(B_{34}+B_{45}) + \frac{1}{3}\left(-B_{34}+\frac{B_{45}}{2}\right) = -B_{34}-\frac{B_{45}}{2}.$$

$$(10)*(10) = \frac{2}{3}\left[\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{I}} * \left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{I}}\right] + \frac{1}{3}\left[\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{II}} * \left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{II}}\right]$$

$$= \frac{1}{3}\left[-(B_{34}+B_{45}) + \frac{2}{3}\left(-B_{34}+\frac{B_{45}}{2}\right)\right] = -B_{34}$$

(Note that $\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{I}} * \left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle_{\mathrm{II}} = -\frac{1}{3}\left[\left|\begin{smallmatrix}\frac{1}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle * \left|\begin{smallmatrix}\frac{3}{2}\\ \frac{1}{2}\end{smallmatrix}\right\rangle + \left|\begin{smallmatrix}\frac{1}{2}\\ -\frac{1}{2}\end{smallmatrix}\right\rangle * \left|\begin{smallmatrix}\frac{3}{2}\\ -\frac{1}{2}\end{smallmatrix}\right\rangle\right] = 0$, by equations (7a) and (7b)).

Clearly, the eigenfunctions of Table 2 do not contain the symmetry necessary for the CB problem, but a check on the spin densities for a fragment (III) gives exact agreement with the π-methyl calculation (reviewed on p. 30):



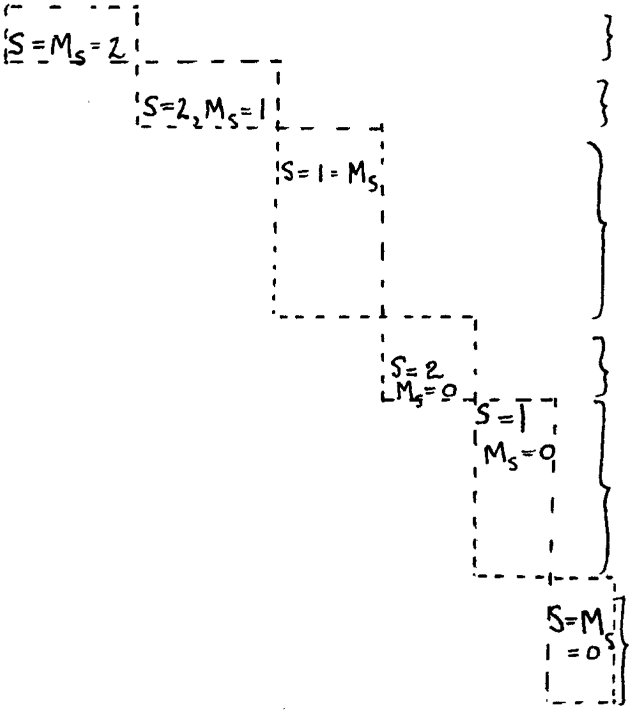
$$\rho_4 = -\rho_3 = \frac{I_{45} - I_{35}}{2B_{34}}$$

$$\rho_1 = -\rho_2 = \frac{I_{25} - I_{15}}{A^S_{12} + A^T_{12}}$$

$$\rho_7 \approx -\rho_6 = \frac{I_{65} - I_{75}}{A^S_{76} + A^T_{76}}$$

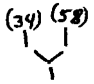
To continue the calculation beyond fragment (III), or a system in which the unpaired spin is localized on <u>one</u> orbital, it was necessary to form wave functions whose spin functions are linear combinations of the vector-coupling functions and whose transformation matrix for the rotation $\rho_3 \rightarrow -\rho_5$, $\rho_4 \rightarrow -\rho_4$, $\rho_5 \rightarrow -\rho_3$ is an irreducible representation of the rotation group C_2. Since the total wave functions in the zeroth-order approximation can be considered to be direct products (properly antisymmetrized) of the wave functions in the allyl and methyl regions, the transformation of the methylene part of the wave functions upon rotation will be considered separately.

It is a well-known fact that the transformations of the spin functions can be used to construct the irreducible representations of the rotation group. Hence it is convenient to know the following facts about spin functions and their irreducible representations (39). There are k + 1 irreducible representations which can be formed from the $\binom{n}{k}$ spin functions of the type $s_1 s_2 \ldots s_k$. (n is the total number of spin orbitals for n electrons; in $s_1 s_2 \ldots s_k$, an orbital assignment is explicitly designated only if the electron has spin $\frac{1}{2}$). Further, $k = \frac{1}{2}n - S$, $M_S = S_z = k$, and the irreducible representations for $k > \frac{n}{2}$ are symmetric with those of $k \leq \frac{1}{2}n$. The identity character of each of the k + 1 irreducible representations is $\binom{n}{k} - \binom{n}{k-1}$, as long as $k \leq \frac{1}{2}n$. Applying this formula, one finds that the dimension of the irreducible representation for $S = M_S = 0$ is two; for S = 1, M_S = 1, 0, -1, it is three. One can see that such must be the case from the following variations of the coupling of angular momentum 1 and 1, or 1 and 0, or 0 and 0.



$$|{}^{2}_{2}\rangle = |{}^{1}_{1}\rangle|{}^{1}_{1}\rangle$$

$$|{}^{2}_{1}\rangle = \tfrac{1}{\sqrt{2}}[|{}^{1}_{1}\rangle|{}^{1}_{0}\rangle + |{}^{1}_{0}\rangle|{}^{1}_{1}\rangle]$$

$$|{}^{1}_{1}\rangle = \tfrac{1}{\sqrt{2}}[|{}^{1}_{1}\rangle|{}^{1}_{0}\rangle - |{}^{1}_{0}\rangle|{}^{1}_{1}\rangle] =$$


$$|{}^{1}_{1}\rangle = |{}^{1}_{1}\rangle|{}^{0}_{0}\rangle =$$


$$|{}^{1}_{1}\rangle = |{}^{0}_{0}\rangle|{}^{1}_{1}\rangle =$$


$$|{}^{2}_{0}\rangle = \tfrac{1}{\sqrt{6}}[|{}^{1}_{1}\rangle|{}^{1}_{-1}\rangle + 2|{}^{1}_{0}\rangle|{}^{1}_{0}\rangle + |{}^{1}_{-1}\rangle|{}^{1}_{1}\rangle]$$

$$|{}^{1}_{0}\rangle = \tfrac{1}{\sqrt{2}}[|{}^{1}_{1}\rangle|{}^{1}_{-1}\rangle - |{}^{1}_{-1}\rangle|{}^{1}_{1}\rangle]$$

$$|{}^{1}_{0}\rangle = |{}^{1}_{0}\rangle|{}^{0}_{0}\rangle$$

$$|{}^{1}_{0}\rangle = |{}^{0}_{0}\rangle|{}^{1}_{0}\rangle$$

$$|{}^{0}_{0}\rangle = \tfrac{1}{\sqrt{3}}[|{}^{1}_{1}\rangle|{}^{1}_{-1}\rangle - |{}^{1}_{0}\rangle|{}^{1}_{0}\rangle + |{}^{1}_{-1}\rangle|{}^{1}_{1}\rangle]$$

$$|{}^{0}_{0}\rangle = |{}^{0}_{0}\rangle|{}^{0}_{0}\rangle$$

From these functions, one can construct the irreducible representations of $P_{(35)}$ for functions having S = 1:

$$P_{(35)} = \begin{pmatrix} 0 & -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & -\frac{1}{2} & -\frac{1}{2} \\ \frac{1}{\sqrt{2}} & -\frac{1}{2} & -\frac{1}{2} \end{pmatrix}$$

$P_{(35)}$ was constructed from the vector-coupling functions for S = 1 by calling s_3, s_5 and <u>vice versa</u>. One may work with the spin part of the wave functions in order to learn how the permutation of orbitals, i.e., space part only, alters the wave function, because the permutations P^S_{ij} and P_{ij}, which are spin and space orbital permutations of spin-orbitals i and j, respectively, satisfy the relation $P^S_{ij} = (-1)^x P_{ij}$ (Relation 1). x is the number of transpositions involved in permuting orbitals i and j, the numbers of their column position in any given Slater determinant. To see that this relation is true, consider the following:

$$P_{(12)}\begin{vmatrix} a_1(1) & \overline{a_2(1)} & \vdots \\ a_1(2) & \overline{a_2(2)} & \vdots \\ a_1(3) & \overline{a_2(3)} & \vdots \\ \vdots & \vdots & \vdots \end{vmatrix} = \begin{vmatrix} a_2(1) & \overline{a_1(1)} & \vdots \\ a_2(2) & \overline{a_1(2)} & \vdots \\ a_2(3) & \overline{a_1(3)} & \vdots \\ \vdots & \vdots & \vdots \end{vmatrix} = - \begin{vmatrix} \overline{a_1(1)} & a_2(1) & \vdots \\ \overline{a_1(2)} & a_2(2) & \vdots \\ \overline{a_1(3)} & a_2(3) & \vdots \\ \vdots & \vdots & \vdots \end{vmatrix} = P^S_{(12)}\begin{vmatrix} a_1(1) & \overline{a_2(1)} & \vdots \\ a_1(2) & \overline{a_2(2)} & \vdots \\ a_1(3) & \overline{a_2(3)} & \vdots \\ \vdots & \vdots & \vdots \end{vmatrix}$$

It will be noted that $P_{(35)}$ involves an odd number of transpositions.

To find how the vector-coupling functions transform under spatial rotations, one must consider the rotation of the space orbitals explicitly as well as relation (1). Rotation of the space orbitals of the allyl section of CB takes p_3 into $-p_5$, p_5 into $-p_3$ and p_4 into $-p_4$. Hence $C_{2\ \text{allyl}} = -P_{(35)}$, where $P_{(35)}$ is the permutation only of the space portions of spin-orbitals 3 and 5 throughout the wave function.

From the trace of the identity representation and of $C_{2\text{allyl}}$, we find that there are two functions of A symmetry and one of B symmetry for the allyl portion of the CB wave function when the spin in that region is 1. Similarly, for $S^2_{\text{allyl}} = 0$, we have one each of A and B symmetry. To find the rotationally-invariant eigenfunctions of $S^2 = 1$, we must find the matrix T such that:

$$\begin{pmatrix} -1 & & 0 \\ & +1 & \\ 0 & & +1 \end{pmatrix} T^{-1} \begin{pmatrix} \overset{(34)\quad(58)}{\underset{1}{{}^{1}\curlyvee{}^{1}}} \\ \underset{1}{{}^{1}\curlyvee{}^{0}} \\ \underset{1}{{}^{0}\curlyvee{}^{1}} \end{pmatrix} = \left(T^{-1} C_{2\text{allyl}} T\right) T^{-1} \begin{pmatrix} \text{column} \\ \text{at left} \end{pmatrix}$$

(Note that the column of functions are here being used to represent the space part of the wave functions). The similarity transformation,

$$T \begin{pmatrix} -1 & & \\ & +1 & \\ & & +1 \end{pmatrix} T^{-1} = C_{2\ \text{allyl}}$$

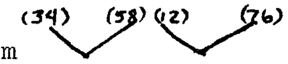
is satisfied for $T = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ -\frac{1}{2} & \frac{1}{2} & \frac{1}{\sqrt{2}} \\ \frac{1}{2} & -\frac{1}{2} & \frac{1}{\sqrt{2}} \end{pmatrix}$, $T^{-1} = \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{2} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & \frac{1}{2} & -\frac{1}{2} \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$.

The singlet functions of the eight electron model treatment of CB, having A and B symmetry in the allyl section and S = 1 in that region, are then:

Table 3

eigenfunction		energy
$B(u) = \frac{1}{2}[\sqrt{2}(10) - (11) + (12)]$	$= \frac{1}{\sqrt{3}}[(J - M) - 2(G - A)]$	$A^{S}_{76} - A^{T}_{12} - B$
$B(1) = \frac{1}{2}[\sqrt{2}(7) - (8) + (9)]$	$= \frac{1}{\sqrt{3}}[(J - M) - 2(B - H)]$	$A^{S}_{12} - A^{T}_{76} - B$
$A_2(u) = \frac{1}{\sqrt{2}}[(11) + (12)]$	$= \sqrt{\frac{2}{3}}[(J - (E + G)]$	$A^{S}_{76} - A^{T}_{12}$
$A_2(1) = \frac{1}{\sqrt{2}}[(8) + (9)]$	$= \sqrt{\frac{2}{3}}[(M - (H + D)]$	$A^{S}_{12} - A^{T}_{76}$
$A_1(u) = \frac{1}{2}[\sqrt{2}(10) + (11) - (12)]$	$= \frac{1}{\sqrt{3}}[(J - M) - 2(E - A)]$	$A^{S}_{76} - A^{T}_{12} - B$
$A_1(1) = \frac{1}{2}[\sqrt{2}(7) + (8) - (9)]$	$= \frac{1}{\sqrt{3}}[(J - M) - 2(B - D)]$	$A^{S}_{12} - A^{T}_{76} - B$

A_1 and A_2 are functions of A-type symmetry, B of B-type symmetry. u and l denote that the upper or lower C-H bond has a triplet pairing, respectively.

A schematic representation of the form  for these same functions is:

$$B(\ell), B(u) = \frac{1}{2}\left[\sqrt{2}\left({}^{1}\underset{1}{Y}{}^{1}\right) - \left({}^{1}\underset{1}{Y}{}^{0}\right) + \left({}^{0}\underset{1}{Y}{}^{1}\right)\right] \times \left[{}^{0}\underset{1}{Y}{}^{1}, {}^{1}\underset{1}{Y}{}^{0}\right]$$

$$A_2(\ell), A_2(u) = \frac{1}{\sqrt{2}}\left[\left({}^{1}\underset{1}{Y}{}^{0}\right) + \left({}^{0}\underset{1}{Y}{}^{1}\right)\right] \times \left[{}^{0}\underset{1}{Y}{}^{1}, {}^{1}\underset{1}{Y}{}^{0}\right]$$

$$A_1(\ell), A_1(u) = \frac{1}{2}\left[\sqrt{2}\left({}^{1}\underset{1}{Y}{}^{1}\right) + \left({}^{1}\underset{1}{Y}{}^{0}\right) - \left({}^{0}\underset{1}{Y}{}^{1}\right)\right] \times \left[{}^{0}\underset{1}{Y}{}^{1}, {}^{1}\underset{1}{Y}{}^{0}\right].$$

It is quite evident from this schematic representation that the coefficients of the exchange integrals, A_{12} and A_{76}, are correct in Table 3. One of the ways to verify that the coefficients of B ($=B_{34} = B_{45}$) are also correct is to determine the six independent matrix elements of $\underset{\approx}{\mathcal{H}}$ in terms of B only for the states (10), (11), and (12), and then to transform this $\underset{\approx}{\mathcal{H}}_B$ to find $\underset{\approx}{\mathcal{H}}'_B$ for B(u), A_1(u) and A_1(1). The energies of the other three states of Table 3 may then be verified by replacing

(10) by (7), (11) by (8), and (12) by (9), as appropriate.

Let us identify these matrix elements of $\underset{\approx}{\mathcal{H}}_B$ by (i) * (j), where i, j = 10, 11, 12. Then

$$\begin{pmatrix} (10)*(10) & (10)*(11) & (10)*(12) \\ (11)*(10) & (11)*(11) & (11)*(12) \\ (12)*(10) & (12)*(11) & (12)*(12) \end{pmatrix} \equiv \underset{\approx}{\mathcal{H}}_B, \quad \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{2} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & \frac{1}{2} & -\frac{1}{2} \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \equiv T;$$

where T is the transformation matrix of the states (10), (11), and (12), used to obtain the functions of Table 3.

Then $T\, H_B\, T^t = \underset{\approx}{\mathcal{H}}'_B$, where $\underset{\approx}{\mathcal{H}}'_B$ is the Hamiltonian matrix in terms of B only for the functions B(u), A_1(u), and A_1(1). T^t is the transpose of T.

Constructing off-diagonal elements of $\underset{\approx}{\mathcal{H}}_{B'}$ by use of the rule given in Section II, we have:

$$(11) * (12) \quad = \tfrac{1}{3}(J-2G)*(J-2E) = \tfrac{1}{3}(J^2-2JG-2JE+4GE), \text{where } X*Y = XY.$$
$$= \tfrac{1}{3}\left[\left(-\tfrac{1}{2}+\tfrac{1}{2}+\tfrac{1}{2}+1\right)B_{45} + (1-1-1+1)\,B_{34}\right] = \frac{B_{45}}{2}$$

$$(11) * (10) \quad = \tfrac{\sqrt{2}}{3}(J-2E)*\left[(J+2A)-(G+E+M)\right] = \tfrac{\sqrt{2}}{3}\left[J^2+2JA-(JG\right.$$
$$\left.+JE+JM)-2JE-4AE+2(EG+E^2+EM)\right] = \tfrac{\sqrt{2}}{3}\left[\left(1+\tfrac{1}{2}\right.\right.$$
$$\left.\left.-\tfrac{1}{2}-\tfrac{1}{2}-\tfrac{1}{2}-1+1+\tfrac{1}{2}-1+\tfrac{1}{2}\right)B_{34}+\left(-\tfrac{1}{2}+\tfrac{1}{2}+\tfrac{1}{4}+\tfrac{1}{4}-\tfrac{1}{2}+\tfrac{1}{2}-2+\tfrac{1}{2}-1+\tfrac{1}{2}\right)B_{45}\right] = -\frac{B_{45}}{\sqrt{2}}$$

$$(12) * (10) \quad = \tfrac{\sqrt{2}}{3}(J-2G)*\left[(J+2A)-(G+E+M)\right]$$
$$= \tfrac{\sqrt{2}}{3}\left[J^2+2JA-(JG+JE+JM)-2JG-4GA+2(G^2+GE+GM)\right]$$
$$= \tfrac{\sqrt{2}}{3}\left[\left(1+\tfrac{1}{2}+\tfrac{1}{4}+\tfrac{1}{4}-\tfrac{1}{2}+\tfrac{1}{2}-2-1+\tfrac{1}{2}+\tfrac{1}{2}\right)B_{34}+\left(-\tfrac{1}{2}+\tfrac{1}{2}\right.\right.$$
$$\left.\left.+\tfrac{1}{4}+\tfrac{1}{4}-\tfrac{1}{2}+\tfrac{1}{2}-2-1+\tfrac{1}{2}+\tfrac{1}{2}\right)B_{45}\right] = -\frac{B_{45}}{\sqrt{2}}$$

The diagonal elements have been given in Table 2, So

$$T\underset{\approx}{H}_B T^t = \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{2} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & \frac{1}{2} & -\frac{1}{2} \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \left[\begin{pmatrix} -B_{34} & & 0 \\ & -B_{34} & \\ 0 & & +B_{34} \end{pmatrix} + B_{45} \begin{pmatrix} 0 & -\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & -\frac{1}{2} & \frac{1}{2} \\ -\frac{1}{\sqrt{2}} & \frac{1}{2} & -\frac{1}{2} \end{pmatrix} \right] T^t$$

$$= \begin{pmatrix} -\frac{1}{2}(B_{34}+B_{45}) & & \\ & -\frac{1}{2}(B_{34}+B_{45}) & \\ & & 0 \end{pmatrix} = \begin{pmatrix} -B & & \\ & -B & \\ & & 0 \end{pmatrix}$$

Hence the eigenvalues given in Table 3 are correct.

To complete the calculation of the spin densities on the β-protons in CB, one must determine the coefficients, $\frac{\langle j | \mathcal{H}_{pert} | 0 \rangle}{\Delta E_{0j}}$, which appear in the first-order expression for ψ and then compute $\langle \psi | \hat{\rho}_{H_1} | \psi \rangle$ and $\langle \psi | \hat{\rho}_{H_7} | \psi \rangle$, where $\hat{\rho}_{H_1}$ is the operator giving the spin density on proton #1 and $\hat{\rho}_{H_7}$ is the operator giving the spin density on the other β-proton. The standard rule of VB theory for calculating matrix elements for singlet states has been given in Section III and the island diagrams which are useful in applying this rule are given in Appendix II. The rule for calculating the spin density in the VB spin-orbital ψ_a is: the matrix element of the spin density operator $\hat{\rho}$ for ψ_a between two CS's is given by the overlap coefficient of the two CS's multiplied by 1, -1, or 0, depending on whether the orbital ψ_a is in the same island as the dummy orbital and is an even (+1) or odd (-1) numbered orbital or is not in the same island as the dummy orbital (0) (40).

In the coefficients, $\frac{\langle j | \mathcal{H}_{pert} | 0 \rangle}{\Delta E_{0j}}$, $|0\rangle$ is the ground state, $\frac{1}{\sqrt{3}}$ (J + M). The j's are the states in Table 3 and the state, ex =(J - M). ex and the ground state are the wave functions of the allyl plus phantom section having S = 0 and have B- and A-type symmetry respectively. Eigenvalues of these two states are $A^S_{12} + A^S_{76} + B$ (ground state) and $A^S_{12} + A^S_{76} - B$ (ex). $\mathcal{H}_{pert}$ is that portion of the Hamiltonian which involves the exchange integrals $J(p_3\sigma_2)$, $J(p_5\sigma_2)$, $J(p_3\sigma_6)$, $J(p_5\sigma_6)$, $J(p_3h_1)$, $J(p_3h_7)$, $J(p_5h_1)$, $J(p_5h_7)$. In the table below each of these exchange integrals is represented by I_{ij}, since the numbering of the orbitals (i and j) involved in any given one of them are distinct. The use of ρ_j in this table is merely to label the contribution from the matrix elements of the spin density operator ρ to the spin density in orbital j.

	$\langle 0 \vert \rho \vert j \rangle$	$\frac{\langle j \vert \mathcal{H}_{pert} \vert 0 \rangle}{\Delta E_{oj}}$, where $\Delta E_{oj} = E_0 - E_j$
(1)	$\langle 0 \vert \rho \vert A_2(\ell) \rangle = \frac{\sqrt{2}}{3}(\rho_6 - \rho_7)$	$\frac{1}{\sqrt{2}}\left[\frac{-I_{36} + I_{37} - I_{56} + I_{57}}{A^T_{76} + A^S_{76} + B}\right]$
(2)	$\langle 0 \vert \rho \vert A_2(u) \rangle = \frac{\sqrt{2}}{3}(\rho_2 - \rho_1)$	$\frac{1}{\sqrt{2}}\left[\frac{-I_{32} + I_{13} - I_{25} + I_{15}}{A^S_{12} + A^T_{12} + B}\right]$
(3)	$\langle 0 \vert \rho \vert A_1(\ell) \rangle = \frac{4}{3}(\rho_7 - \rho_6)$	0
(4)	$\langle 0 \vert \rho \vert A_1(u) \rangle = \frac{4}{3}(\rho_1 - \rho_2)$	0
(5)	$\langle 0 \vert \rho \vert ex \rangle = \frac{1}{\sqrt{3}}(\rho_5 - \rho_3)$	0
(6)	$\langle 0 \vert \rho \vert B(\ell) \rangle = \langle 0 \vert \rho \vert B(u) \rangle = 0$	. . . . .

Direct substitution in

$$\langle \psi | \rho | \psi \rangle = 2 \sum_j \frac{\langle j | \mathcal{H}_{pert} | 0 \rangle}{\Delta E_{oj}} \langle 0 | \rho | j \rangle$$

gives eq. 4 of this section.

This result holds even if the portion of the zeroth-order wave functions in the methylene region of CB has A or B-type symmetry explicitly. This fact is demonstrated below. Only the non-zero contributions are considered.

$$\psi_A = \frac{1}{\sqrt{2}}\left[A_2(u) + A_2(\ell)\right] = A$$

$$\Delta E_{oA} = A^S_{12} + A^S_{76} + B - \tfrac{1}{2}(A^S_{76} - A^T_{12} + A^S_{12} - A^T_{76}) = \frac{A^S_{12} + A^S_{76} + A^T_{12} + A^T_{76}}{2} + B.$$

Note that (9) * (11) = (J - 2B)*(J-2E) = $J^2 - 2(JB + JG) + 4BG$

$$= (1-1-1+1)B_{34} + \left(-\tfrac{1}{2} + \tfrac{1}{2} + \tfrac{1}{2} - \tfrac{1}{2}\right)B_{45} = 0$$

$$(9)*(12) = (J-2B)*(J-2E) = J^2 - 2(JB + JE) + 4BE$$

$$= (1-1-1+1)B_{34} + \left(-\tfrac{1}{2} + \tfrac{1}{2} + \tfrac{1}{2} - \tfrac{1}{2}\right)B_{45} = 0$$

The same result holds for $(8)*(11), (8)*(12)$, as may be deduced from symmetry.

So $A_2(u) * A_2(\ell) = 0$. $\langle A|\rho|A\rangle = \frac{1}{\sqrt{2}}\left(\frac{\sqrt{2}}{3}\right)\left[(\rho_6 - \rho_7) + (\rho_2 - \rho_1)\right]$.

$$\frac{\langle A|\mathcal{H}_{pert}|0\rangle}{\Delta E_{OA}} = \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)\left[\frac{-I_{36} + I_{37} - I_{56} + I_{57} - I_{32} + I_{13} - I_{25} + I_{15}}{\Delta E_{OA}}\right]$$

Hence $\langle \Psi|\rho|\Psi\rangle = \frac{2}{2(3)}\left[\frac{-I_{36} + I_{37} - I_{56} + I_{57} - I_{32} + I_{13} - I_{25} + I_{15}}{A^S_{12} + A^S_{76} + A^T_{12} + A^T_{76} + 2B}\right]\left[(\rho_6 - \rho_7) + (\rho_2 - \rho_1)\right]$.

This result is equivalent to that of equations (4) for $I_{36} = I_{56}$, $I_{32} = I_{52}$, $I_{37} = I_{57}$, and $I_{13} = I_{15}$. For convenience, equations (4) are repeated here:

$$\rho_6 = -\rho_7 = \frac{2}{3}\left[\frac{-I_{36} + I_{37} - I_{56} + I_{57}}{A^T_{76} + A^S_{76} + B}\right]$$

$$\rho_2 = -\rho_1 = \frac{2}{3}\left[\frac{-I_{32} + I_{13} - I_{25} + I_{15}}{A^S_{12} + A^T_{12} + B}\right]$$

The conclusion then is that the spin density on the β-protons is dependent on the π-electron excitation energies. It has been shown that Q_{β_i}, in the relation

> $a_{H_{\beta_i}} = Q_{\beta_i}\rho_{allyl}$, where $a_{H_{\beta_i}}$ is the ESR isotropic hyperfine splitting on β-proton number i and ρ_{allyl} is the total (to within a good approximation) spin density residing in the allyl section of an allyl - β - proton type fragment,

is estimated for the β-protons of MCAALCP to be 22g, at high temperatures. This Q, for the cyclobutenyl - β-proton - type radical (with hindered rotation), is calculated to be 66.2g.

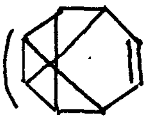
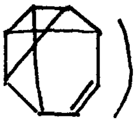
V. THE RESOLUTION OF THE FOURTEEN VECTOR-COUPLING STATES IN TERMS OF THE FOURTEEN CANONICAL STATES FOR AN EIGHT ELECTRON SYSTEM

The methods of the resolution of the entire vector-coupling set in terms of the CS's as given in Table 2 (Section IV) and Tables 4 and 5 below will now be outlined. State (14) was obtained by inspection; (12), (10), (9), (8), (7), (6), (4), and (3) by suitable permutation of the orbitals in states (11) and (13). The identities of Section II were used extensively. (13) was resolved by use of identity (2), p. 10. (11) also involved this identity:

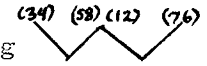
$$\begin{aligned}
(11) &= \tfrac{1}{2\sqrt{3}}\Big[s_3 s_4 (s_5 - s_8)(s_7 - s_6) - \frac{(s_3+s_4)(s_5-s_8)(s_1+s_2)(s_7-s_6)}{2} + s_1 s_2 (s_5 - s_8)(s_7 - s_6)\Big] \\
&= \tfrac{1}{4\sqrt{3}}\left[s_3 s_4 - s_1 s_3 + s_3 s_4 - s_1 s_4 + s_1 s_2 - s_2 s_3 + s_1 s_2 - s_2 s_4 \right](s_5 - s_8)(s_7 - s_6) \\
&= \tfrac{1}{4\sqrt{3}}\left[(s_3 - s_1)(s_4 - s_2) + (s_2 - s_3)(s_1 - s_4)\right](s_5 - s_8)(s_7 - s_6) \\
&= \tfrac{1}{4\sqrt{3}}\left[(s_1 - s_2)(s_3 - s_4) + 2(s_2 - s_3)(s_1 - s_4)\right](s_5 - s_8)(s_7 - s_6) \\
&= \tfrac{1}{\sqrt{3}}\left[J - 2E \right]
\end{aligned}$$

Both identities (2) and (3) were used to resolve (5):

$$\begin{aligned}
(5) &= \tfrac{1}{3}\left[s_{34} - \tfrac{1}{2}(s_3+s_4)(s_5+s_8) + s_{58}\right]\left[s_{12} - \tfrac{1}{2}(s_1+s_2)(s_7+s_6) + s_{76}\right] \\
&= \tfrac{1}{3}\left[(\tfrac{1}{2})(s_3-s_4)(s_5-s_8) - (s_3-s_8)(s_5-s_4)\right]\left[(\tfrac{1}{2})(s_1-s_2)(s_7-s_6) - (s_1-s_6)(s_7-s_2)\right] \\
&= \tfrac{1}{3}\Big[(\tfrac{1}{4})(s_3-s_4)(s_5-s_8)(s_1-s_2)(s_7-s_6) - (\tfrac{1}{2})(s_3-s_4)(s_5-s_8)(s_1-s_6)(s_7-s_2) \\
&\qquad - \tfrac{1}{2}(s_1-s_2)(s_7-s_6)(s_3-s_8)(s_5-s_4) + (s_1-s_6)(s_7-s_2)(s_3-s_8)(s_5-s_4)\Big]
\end{aligned}$$

$= \tfrac{1}{3}\Big[J - 2\Big($  $\Big) - 2M + 4\Big($  $\Big)\Big]$

$$\begin{aligned}
&= \tfrac{1}{3}\left[J - 2(J + L - G - B + C) - 2M + 4(K + M - H - A + F)\right] \\
&= -\tfrac{1}{3}\left[J + 2((L + C) - (G + B + M)) + 4((H + A) - (K + F))\right]
\end{aligned}$$

For the resolution of state (2), let $\left|{L \atop M_L}\right\rangle_L$, $\left|{L \atop M_L}\right\rangle_R$ refer to the total spin angular momentum states of the electrons in the orbitals numbered 3, 4, 5 and 8 and 1, 2, 7, and 6 respectively. This corresponds to the numbering  of the orbitals in the coupling diagrams given above. Similarly, let j in $\left|{L \atop M_L}\right\rangle_j$ have the range 1, 2, 3, 4 and refer to the pairs of electrons, (3, 4), (5, 8), (1, 2), (7, 6), respectively. Then

$$
\begin{aligned}
(2) &= \tfrac{1}{\sqrt{3}}\left[\left|{1 \atop 1}\right\rangle_L \left|{1 \atop -1}\right\rangle_R - \left|{1 \atop 0}\right\rangle_L \left|{1 \atop 0}\right\rangle_R + \left|{1 \atop -1}\right\rangle_L \left|{1 \atop 1}\right\rangle_R \right] \\
&= \tfrac{1}{2\sqrt{3}}\Big\{ \left[(\uparrow_1 \rightarrow_2 - \rightarrow_1 \uparrow_2)(\rightarrow_3 \downarrow_4 - \downarrow_3 \rightarrow_4) = A \right] \\
&\qquad - \left[(\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2)(\uparrow_3 \downarrow_4 - \downarrow_3 \uparrow_4) = Y \right] \\
&\qquad + \left[(\rightarrow_1 \downarrow_2 - \downarrow_1 \rightarrow_2)(\uparrow_3 \rightarrow_4 - \rightarrow_3 \uparrow_4) = B \right],
\end{aligned}
$$

where $\uparrow_j = \left|{1 \atop 1}\right\rangle_j$, $\rightarrow_k = \left|{1 \atop 0}\right\rangle_k$, $\downarrow_\ell = \left|{1 \atop -1}\right\rangle_\ell$.

Expanding A and B,

$$
\begin{aligned}
A &= (\rightarrow_{2,3} \uparrow_1) - (\rightarrow_{2,4} \uparrow_1) - (\rightarrow_{1,3} \uparrow_2) + (\rightarrow_{1,4} \uparrow_2) \\
B &= (\rightarrow_{1,4} \uparrow_3) - (\rightarrow_{1,3} \uparrow_4) - (\rightarrow_{2,4} \uparrow_3) + (\rightarrow_{2,3} \uparrow_4),
\end{aligned}
$$

where $\rightarrow_i \rightarrow_j \equiv \rightarrow_{i,j}$.

$$
\begin{aligned}
A + B &= [\rightarrow_{2,3} - (\rightarrow_{2,4})]\uparrow_1 + [\rightarrow_{2,3} - (\rightarrow_{1,3})]\uparrow_4 \\
&\quad + [\rightarrow_{1,4} - (\rightarrow_{1,3})]\uparrow_2 + [\rightarrow_{1,4} - (\rightarrow_{2,4})]\uparrow_3 \\
&= \tfrac{1}{2}(s_5 + s_8)s_{34}[(s_1 + s_2) - (s_7 + s_6)] + \tfrac{1}{2}[s_5 + s_8 - (s_3 + s_4)](s_1 + s_2)s_{76} \\
&\quad + \tfrac{1}{2}(s_3 + s_4)s_{58}[s_7 + s_6 - (s_1 + s_2)] + \tfrac{1}{2}(s_7 + s_6)s_{12}[s_3 + s_4 - (s_5 + s_8)] \\
&= \tfrac{1}{2}(s_5 + s_8)s_{34}[(s_1 - s_6) - (s_7 - s_2)] + [(s_5 - s_4) - (s_3 - s_8)](s_1 + s_2)s_{76}(\tfrac{1}{2}) \\
&\quad + \tfrac{1}{2}(s_3 + s_4)s_{58}[(s_7 - s_2) - (s_1 - s_6)] + \tfrac{1}{2}(s_7 + s_6)s_{12}[-(s_5 - s_4) + (s_3 - s_8)].
\end{aligned}
$$

Combining the first and third and second and fourth terms of this expression we have

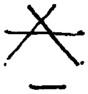
$$
\begin{aligned}
A + B = (\tfrac{1}{2})\Big\{ & [-(s_7 - s_2) + (s_1 - s_6)][s_{45}(s_3 - s_8) - s_{38}(s_5 - s_4)] \\
& + [-(s_5 - s_4) + (s_3 - s_8)][-s_{16}(s_7 - s_2) + s_{27}(s_1 - s_6)] \\
= (\tfrac{1}{2})\Big\{ & -(s_{16} + s_{45})(s_3 - s_8)(s_7 - s_2) + (s_{45} + s_{27})(s_3 - s_8)(s_1 - s_6) \\
& - (s_{38} + s_{27})(s_5 - s_4)(s_1 - s_6) + (s_{38} + s_{16})(s_7 - s_2)(s_5 - s_4)\Big\}.
\end{aligned}
$$

At this point, recall of identity (2), which allows one to express $[s_{16}+s_{45}-\frac{1}{2}(s_1+s_6)(s_4+s_5)](s_7-s_2)(s_3-s_8)$, and so on, in terms of CS's, leads to further progress. It turns out that the term Y is given by:

$$\begin{aligned}
Y = \tfrac{1}{4}\{ &(s_1+s_6)(s_4+s_5)(s_7-s_2)(s_3-s_8)-(s_4+s_5)(s_2+s_7)(s_3-s_8)(s_1-s_6)\\
&+(s_3+s_8)(s_2+s_7)(s_5-s_4)(s_1-s_6)-(s_3+s_8)(s_1+s_6)(s_7-s_2)(s_5-s_4)\}\\
= \tfrac{1}{4}\{ &[(s_1+s_6)(s_7-s_2)-(s_1-s_6)(s_2+s_7)](s_3-s_8)(s_4+s_5)\\
&+[(s_2+s_7)(s_1-s_6)-(s_1+s_6)(s_7-s_2)](s_3+s_8)(s_5-s_4)\}\\
= \tfrac{1}{4}\{ &[(s_{12}+s_{17}-s_{26}-s_{76})-(s_{17}+s_{67}-s_{12}-s_{26})](s_3+s_8)(s_5-s_4)\\
&+[(s_{17}+s_{67}-s_{12}-s_{26})-(s_{12}+s_{17}-s_{26}-s_{67})](s_3-s_8)(s_4+s_5)\\
= -(&s_{12}-s_{67})(s_{34}-s_{58}) = -[(\uparrow_1\downarrow_2-\downarrow_1\uparrow_2)(\uparrow_3\downarrow_4-\downarrow_3\uparrow_4)] = Y.
\end{aligned}$$

So (2) $= \frac{1}{4\sqrt{3}}\{-[s_{16}-\frac{1}{2}(s_1+s_6)(s_4+s_5)+s_{54}](s_3-s_8)(s_7-s_2)$

$$\begin{aligned}
&+[s_{45}-\tfrac{1}{2}(s_4+s_5)(s_2+s_7)+s_{27}](s_3-s_8)(s_1-s_6)\\
&+[s_{38}-\tfrac{1}{2}(s_3+s_8)(s_1+s_6)+s_{16}](s_7-s_2)(s_5-s_4)+z^*\\
= \tfrac{1}{4\sqrt{3}}\{&[-\tfrac{1}{2}(s_1-s_6)(s_5-s_4)(s_3-s_8)(s_7-s_2)+(s_1-s_4)(s_5-s_6)(s_3-s_8)(s_7-s_2)]\\
&+[\tfrac{1}{2}(s_5-s_4)(s_7-s_2)(s_3-s_8)(s_1-s_6)-(s_5-s_2)(s_7-s_4)(s_3-s_8)(s_1-s_6)]\\
&-[\tfrac{1}{2}(s_3-s_8)(s_7-s_2)(s_5-s_4)(s_1-s_6)-(s_3-s_2)(s_7-s_8)(s_5-s_4)(s_1-s_6)]\\
&+[\tfrac{1}{2}(s_3-s_8)(s_1-s_6)(s_7-s_2)(s_5-s_4)-(s_3-s_6)(s_1-s_8)(s_7-s_2)(s_5-s_4)]
\end{aligned}$$

$= \frac{1}{\sqrt{3}}\Big[$  $-$  $+K-F\Big]$

$$\begin{aligned}
&= \tfrac{1}{\sqrt{3}}[L+D+N-(B+I)-(B+M+G+F+I+K+E)\\
&\qquad +(J+H+L+2A+N)+(K-F)]\\
&= \tfrac{1}{\sqrt{3}}[2(L+N+A)+(D+J+H)-2(B+I+F)-(M+G+E)].
\end{aligned}$$

---

* $z = -[s_{38}-\frac{1}{2}(s_3+s_8)(s_1+s_6)+s_{16}](s_7-s_2)(s_5-s_4)$.

Only state (1) remains to be resolved. Orthogonality between (1) and the remaining vector-coupling states and normalization of (1) gave the expression for (1) found in Table 4. The normalization of (1) is most easily accomplished by use of the overlap coefficients (Appendix II) of the seven A-type symmetry functions of Section II.

Table 4

eigenfunction	energy
$(6) = \frac{1}{\sqrt{3}}(J + 2(L + C) - 2(G + B))$	$-A^T_{12}\ -A^T_{76}\ +B_{34}\ -\frac{1}{2}B_{45}$
$(5) = \frac{1}{3}[J + 2((L + C) - (G + B + M)) + 4((H + A) - (K + F))]$	$-A^T_{12}\ -A^T_{76}\ -B_{34}\ +\frac{1}{2}B_{45}$
$(4) = \sqrt{\frac{2}{3}}(C - L)$	$-A^T_{12}\ -A^T_{76}\ +B_{34}\ -\frac{1}{2}B_{45}$
$(3) = \sqrt{\frac{2}{3}}[(E + G + M) - (L + C + J + D + H) + 2(I + K + B - (N + A))]$	$-A^T_{12}\ -A^T_{76}\ -B_{34}\ -\frac{1}{2}B_{45}$
$(2) = \frac{1}{\sqrt{3}}[2(L + N + A) + (D + J + H) - 2(B + I + F) - (M + G + E)]$	$-A^T_{12}\ -A^T_{76}\ -B_{34}$
$(1) = \frac{2}{3\sqrt{5}}[-(A + B) + 3(I + N) + \frac{1}{2}((J + M) + (G + H)) + (F + C)$ $-2(K + L) - 3/2(D + E)]$	$-A^T_{12}\ -A^T_{76}\ -B_{34}$

All of the above states, with the exception of (1) have been checked using rule (1) (Section II) to verify that they do indeed give the energies indicated. By inspection of the vector-coupling functions, it is apparent that the energies of the allyl section of the states (2) through (6) can be associated with those of the states (7) through (13). Groups of three states which have the same B_{34} and B_{45} coefficients are: (12), (9), and (4); (11), (8), and (3); and (10), (7), and (2). The cases in which the exchange integral J(ch) in a C-H bond has a minus sign (triplet spin coupling) and those in which it has a plus sign (singlet spin coupling) are recognizable by inspection. The energy of (1) is also obtainable by inspection, and the result confirmed by the fact that the trace of $\underset{\approx}{\mathcal{H}}$ is then identical to that obtained by the computer for another orthogonal set of functions. The trace in either case is: $-4(A_{12} + A_{76} + B_{34} + B_{45})$. The completed set of orthogonal functions is of use in analyzing other orthogonal functions and their expansion properties for any eight electron system. To the author's knowledge, Table 5 below, giving all fourteen vector-coupling functions in terms of canonical states, has not been published:

TABLE 5

	J	M	A	B	G	H	E	D	C	F	K	L	I	N
(1) $\frac{3\sqrt{5}}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	-1	-1	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{3}{2}$	1	1	-2	-2	3	3
(2)	$\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$\frac{2}{\sqrt{3}}$	$-\frac{2}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$		$-\frac{2}{\sqrt{3}}$		$\frac{2}{\sqrt{3}}$	$-\frac{2}{\sqrt{3}}$	$\frac{2}{\sqrt{3}}$
(3)	$\sqrt{\frac{2}{3}}$	$-\sqrt{\frac{2}{3}}$	$2\sqrt{\frac{2}{3}}$	$-2\sqrt{\frac{2}{3}}$	$-\sqrt{\frac{2}{3}}$	$+\sqrt{\frac{2}{3}}$	$-\sqrt{\frac{2}{3}}$	$\sqrt{\frac{2}{3}}$	$\sqrt{\frac{2}{3}}$		$-2\sqrt{\frac{2}{3}}$	$\sqrt{\frac{2}{3}}$	$-2\sqrt{\frac{2}{3}}$	$2\sqrt{\frac{2}{3}}$
(4)									$\sqrt{\frac{2}{3}}$			$-\sqrt{\frac{2}{3}}$		
(5)	$\frac{1}{3}$	$-\frac{2}{3}$	$\frac{4}{3}$	$-\frac{2}{3}$	$-\frac{2}{3}$	$\frac{4}{3}$			$\frac{2}{3}$	$-\frac{4}{3}$	$-\frac{4}{3}$	$\frac{2}{3}$		
(6)	$\frac{1}{\sqrt{3}}$			$-\frac{2}{\sqrt{3}}$	$-\frac{2}{\sqrt{3}}$				$\frac{2}{\sqrt{3}}$			$\frac{2}{\sqrt{3}}$		
(7)						$\sqrt{\frac{2}{3}}$		$-\sqrt{\frac{2}{3}}$						
(8)	$\frac{1}{\sqrt{3}}$	$-2\sqrt{\frac{1}{3}}$		$-2\sqrt{\frac{1}{3}}$		$2\sqrt{\frac{1}{3}}$		$2\sqrt{\frac{1}{3}}$						
(9)	$\sqrt{\frac{1}{3}}$			$-2\sqrt{\frac{1}{3}}$										
(10)	$\sqrt{\frac{2}{3}}$	$-\sqrt{\frac{2}{3}}$	$2\sqrt{\frac{2}{3}}$		$-\sqrt{\frac{2}{3}}$		$-\sqrt{\frac{2}{3}}$							
(11)	$\frac{1}{\sqrt{3}}$						$-\frac{2}{\sqrt{3}}$							
(12)	$\frac{1}{\sqrt{3}}$				$-\frac{2}{\sqrt{3}}$									
(13)	$\frac{1}{\sqrt{3}}$	$-\frac{2}{\sqrt{3}}$												
(14)	1													

VI. THE INTERPRETATION OF CONFIGURATION INTERACTION IN MOLECULAR THEORY AND CONSIDERATIONS OF THE EFFECTS OF HYBRIDIZATIONS OF THE EXCITED STATES IN VALENCE BOND FIRST-ORDER PERTURBATION THEORY

The use of configuration interaction introduces elements of antisymmetry in the otherwise symmetric spatial portions of a valence bond ground state wave function. (43). The validity of this statement is shown in the case of the valence bond theory by the following well-known results: (1) Interchange of any two spin-orbitals of a wave function (of the form of Ψ below) multiplies that function by -1. With the ground-state valence bond function expressed as the sum of Slater determinants, written compactly as:

$$\Psi = \left| (abcd \ldots) \left(\frac{\alpha\beta - \beta\alpha}{\sqrt{2}}\right)\left(\frac{\alpha\beta - \beta\alpha}{\sqrt{2}}\right) \ldots \right|,$$

where the order on the expression for Ψ is such that a and b, c and d, etc., are orbitals of the same bond, it is clear that the interchange of the spins of spin-orbitals $a\alpha$ and $b\beta$, for instance, is an operation equivalent to the multiplication of Ψ by -1. Hence the outcome of the space permutation of two paired orbitals is multiplication by +1. (The more general case of the relation between spin- and space-permutations was discussed in Section IV.) (2) Appropriate linear combinations of the canonical states of the valence bond theory are eigenfunctions of the spin of the perfect-pairing (or electron-pair)bonds. An example of such a spin-coupled state (Ψ_{ex} below) which is antisymmetric in its spatial part for the orbitals a and b is:

$$\Psi_{ex} = \left| (abcd \ldots) \left[\alpha\alpha\beta\beta - \tfrac{1}{2}(\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha) + \beta\beta\alpha\alpha \right] \frac{1}{\sqrt{3}} \right|.$$

For such a case, the spins of the electrons in orbitals a and b form a triplet spin state, of themselves.

The inclusion of such antisymmetric components tends to correct for the error inherent in a symmetrical space function, which allows for two electrons to occupy the same point in space (43). The exclusion principle is operative in the anti-symmetrical spatial parts, and hence they are effective in reducing contributions to the total energy from electron-electron repulsion. These ideas have been particularly emphasized by Lennard-Jones and Pople (43). It follows, by the variational principle, that a better ground-state wave function is secured by the interaction of antisymmetrical spatial portions of the valence-bond excited states with the perfect-pariing state.

This antisymmetry of components of the electronic wave function, in the case of the vector-coupling functions, is concentrated in the same regions of the molecule as that of the perfect pairing bonds. The fact that the electrons always experience electron-electron repulsion and doubtlessly most strongly in an electron-pair is some explanation of the success of first-order calculations using vector-coupling functions, such as were discussed in Sections IV and V.

The electron pair theory of molecular structure is thus seen to be well represented in the vector-coupling theory. The concepts of the atoms-in-molecule theory (46) are employed in the choice of perturbations which mix the various vector-coupling states. This is particularly noticeable in the case of the C-H fragment, of which it is argued that the spin polarization of the electron in the 1s orbital of the proton is opposite to that of the π-orbital because of a Hund's rule-type phenomenon (4, 17). The direction of the electron spin at the proton can be verified experimentally to be opposite to that of the π-orbital (4).

The excited state to which the Hund's rule argument refers is the ^3P state of the carbon atom. An investigation to determine the relation between the excited doublet state of the C-H fragment and the carbon ^3P state yields:

$$(^3P)\times(1s) = \left|(p\,p^{0}1s)\left(\frac{1}{\sqrt{3}}\left[\left|{}^{1}_{0}\right\rangle\left|{}^{\frac12}_{\frac12}\right\rangle-\sqrt{2}\left|{}^{1}_{1}\right\rangle\left|{}^{\frac12}_{-\frac12}\right\rangle\right]\right)\right|$$

$$= \left|p\,p^{0}1s\left[\frac{1}{\sqrt{3}}\left(\frac{(s_1+s_2)s_3}{\sqrt{2}}-\sqrt{2}\,s_1s_2\right)\right]\right|$$

$$= \left|(p\,p^{0}1s)\left[-\frac12\left(\frac{1}{\sqrt{3}}\right)\left[\frac{s_1(s_3+s_2)}{\sqrt{2}}-\sqrt{2}\,s_2s_3\right]\right]\right| + \left|p\,p^{0}1s\left(\frac{\sqrt{3}}{2}\,\frac{s_1(s_3-s_2)}{\sqrt{2}}\right)\right| \quad \text{(eq. 8)},$$

where $(^3P) \times (1s)$ is the total electronic wave function formed from the carbon ^3P state and the ground doublet state of hydrogen, $P^{o} = P_z$ (in terms of Fig. 5), $P = P_x = \frac12(P^+ + P^-)$.

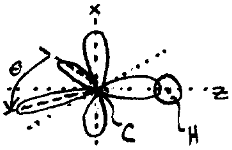


Fig. 5

The first term of the sum is the doublet excited state of the C-H fragment for the case in which the in-plane orbital is a pure p orbital. The term $\left|(p\,p^{0}1s)\frac{\sqrt{3}}{2\sqrt{2}}s_1(s_3-s_2)\right|$ does not contribute to the unpaired spin density on the proton regardless of the hybridizations of the perfect-pariing and the excited states.

The hybridication of the excited doublet state can significantly alter the dependence of the $Q_{\sigma\text{-proton}}$ values on the in-plane hybrid angle θ, as will be shown below. The evidence that the hybridization of the in-plane orbital, $\frac{s+\lambda p_z}{\sqrt{1+\lambda^2}}$, may be different in the excited state from that of the ground-state is as follows. The character of (or a hybridization peculiar to) the excited doublet state appears to be important in determining the amount of electron spin density present on the σ-hydrogen of the C-H fragment in a variety of aromatic hydrocarbon free radicals. The hyperfine splitting dependence of such protons on the angle θ (given in Fig. 5) is estimated by conventional VB theory (44) to be 2g/°. This effect is not observed. The Q_σ 's observed experimentally are: -21.20g (cyclobutyl) (13), -22.5g (cases in which the carbon atom has sp^3 hybridization) (4), -21.5g (cyclopentyl) (13), -25.7g (cyclooctatetraene anion) (44). Hence there is a nearly constant coupling constant Q_σ between the spin of the π-orbital and the hyperfine splitting of the σ -proton, both for cases in which the hybrid angle θ is less than 120° (cyclobutyl) and in which it is greater (cyclooctatetraene anion (135°)). As mentioned on p. 8 , the latter is not disqualified on the basis of non-planarity, because ^{13}C splittings, which, according to standard variational VB theory magnify out-of-plane distortions (20), show that its in-plane σ -hybrids lie in the same plane. In view of the fact that the in-plane hybrid angle for <u>isolated triplets</u> is invariably vary large (12), it seems possible that the components of the excited (intermixing) doublet, whose effect is essentially that of a triplet pairing between the π and σ-carbon orbitals, may affect the in-plane hybridization. To see that the excited doublet has essentially the same effect as far as determining the σ -proton spin density is concerned as a wave function having a triplet spin coupling of the electrons in these two carbon orbitals, one may subtract the second term on the right in eq. 8 from both sides. (eq. 8 is easily generalized to the case in which the in-plane hybrid extending toward the σ-proton is of the type $\frac{s+\lambda p_z}{\sqrt{1+\lambda^2}}$ instead of p_z alone). The fact that bent-bonds accompany the large in-plane hybrid angles for isolated triplets is apparently of lesser significance than the tendency of the carbon atom, at which the triplet pairing is localized to exist in a state quite similar to a carbon ^3P atomic state. Discussion of the theoretical analyses of the properties of isolated triplets is included in the next section.

Possibly then, the wave function component with the triplet pairing between the electrons of the π-orbital and the hybrid orbital should assume more ^3P atomic state character than the perfect-pairing ground state. The failure to do this has led to a somewhat curious result: the spin polarization of the electron on the in-plane σ-proton of the C-H fragment becomes increasingly negative as the in-plane carbon hybrid is removed -- removed in accordance with standard concepts of hybridization as a function of the carbon in-plane hybrid angle θ (see Fig. 6 below).

The dependence of the hyperfine splitting of the σ-proton of the C-H fragment as a function of the hybridizations of the ground state and of the excited doublet state was analyzed using first-order theory. In accord with the work of (44), the in-plane hybrid orbital was taken to be:

$$\sigma_{CH} = \frac{1}{(1+\lambda^2)^{\frac{1}{2}}}\left[(2s)+\lambda(2p)\right], \text{ where } \lambda = \left[\frac{(-2\cos\theta)}{1+\cos\theta}\right]^{\frac{1}{2}}.$$

The values of the exchange integrals involved were assumed to be:

(1) $J(\pi,\sigma_{CH}) = \frac{1}{1+\lambda^2}\left[J(\pi,s) + \lambda J(\pi,p)\right]$, where $J(\pi,s) = J(p,s)$, the atomic exchange integral between the atomic 2p and 2s orbitals; $J(\pi,p) = J(p_x,p_y)$, the atomic exchange integral between two atomic p orbitals; $J(\pi,s) = 2.4$, $J(\pi,p) = .69$ (44, 45).

(2) $J(\pi,s_H) = .792$, where s_h is the 1s orbital of the proton;

(3) $J(\sigma_{CH},s_H) = -3.916$.

The hybridization dependence of $J(\pi,s_H)$ and $J(\sigma_{CH},s_H)$ was neglected because of computational difficulties. The result of the variational calculation (44) using these integrals on the C-H fragment was similar to that obtained by using first-order perturbation theory for the case of identical ground and excited state hybridizations. The dependence of the energy denominators on hybridization must be ignored in the first-order approach, and hence the variational approach is presumably preferable in such studies. However, using well-known equations for calculating the spin densitiy on the proton of the C-H fragment (4), one has:

$$\Psi = gr + \frac{\langle ex | \mathcal{H}_{pert} | gr \rangle}{(-\Delta E_{21})} ex,$$

$$gr = \left| (phs)\left(\frac{\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha}{\sqrt{6}}\right) \right| .$$

$ex = \left| (phs)\frac{(\alpha\beta\alpha + \alpha\alpha\beta - 2\beta\alpha\alpha)}{\sqrt{6}} \right|$, where p is the p_z orbital of the carbon h is the in-plane hybrid, and s is the ls orbital of hydrogen.

$h \equiv \sigma_{CH}$.

$$\langle \Psi | \rho | \Psi \rangle = \frac{2 \langle gr | \mathcal{H}_{pert} | ex \rangle}{-\Delta E_{21}} \langle gr | \hat{\rho}_H | ex \rangle$$

$$2\sqrt{3} \langle gr | \hat{\rho}_H | ex \rangle = -2$$

$$\frac{1}{3}\left(\frac{2\sqrt{3}}{\Delta E_{21}}\right) \langle gr | \mathcal{H}_{pert} | ex \rangle = J(\pi, \sigma_{CH}) - J(\pi, s)$$

$$= \frac{1}{1+\lambda^2}\left[2.4 + \lambda^2(.69)\right] - .79 = \left(\frac{1.7}{1+\lambda^2} - .1\right)$$

$$\langle \Psi | \hat{\rho}_H | \Psi \rangle = \frac{2}{-\Delta E_{21}}\left(\frac{\sqrt{3}}{2}\right)\left(J(\pi,\sigma_{CH}) - J(\pi,s)\right)\left(\frac{2}{2\sqrt{3}}\right)|s(0)|^2 = -\frac{(J(\pi,\sigma_{CH}) - J(\pi,s))}{\Delta E_{21}}|s(0)|^2$$

$$\text{So } a_{CH_{vb}} = -\frac{(J(\pi,\sigma_{CH}) - J(\pi,s))}{\Delta E_{21}} (a_H = 507.6g)$$

$a_{CH_{vb}} = -\frac{1}{\Delta E_{21}}\left(\frac{1.7}{1+\lambda^2} - .1\right)$. This equation is graphed as Case (1) below.

For comparison, let

$$ex = \left| (pp_x s) \frac{(\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha)}{\sqrt{6}} \right| .$$

ex has the hybridization of the ^3P carbon state in this case. Then

$$(2\sqrt{3}) \langle gr | \hat{\rho}_H | ex \rangle = -2\left(\frac{\lambda}{\sqrt{1+\lambda^2}}\right)$$

$$J(\pi,\sigma_{CH}) = \int p(1) \frac{(s+\lambda p_x)(2)}{\sqrt{1+\lambda^2}} \mathcal{H}_{pert}\, p_x(1) p(2) d\tau_1 d\tau_2 = \frac{\lambda\, J(\pi,p)}{\sqrt{1+\lambda^2}} = \frac{\lambda}{\sqrt{1+\lambda^2}}(.69)$$

$$J(\pi, 1s) = \int p(1)\, 1s(2) \frac{(s+\lambda p_x)(3)}{\sqrt{1+\lambda^2}} \mathcal{H}_{pert}\, p(2)\, 1s(1) p_x(3)\, d\tau_1 d\tau_2 d\tau_3$$

$$= \frac{\lambda}{\sqrt{1+\lambda^2}}(.792)$$

So $$\left(\tfrac{1}{3}\right)\left(\tfrac{2\sqrt{3}}{\Delta E_{21}}\right)\langle gr|\mathcal{H}_{pert}|ex\rangle = \frac{\lambda}{\sqrt{1+\lambda^2}}(.69-.792) = \frac{\lambda}{\sqrt{1+\lambda^2}}(-.10)$$

$$\langle \psi|\hat{\rho}_H|\psi\rangle = \frac{2}{-\Delta E_{21}}\left(\frac{\sqrt{3}}{2}\right)\frac{\lambda}{\sqrt{1+\lambda^2}}\frac{(-.10)\lambda}{\sqrt{1+\lambda^2}}\left(\frac{2}{2\sqrt{3}}\right) = \frac{-1}{\Delta E_{21}}\left(\frac{\lambda^2}{1+\lambda^2}\right)(-.10)$$

$$a_{CH_{vb}} = \frac{1}{-\Delta E_{21}}\left(\frac{\lambda^2}{1+\lambda^2}\right)(-.10)$$ (Case (2)).

Cases (3a), (3b) have the hybridization in the excited state ex given by $$ex = \left|(ph's)\left(\frac{\alpha\alpha\beta+\alpha\beta\alpha-2\beta\alpha\alpha}{\sqrt{6}}\right)\right|,$$

where $h' = \frac{1}{\sqrt{1+\lambda'^2}}(2s+\lambda'(2p_x))$; λ' =3, 4 for Cases (3a), (3b), respectively.

$$(2\sqrt{3})\langle gr|\hat{\rho}_H|ex\rangle = \frac{-2(1+\lambda\lambda')}{\sqrt{1+\lambda^2}\sqrt{1+\lambda'^2}}.$$

$$J(\pi,\sigma_{CH}) = \int p(1)\frac{(s+\lambda p_x)(2)}{\sqrt{1+\lambda^2}}\mathcal{H}_{pert}\,p(2)\frac{(s+\lambda' p_x)(1)}{\sqrt{1+\lambda'^2}}d\tau_1 d\tau_2$$

$$= \frac{J(p,s)+\lambda\lambda' J(p,p_x)}{\sqrt{1+\lambda^2}\sqrt{1+\lambda'^2}} = \frac{2.4+\lambda\lambda'(.69)}{\sqrt{1+\lambda^2}\sqrt{1+\lambda'^2}}$$

$$J(\pi,s) = \int p(1)\,s(2)\frac{(s+\lambda p_x)(3)}{\sqrt{1+\lambda^2}}\mathcal{H}_{pert}\,p(2)\,s(2)\frac{(s+\lambda' p_x)(3)}{\sqrt{1+\lambda'^2}}d\tau_1 d\tau_2 d\tau_3$$

$$= J(\pi,s_H)\frac{1+\lambda\lambda'}{\sqrt{1+\lambda^2}\sqrt{1+\lambda'^2}},$$ neglecting three-center integrals.

$$= .792\,\frac{1+\lambda\lambda'}{\sqrt{1+\lambda^2}\sqrt{1+\lambda'^2}}$$

So $$\langle \psi|\hat{\rho}_H|\psi\rangle = \left(\frac{2}{-\Delta E_{21}}\right)\frac{2.4+\lambda\lambda'(.69)-.792(1+\lambda\lambda')}{\sqrt{1+\lambda^2}\sqrt{1+\lambda'^2}}\left(\frac{\sqrt{3}}{2}\right)\left(\frac{2}{2\sqrt{3}}\right)\left(\frac{1+\lambda\lambda'}{\sqrt{1+\lambda^2}\sqrt{1+\lambda'^2}}\right)$$

$$= -\frac{1}{\Delta E_{21}}\left[(2.4)+\lambda\lambda'(.69)-.792(1+\lambda\lambda')\right]\frac{(1+\lambda\lambda')}{(1+\lambda^2)(1+\lambda'^2)}$$

For $\lambda'=3$, $\langle \psi|\hat{\rho}_H|\psi\rangle = -\frac{1}{\Delta E_{21}}[1.61-.0306\lambda]\left[\frac{1+3\lambda}{1+\lambda^2}\right]$ (Case 3a);

$\lambda'=4$, $\langle \psi|\hat{\rho}_H|\psi\rangle = -\frac{1}{\Delta E_{21}}[.0645-.0164\lambda]\left[\frac{1+4\lambda}{1+\lambda^2}\right]$ (Case 3b).

$\langle \psi|\hat{\rho}_H|\psi\rangle$ for these four cases is graphed on page 60 (Fig. 6).

The information given on the graph is also contained in the table below:

λ	θ	ρ = σ-proton spin density, (ratio: ρ/ρ at $\theta = 120^\circ$)			
		Case (1)	Case (2)	Case (3a)	Case (3b)
0	90°	1.6, ...	0.,....	.16, ...	.07, ...
$\sqrt{\frac{1}{2}}$	101.5°	1.03, (.59)	-.033, (.86)	.289, (.73)	.12, (.769)
1	109.5°	.75, ...	-.05, ...	.262, ...	....
$\sqrt{2}$	120°	.44, (1.)	-.067, (1.)	.192, (1.)	.092, (1.)
$\sqrt{3}$	127°	.32, ...	-.075, ...	....	....
2	132°	.24, (1.83)	-.080, (1.19)	.14, (1.37)	.057, (1.61)
3	145°	.07, ...	-.090, ...	.07, ...	.021, ...

Note: $\theta' = 145^\circ$, (153°) in Case (3a), (Case (3b)).

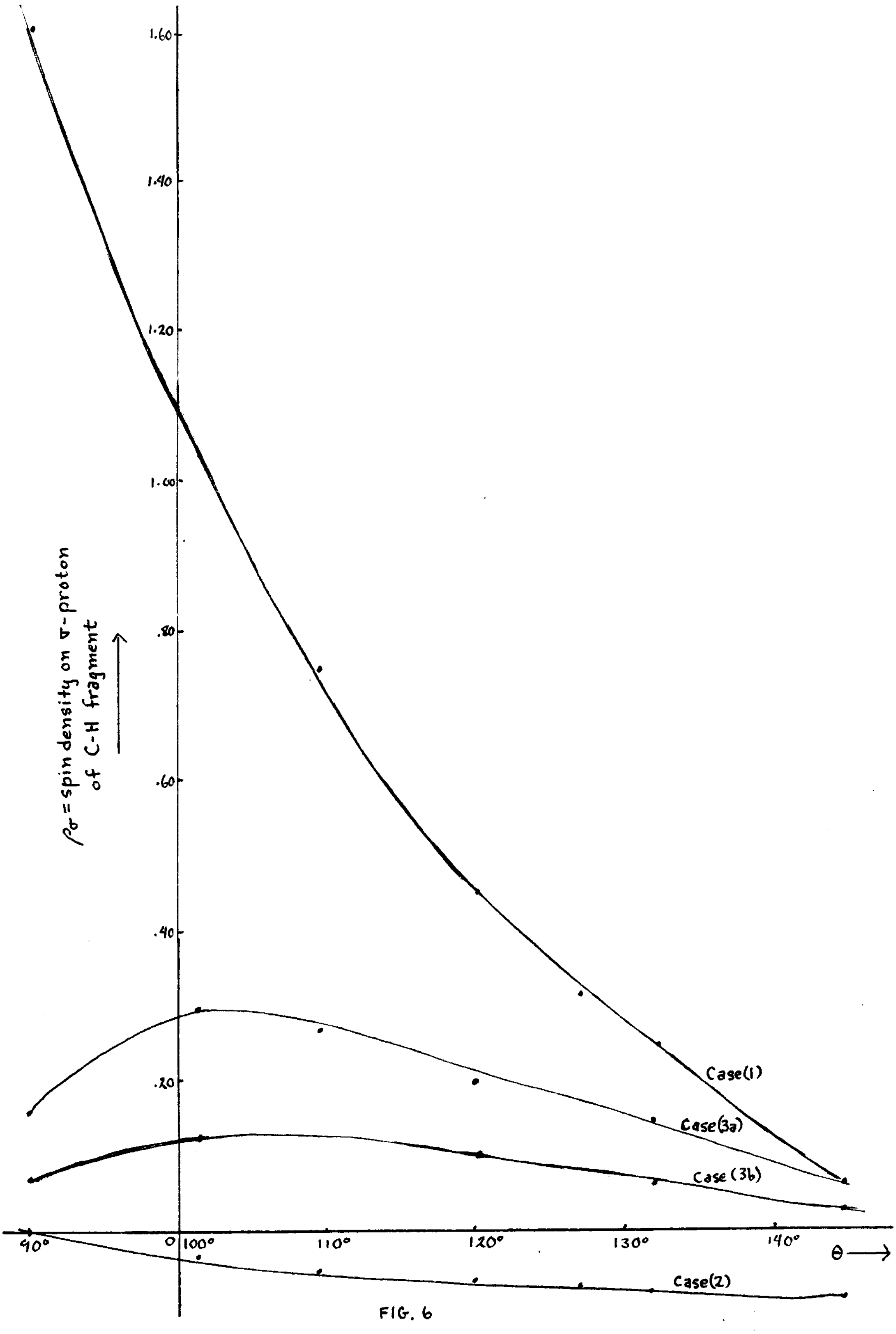

ρσ = spin density on σ-proton of C-H fragment →
1.60
1.40
1.20
1.00
.80
.60
.40
.20
0
90°
100°
110°
120°
130°
140°
θ ⟶
Case(1)
Case(3a)
Case (3b)
Case(2)

FIG. 6

Case (2) would imply a spin polarization of the electrons at the proton in the same direction as that of the π-orbital, contrary to experiment ($\Delta E_{\lambda J} > 0$). One still obtains a positive spin density on the proton in cases 3a and 3b, where the 2g/$^{\circ}$ dependence of a_{H_σ} on θ has been decreased to 1g/$^{\circ}$ and 1.3g/$^{\circ}$, respectively. Thus a considerable variation with the excited state hybridization has been found in both the size and θ -dependence of the σ-proton spin densities.

From the foregoing discussion on the significance of configurational interaction using vector-coupling functions and the effects of intraatomic electron correlation as exemplified by the study of the C-H fragment above, one can see extensions which should be made in the extended valence-bond theory as discussed on p. 9 of Section III. Vector-coupling states with a triplet spin coupling of electrons in the electron-pair bonds would reduce the inaccuracy arising in the extended VB ground state wave function due to neglect of electron-electron repulsion. Suitably perturbed, they also account for the presence of an unpaired electron spin density of β-and σ-protons. With the use of orthogonal bond orbitals, in addition to the orthogonal characteristics of the vector-coupling functions themselves, a configurational interaction, within the precision of the extended VB theory, would be considerably less difficult than that envisioned for the canonical states (22). The use of variational parameters which are dependent upon whether the bond has a triplet or singlet pairing is feasible; a method has been given by Lowdin for determining the matrix elements of the Hamiltonian for two Slater determinants in which the bond orbitals for a given bond are different (47).

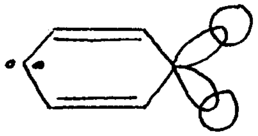
VII. THE EXISTENCE OF A NEW ESR SPECTRUM SOURCE IN IRRADIATED BENZENE: A CONCLUSION BASED PRIMARILY ON THEORETICAL CONSIDERATIONS

The work of Fischer and of Ohnishi, Tanei, and Nitta on the free radical derivatives of benzene and various substituted benzenes (toluene, chlorobenzene, benzenecyclohexane, benzoic acid, xylenes, ethyl benzene, cumene, and fluorobenzene) has revealed the existence of two distinct radical species for benzene, only one of which is also characteristic of the related compounds (38), (48). The common radical produces an ESR spectrum, consisting of a triplet of splitting 50 ± 2g on which is superimposed a quartet of splitting 10.6g, itself subdivided into a triplet of splitting 2.6g. Values of 47.5g and 45g have also been given for the major triplet splitting. This spectrum has been attributed to the cyclohexadienyl radical with the splittings, in order of decreasing magnitude, assigned to the following equivalent sets of protons: the methylene, the ortho and para, the meta. Estimates of the magnitude of the spin density on the methylene protons indicate that this assignment is correct. The results of two sets of calculations are given below (12), (28):

Theory	Q_α	Q_β	^{C}Meth- ^{C}Ortho distance	spin density of orbital			
				methylene β- proton	ortho	meta	para
(1)	26	38	1.54A	first order	.482	.585	-.274
(2)	"	"	"	"	.400	.400	-.100
(3)	"	..	"	.086	.508	.551	-.291
(4)	"	..	1.39A	.180	.495	.507	-.281

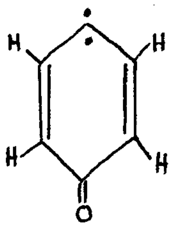
The Q_β applied in (1) and (2) was unsuitable, as has been demonstrated by this thesis, since it was derived for the π-β-proton fragment with hindered rotation of the β-protons (16). The spin densities in the orbitals for (1) and (2) were obtained by use of the VB and MO theories, respectively. In (3) and (4) the VB theory with a reduced set of CS's and sp^3 hybridization of the methylene carbon was employed.

The noteworthy point is that even if the spin density on the ortho π -orbitals were to drop as low as .04 units for some cyclohexadienyl-like structure, one should detect a methylene triplet of separation ∼6g. Hence it is not surprising that Ohnishi *et.al.* labelled their second benzene radical spectrum (a singlet of 25g) as due to the phenyl radical rather than to cyclohexadienylidene (IV). Either would qualify on the basis that the spectrum exhibited the characteristic of a triplet, in that it persisted at higher temperatures than the more elaborate one previously described (49).

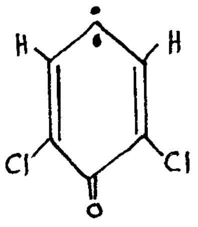


IV

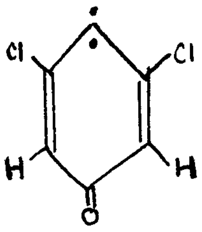
However, their assignment of the singlet spectrum to phenyl is questionable on the basis that the in-plane π -orbital of the divalent carbon should induce a large π -proton-type spin density on its neighboring in-plane σ -protons. This is easily shown by valence bond calculations (28b) (there should be a 21g splitting for sp^2 divalent carbon (50)) and appears to be confirmed by the triplet splitting (18±2g) observed by Tolkachev *et.al.* on a radical derivative of phenyl iodide and by the magnitude and numbers of components observed in the hyperfine structure of the following ground-state triplet molecules:



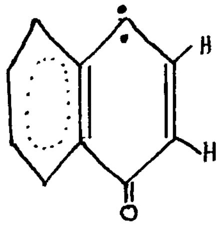
IVa



IVb



IVc



IVd

IVa produced a triplet of magnitude 8g; IVb and IVd a triplet and doublet, respectively, of 10-12g (52). IVc significantly produced a singlet. Such a result can be interpreted to mean that the triplet is mainly localized on the divalent carbon and direct interaction between the appropriate in-plane orbitals should be detectable by a large splitting.

Other work by Wassermann and his colleagues also points to a localization of the in-plane "component" of the triplet, with delocalization of the π-"component". D zero-field splittings of order .4cm^{-1}, indicating appreciable one-center interaction (53), have been observed in the following compounds: fluorenylidene (Va), cyclopentadienylidene (Vb), indenylidene (Vc).

Va

Vb

Vc

	Va	Vb	Vc
D =	.4078 cm^{-1}	.4089	.3777
E =	.0283	.0120	.0160

Low E values in Vb and Vc are attributed to increased delocalization (unfortunately, the hyperfine structure on Vb was not reported though a spin density of .26 units was estimated to reside on C_3 and C_4). Hence, it seems one can rule out cyclohexadienylidene on two counts.

Other possibilities (though quite remote) are an excited triplet state of benzene or an anion. Characteristically, these two species of an aromatic ring compound give similar and detectably large spin densities on in-plane hydrogens (54); but even if these two states were distorted variously, we would still expect at least one doublet splitting. A similar consideration eliminates a complex between a phenyl and benzene molecules such that a proton is shared equally (VI).

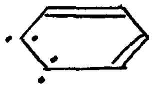
VI

A further case is of course the presence of an impurity, such as oxygen with a ground state triplet. However, it is most unlikely that one would see EPR absorptions by O_2 dissolved in organix solvents in the usual magnetic resonance setup (9.5 Gc at 3400 Oe) (41). Higher frequencies would be needed (41).

It seems worthwhile to consider the products of the radiolysis of liquid benzene in order to ascertain their precursors, which may be common to both the liquid and solid states. The major products were: bicyclohexadiene, phenylcyclohexadiene, biphenyl, and terphenyl; the fraction of compounds having twelve carbon atoms was 18.8%; 18, 57.6%; and higher, 23.6% (57). There is evidently a good possibility of γ-irradiation striking the same molecule twice in the course of an irradiation. Hence, further possibilities for the unidentified source are:

VIIa

VIIb



VIIc

VIIb should go quickly to VIIa or VIIc. VIIc (benzyne) is highly reactive, becoming phenyl or benzene with the addition of the appropriate number of hydrogen atoms.

The disappearance of the cyclohexadinyl spectrum at a temperature (-32°C) considerably below the melting point of benzene (5.5°C), with its replacement by the singlet spectrum, may indicate that motion due to rising temperature has allowed cyclohexadienyl to borrow an additional hydrogen atom from its neighbors. If so, the concentration of both phenyl and VIIa should rise. The singlet spectrum does not corroborate the presence of either.

Known cases in which an ESR singlet spectrum has been observed are in the charge-transfer complexes involving organic acids (58). However, it is difficult to see what charge-transfer complex is involved in the case at hand.

The foregoing comments were presented as a further illustration of the usefulness of simplified VB theory calculations of spin densities in free radicals.

SUMMARY AND CONCLUSIONS

For the case of hindered rotation of the methylene β-protons in cyclobutenyl, the variational valence bond calculation, using a large number of exchange integrals gave an appreciably lower estimate of the electron spin densities on the β-protons that does the first-order calculation. This situation, however, was seen to be the reverse of the results obtained using the two methods in calculating the spin densities of β-protons which are adjacent to a π-orbital in a long-chain polymer. The first-order calculation, which agrees with experiment, was given in this thesis; the variational calculation was deduced from results previously applied to the calculation of the spin densities of β-protons which are adjacent to an allyl section in a long-chain polymer. The original calculation (on the long-chain polymer with a β-proton-allyl section) was applied since in it the effects of two of the three π-orbitals of the allyl section on the β-proton spin densities were ignored until a multiplicative constant, the spin density of the terminal π-orbital of the allyl radical, was introduced as the very end.

It was further demonstrated that the spin densities of the β-protons which are adjacent to an allyl section, whether it is present in a long-chain polymer or part of the cyclobutenyl radical or any other aromatic hydrocarbon, are dependent on the π-electron excitation energies of the allyl section. This result was in accord with experimental results, which enabled one to make a comparison between the hyperfine splittings of the β-protons of a long-chain polymer which are adjacent to an allyl section and of those which are adjacent to a single π-orbital. The effect of the contribution of the π-electron excitation energies is to reduce the size of the hyperfine splitting.

Expressions were obtained for all fourteen vector-coupling states of an eight electron system in terms of canonical states. The latter were found to be especially amenable to computer computations, as indicated by the program given in Appendix II.

The reasons for the suitability of the use of the vector-coupling functions in configuration interaction was discussed. A case was given in which the hybridization of the perturbing excited state, different from that of the perfect-pairing "ground" state, alters the magnitude and dependence on hybrid angles of a proton splitting. The particular system considered was that of the C-H "fragment". The use of such distinct hybridizations, dependent upon whether two electrons have a singlet or triplet spin coupling, corresponds to having the antisymmetrical spatial components (triplet) of the ground state wave function somewhat differently distributed in space than that of the symmetrical spatial components (singlet) for electron pairs.

For the radical in irradiated benzene giving the singlet spectrum, it was concluded that all radicals, thought most likely to be present, would not give such a spectrum.

APPENDIX I. A COMPUTER PROGRAM FOR COMPUTING THE SPIN DENSITIES OF AN EIGHT (OR LESS) ORBITAL SYSTEM USING THE EMPIRICAL, NON-OVERLAP VALENCE BOND THEORY

The computer program below was designed to calculate spin densities according to the non-overlap, empirical VB theory for an eight electron (one phantom) system. Orbital number 8 was chosen to be the phantom. The program was divided into three separate smaller programs, with the information of Parts I and II being introduced as data in the final Part III. The three parts could be made into one entire program with the removal of the parts within dotted lines and other minor adjustments. The more general dimension statements are:

B$\left(\frac{n}{2}\right)!$, $\frac{1}{2}$n), G($\left(\frac{n}{2}\right)!$, $\frac{1}{2}$n), KC(j), A(n,n,j), HH(j), RHO(n-1), H(i,i), U(i,i), D(i), where i = $n!\left[\left(\frac{n}{2}\right)!\left(\frac{n}{2}+1\right)!\right]^{-1}$, j = $\frac{i(i-1)}{2}$. n is the number of orbitals = N; RR = i, MMR = j, MF = $\left(\frac{n}{2}\right)!$, M = $\frac{1}{2}$n.

The values of the exchange integrals were introduced (line 12a below) according to the numbers of the orbitals involved, with J(i, j) before J(i, j+1), and J(i,j) before J(i - 1, j).

The program may be outlined as follows:

1) First, all permutations of the even integers between and including 2 and n were generated. Each integer of an even-integer permutation was associated on the basis of its position, as counted from left to right, with the odd integers between and including 1 and (n-1). Only one ordering of the odd integers was allowed, the one 1 3 5 ...(n-1) (= 2I =1, where I = 1,2,3, ...). This correspondence of the even integers to the odd integers is exactly that of the even and odd integers labelling orbitals in the Rumer diagrams, in which lines are drawn between even-numbered

and odd-numbered sites only. Hence we have all the canonical states represented and a few extra $\left[(\frac{1}{2}n)! \;\; -n!\;\; \left((\frac{n}{2})!\,(\frac{n}{2}+1)!\right)^{-1}\right]$ crossed structures, interspersed with them (at this point).

The permutations of the even integers were obtained as follows:

a) A matrix of size $\frac{n}{2} \times ((\frac{n}{2})!)$ containing the ordering of even integers, 2 4 6 ... n, across all its rows was constructed (line 1).

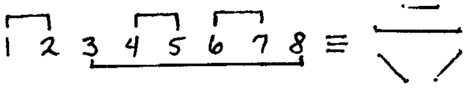
b) Then in one-half of the rows the integers n and n-2 were permuted. The second half remained unchanged. Next the two halves were each subdivided into thirds and the following permutations constructed:

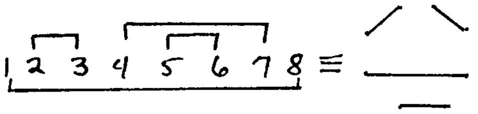
$$\begin{array}{cccccc}
2 & 4 & \cdots & n-4 & n-2 & n \\
\vdots & \vdots & & \vdots & \vdots & \vdots \\
2 & 4 & , & n-4 & n-2 & n \\
 & & & n-4 & n-2 & n \\
\vdots & \vdots & , & \vdots & \vdots & \vdots \\
 & & & n-4 & n & n-2 \\
2 & 4 & & n-4 & n & n-2 \\
\vdots & \vdots & & \vdots & \vdots & \vdots \\
2 & 4 & \cdots & n-4 & n & n-2
\end{array}
\longrightarrow
\begin{array}{cccccc}
2 & 4 & \cdots & n & n-2 & n-4 \\
\vdots & \vdots & & \vdots & \vdots & \vdots \\
2 & 4 & & n-4 & n & n-2 \\
 & & & n-4 & n-2 & n \\
\vdots & \vdots & & \vdots & \vdots & \vdots \\
 & & & n-2 & n & n-4 \\
2 & 4 & & n-4 & n-2 & n \\
\vdots & \vdots & & \vdots & \vdots & \vdots \\
2 & 4 & \cdots & n-4 & n & n-2
\end{array}$$

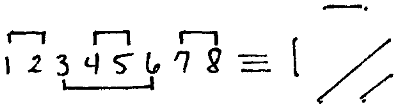
c) The pattern indicated was continued; each time a new number, located one column further to the left, was introduced by all possible single interchanges (or no interchange) between its position and the position of the integers to its right. In this way all $(\frac{n}{2})!$ distinct permutations were generated (line (2) to line (3)).

Simultaneously, a matrix containing all possible ways of adding $\frac{1}{2}$n 2's was constructed to be used later in calculating the overlap coefficients (the $\underset{\approx}{O}$ matrix elements) of every pair of CS's. Between lines (5) and (6), the rows of this matrix were tested and arranged so that only rows, in which the integers to the left were each greater than or equal to the integers to the right in the row, were present in the initial rows of this matrix.

2) The next problem was to sort out and to "remove" the non-canonical states. This was accomplished by noting that all CS's could be written in terms of nested "blocks" of integer intervals, with all larger "blocks" containing one or more smaller blocks of variable length. These blocks are defined by the following technique: arrange the integers from one to n thus: 1 2 3 4 5 6 7 8 (n = 8, for example). Then draw lines between every two integers which correspond to the orbitals between which lines are drawn in a given Rumer diagram (for a CS only). Examples are:







The test which will check the integer intervals indicated by the even-integer permutations are properly structured and exclude those which are not, is given from line (4) to line (5).

3) At this point, the CS's having been constructed and isolated, the calculation of the matrix elements of the $\underset{\approx}{\mathcal{H}}$ and $\underset{\approx}{\mathcal{O}}$ matrices begins. For both matrices, it was necessary to determine whether two orbitals lay in the same island, or on an unbroken line chain of the superposition diagram of the two CS's involved. (See also Appendix II.) In addition, it was necessary to know, for the computation of $\underset{\approx}{\mathcal{H}}$, whether they were both at odd (even) numbered sites or not, i.e. whether they were both at odd (even) numbered sites or not. The technique employed was essentially to work through each of the odd integers in succession (1, 3, 5, ...)

and to determine the extent of the island in which the orbital, to which the odd integer corresponded, lay. A three-dimensional matrix (A) was used to record whether two orbitals were in the same island of a given superposition diagram and what coefficient should be assigned to the exchange integral between any two orbitals, on the basis of rule (1), Section II (lines (8) through (9)).

The information as to whether or not any given pair of orbitals occurred in the same island was stored separately in A; from it the total number of distinct pairs of orbitals within some island of a given superposition diagram was determined (lines (8) through (9)). (This part of A also contained the information as to whether an orbital lay in the same island as the phantom orbital, which was used in phase (5) below). For any superposition diagram, this total number of in-island pairs is $\sum_{i=\text{island}} \frac{n_i(n_i-1)}{2}$, where n_i is the number of orbitals occurring in any given island i. The total number was then compared with the matrix (G) containing all combinations (ordered as previously mentioned) of even integers whose sum is n. The integers $\sum_c \frac{n_c(n_c-1)}{2}$, where the summation is over all columns of any given row of G and n_c is the even integer appearing in column c, may be uniquely identified with the numbers $\sum_{i=\text{island}} \frac{n_i(n_i-1)}{2}$.

One proof that this identification is unique is: Assume that there were two possible choices. Then

$$n_{1a}^2 - n_{1a} + n_{2a}^2 - n_{2a} + \cdots + n_{ia}^2 - n_{ia} = n_{1b}^2 - n_{1b} + \cdots + n_{jb}^2 - n_{jb} \, .$$

But $n_{1a} + \cdots + n_{ia} = n_{1b} + \cdots + n_{jb} = n$

Thus $n_{1a}^2 + n_{2a}^2 + \cdots + n_{ia}^2 = n_{1b}^2 + \cdots + n_{jb}^2$, which is true when (1) holds only when $n_{1a} = n_{1b}; \; n_{2a} = n_{2b}, \ldots, n_{ia} = n_{ib}$.

In lines (10) through (11), the matrix elements of $\underset{\approx}{\mathcal{O}}$, 2^{x-n}, were calculated, using G and the numbers $\sum_i \frac{n_i(n_i-1)}{2}$.

4) Suitable values were than introduced for the exchange integrals (line 11a), and the eigenvectors $\underset{\sim}{X}$ and eigenvalues E such that $\underset{\approx}{\mathcal{H}}\,\underset{\sim}{x} = E\,\underset{\approx}{\mathcal{O}}\,\underset{\sim}{x}$ computed (lines (12) through (13)). The subroutine EIGEN used two Jacobi diagonalization procedures to determine the eigenvalues E and eigenvectors $\underset{\sim}{x}$.

5) The coefficients of the CS's in the ground-state wave function, the overlap coefficients of the CS's themselves, and the information as to whether an orbital lay in the same island as the phantom orbital, were then used to compute spin sensities for the various orbitals, according to the rule given in Section IV on p. 15 (lines (14) - (15)).

PART I

```
      DIMENSION B(24,4), G(24,4)
      INTEGER B, G
      INTEGER MOV, C, PT, PTV, RR, SS, P, RD, BC, BOV, GR1, GR2, P, V,
     X T, EL1, EL2, SW, S, AB, BB, R, AP, BP, QR, EE1, EE2
      N=8
      M=4
      RR=14
      IPAR=5
      MMR=105
      MF=24
      LOGICAL X, Y, XX, YY, X1, Y1, XX1, YY1
      DO 3 K=1, M
      DO 3 J=1, MF
      B(J,K) =0
      B(J,K) =2*K                                         line 1
 3    G(J,K) =2                                           line 2
      I = 1
      V = MF/(I+1)
      GO TO 4
 6    I = I+1
      IF(I.GT.(M-1)) GO TO 7
      V= V/(I+1)
 4    LL = MF/(V*(I+1))
      DO 5 K=1,LL
      L =I+1
      DO 5 J=1,L
      DO 5 T=1,V
      MV=T+V*(J-1+(K-1)*(I+1))
      LM =M-I
      EL1 =B(MV,LM)
      LN =M+1-J
      EL2 =B(MV,LN)
      B(MV,LM) =EL2
      B(MV,LN) =EL1
      IF(LM.EQ.LN) GO TO 5
      EL1 =G(MV,LM)
      EL2 =G(MV,LN)
      G(MV,LM) =EL1 + EL2
      G(MV,LN) =0
 5    CONTINUE
      GO TO 6
 7    CONTINUE                                            line 3
CC    ELIMINATION OF CROSSED STRUCTURES
      DO 14 I =1,MF                                       line 4
      LL=M-1
      DO 14 J = 1, LL
      L = J + 1
      DO 14 T = L, M
      IP = B(I, J)
10    IPTP = B (I, T)
      IPT = 2*T-1
      IT = 2*J-1
```

```
      X = IP.LT.IPT
      Y = IP.LT.IPTP
      XX=IT.GT.IPT
      YY=IT.GT.IPTP
      X1=IP.GT.IPT
      Y1=IP.GT.IPTP
      XX1=IT.LT.IPT
      YY1=IT.LT.IPTP
      IF(((Y1.AND.YY).AND.(X.AND.XX1)).OR.((X1.AND.Y1).AND.(XX1.AND.
     I YY1)).OR.((X.AND.Y).AND.(XX1.AND.YY1))) GO TO 14
      B(I,1)=0                                                  line 5
 14   CONTINUE
      DO 322 IN=1,2                                             line 6
      LR=RR
      IR(IN.EQ.1) GO TO 333
      LR=IPAR
      L=M-1
      DO 358 I=1,L
      DO 358 R=1,MF
      GR1 =G(R,I)
      GR2 =G(R,I+1)
 358  IF(GR1.LT.GR2) GO TO 336
      GO TO 322
 336  G(R,1)=0
332   DO 335 I=1,MF
      DO 335 J=1,M
 335  B(I,J)=G(I,J)                                             line 7*
 333  DO 15 I=1,LR
      IF(B(I,1).NE.0) GO TO 15
      L=I+1
      DO 17 R=L,MF
 17   IF((B(I,1).EQ.0).AND.(B(R,1).NE.0)) GO TO 18
      GO TO 15
 18   DO 19 K=1,M
      EL1=B(I,K)
      EL2=B(R,K)
      B(I,K)=EL2
 19   B(R,K)=EL1
 15   CONTINUE
 160  FORMAT (1X,4I3)
 322  WRITE (6,160) ((B(I,J),J=1,M),I=1,MF)
      STOP
      END
```

*For the use of the results of this part in Parts II and III, information on B must be stored prior to this operation.

PART II

```
       N=8
       INTEGER MOV, C, PT, PTV, RR, SS, P, RD, BC, BOV, GR1, GR2, P, V,
     X T, EL1, EL2, SW, S, AB, BB, R, AP, BP, QR, EE1, EE2
       DIMENSION KC(4), B(24,4), FIS(4)
       DIMENSION G(6,4)
       INTEGER B, G
       MMR=5
       MF=6
       M=4
       READ (5,1000) ((G(I,J), J=1,M), I=1,MF)
       READ (5,1001) (KC(I),I=1,MMR)
1000   FORMAT (72I1)
1001   FORMAT (26I2)
 556   S=1                                                    line 10
  66   R=1
  62   IP=G(R,1)
       IF(IP.EQ.0) GO TO 69
       SS = 0
       DO 64 I=1,M
  64   SS=(G(R,I))*(G(R,I)-1)+SS
       IKC=2*KC(S)
       IF(IKC.EQ.SS) GO TO 65
  69   R=R+1
       IF(R.GT.MF) GO TO 100
       GO TO  62

  65   I=0
 265   I =I+1
       IF(I.EQ.M) GO TO 70
       GR1=G(R,I)
       GR2=G(R,I+1)
       IF((GR1.NE.0).AND.(GR2.EQ.0)) GO TO  67
       GO TO 265
  70    KM
       GO TO 83
  67   K=I
  83   FIS(S)=0.5**(FLOAT(M-K))
 170   S=S+1
       IF(S.GT.MMR) GO TO 671
       GO TO 66                                               line 11
 671   DO 675 S=1, MMR
       WRITE(6,77) (S,FIS(S))
  77   FORMAT(1X,///2HS=I3,4X,4HFIS=F8.6)
 675   CONTINUE
 100   WRITE (6,960) SS
 960   FORMAT (1X,2I3)
```

PART III

```
      INTEGER V
      V=0
      LUCK =12
      DIMENSION B(24,4), G(24,4)
      DIMENSION A(8,8,105), FIS(105), HH(105), RHO(7), KC(105),
     X H(14,14), U(14,14), D(14)
      N=8
      INTEGER B, G
      LOGICAL X, Y
      INTEGER MOV, C, PT, PTV, RR, SS, P, RD, BC, BOV, GR1, GR2, P,
     X V, T, EL1, EL2, SW, S, AB, BB, R, AP, BP, QR, EE1, EE2
      RR=14
      MMR=105
      MF=24
      M=4
      READ(5,500) ((B(I,J),J=1,M),I=1,MF), ((G(I,J),J=1,M),I=1,MF)
  500 FORMAT (16(4I1,1X))
   CC IN INSLAND CHECK. SIMPLE ISLAND (TO LINE 33), SAME SPIN AND
   CC MIXED SPIN ON A (37 TO 50).
      DO 21 S=1, MMR                                       line 8*
      L=N-1
      DO 23 J=1,L
      LL=J+1
      DO 23 I=LL,N
   23 A(I,J,S)=-.5
      DO 21 I=1,L
      LL=I+1
      DO 21 J=LL,N
   21 A(I,J,S)=0.
      DO 440 J=1,RR
  224 L=RR+1-J
      DO 140 K=1,L
      DO 140 I=1,M
      AP=2*I-1
      BP=B(J,I)
      LP=K+V
   26 A(AP,BP,LP)=1.0
      A(BP,AP,LP)=1.0
  140  CONTINUE
      V=RR+1-J+V
  440 CONTINUE
      L =RR-1
      DO 30 K=1,L
      V=K*(K+1)/2
      LP=MMR-V+1
      DO 30 J=K,L
      V=V+J
      QR=MMR+1-V
      LM=N-1
      DO 30 K=1,LM
      LL=K+1
      DO 30 J=LL,N
      IF(((A(K,J,LP)).EQ.(1.0)).OR.((A(K,J,QR)).EQ.(1. ))) GO TO 460
```

```
      GO TO 30
460   A(K,J,QR)=1.0
      A(J,K,QR)=1.0
 30   CONTINUE
      S=0
      IR=RR-1
      DO 36 C=1,IR
      IL=C+1
      S=S+1
      DO 38 MOV=IL,RR
      S=S+1
      IM=N-1
      DO 38 PT=1,IM,2
      K=(PT+1)/2
 49   R=1
      BC= B(C,K)
 41   BOV=B(MOV,R)
      IF(BC.EQ.BOV) GO TO 42
      R=R+1
      GO TO 41
 42   LR=2*R-1
      IF(LR-PT) 43,38,44
 44   A(LR,PT,S)=-2.0
      A(PT,LR,S)=1.0
      GO TO 146
 43   A(PT,LR,S)=-2.0
      A(LR,PT,S)=1.0
146   LL=(PT+1)/2
      EE1=B(C,LL)
      EE2=B(C,R)
      IF(EE1-EE2) 45,38,46
 46   A(EE1,EE2,S)=-2.0
      A(EE2,EE1,S)=1.0
      GO TO 145
 45   A(EE2,EE1,S)=-2.0
      A(EE1,EE2,S)=1.0
145   MM1=PT
      MM2=B(C,R)
      IF(MM1-MM2) 47,38,48
 48   A(MM1,MM2,S)=1.0
      A(MM2,MM1,S)=1.0
      GO TO 147
 47   A(MM2,MM1,S)=1.0
      A(MM1,MM2,S)=1.0
147   PTV=R
      K=PTV
      GO TO 49
 38   CONTINUE
 36   CONTINUE                                          line 9
      READ (5,701) (FIS(S),S=1,MMR)
      S=1
      DO 679 J=1,RR
```

```
      DO  679 I=J,RR
      U(J,I)=0.0
      FJ=FIS(S)
      U(J,I)=FJ
      S=S+1
679   CONTINUE
      WRITE (6,183) ((U(I,J),J=1,RR),I=1,RR)
701    FORMAT (7F10.8)
      DO 135 I=1,LUCK                                     line 12
183   FORMAT (1X,14F9.6)
      WRITE (6,134) I
134   FORMAT (2X,5HLUCK=I3)
      LL=N-1
      DO 71 I=1,LL
      L=I+1
 71   READ (5,72) (A(I,J,1),J=L,N)                        line 12a
 72   FORMAT (7F10.8)
      DO 132 S=2,MMR
      L=N-1
      DO 132 J=1,L
      LL=J+1
      DO 132 I=LL,N
132   A(J,I,S)=A(J,I,1)
      DO 75 S=1,MMR
      HH(S)=0.0
 89   L=N-1
      DO 75 J=1,L
      LL=J+1
      DO 75 I=LL,N
      A(J,I,S)=A(I,J,S)*FIS(S)*A(J,I,S)
      HH(S)=A(J,I,S)+HH(S)
 75   CONTINUE
      DO 76 S=1,2
      WRITE (6,131) S
131   FORMAT (1X,2HI=I3)
      IM=N-1
      DO 76 I=1,IM
      L=I+1
      WRITE (6,137) (A(I,J,S),J=L,N)
137   FORMAT (1X,13F10.7)
 76   CONTINUE
192   S=1
      DO 79 J=1,RR
      DO 79 I=J,RR
      H(I,J)=0.0
      H(J,I)=0.0
      FJ=HH(S)
      H(J,I)=FJ
      S=S+1
 79   CONTINUE
```

```
      WRITE (6,183) ((H(I,J),J=1,RR),I=1,RR)
      CALL EIGEN(H,U,MMR,RR,D)                                line 13
      XX=.0                                                   line 14
      DO 211 I=1,RR
211   D(I)=U(I,1)
212   S=1
      DO 179 J=1,RR
      DO 179 I=J,RR
      U(I,J)=0.0
      U(J,I)=0.0
      FJ=FIS(S)
      U(I,J)=FJ
      U(J,I)=FJ
      S=S+1
179   CONTINUE
213   DO 214 I=1,RR
      DO 214 J=1,RR
214   XX=(U(I,J))*D(I)*D(J)+XX
      L=N-1
      DO 133 K=1,L
      DO 92 S=1,MMR
      IF(A(N,K,S)+0.500) 90,106,90
106   A(K,N,S)=0.0
      GO TO 92
 90   IF(MOD(K,2).EQ.0) GO TO 93
      A(K,N,S)=FIS(S)
      GO TO 92
 93   A(K,N,S)=-1.0*FIS(S)
 92   CONTINUE
      S=1
      DO 94 J=1,RR
      DO 94 I=J,RR
      H(I,J)=A(K,N,S)
      S=S+1
 94   CONTINUE
      DO 95 J=1,RR
      DO 95 I=J,RR
 95   H(J,I)=H(I,J)
      RHO(K)=0.0
      DO 96I=1,RR
      DO 96 J=1,RR
 96   RHO(K)=H(I,J)*D(I)*D(J)+RHO(K)
      RHO(K)=RHO(K)/XX
      WRITE (6,99) K,RHO(K)
 99   FORMAT (1X,4HRHO (,I3,3H) =,F10.7)
133   CONTINUE                                                line 15
135   CONTINUE
100   CONTINUE
      STOP
      END
```

*The number 671 should be inserted at↓(line 8) if Part II added.

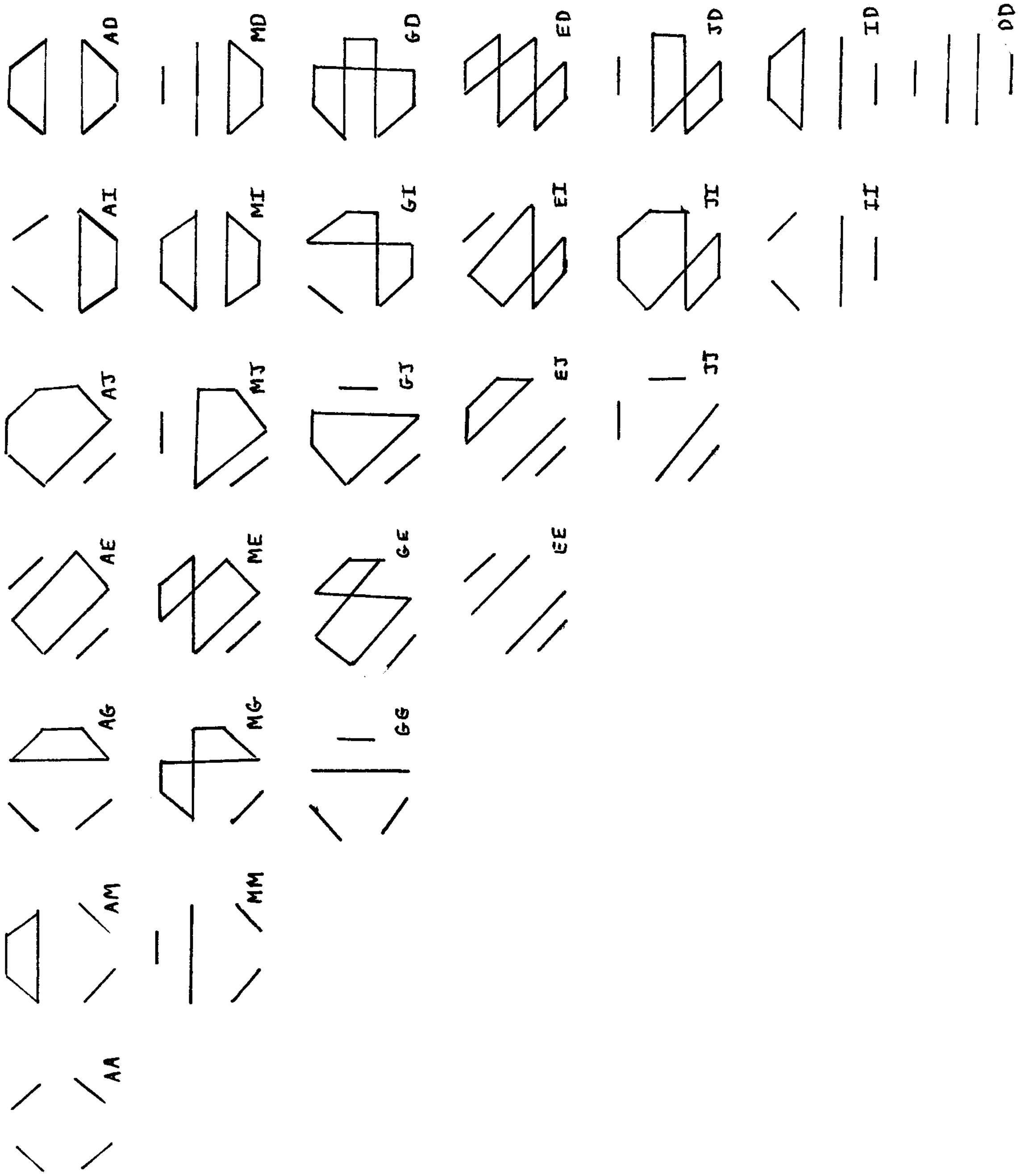
APPENDIX II. THE PAULING SUPERPOSITION DIAGRAMS FOR THE FOURTEEN CANONICAL STATES OF AN EIGHT ORBITAL SYSTEM; A TABLE OF OVERLAP COEFFICIENTS FOR THESE SUPERPOSITION DIAGRAMS; AND A TABLE OF OVERLAP COEFFICIENTS FOR THE SEVEN FUNCTIONS OF A-TYPE SYMMETRY DISCUSSED IN SECTION II

The 132 distinct Pauling superposition diagrams of the fourteen canonical states possible for an eight electron system are given on the next three pages. The Rumer diagrams of the fourteen canonical states were given on p. 12. Their superposition diagrams will be labelled Y and Z, where Y and Z are the two canonical states involved. The diagrams give x in rule (1) of Section II, since x is also the number of "islands". An "island" is defined as an entity composed of all orbitals, which are connected by an unbroked chain of lines in the superposition diagram. These lines are the composite collection of those present in the initial Rumer diagrams of the two CS's, prior to superposition. (A double line between two orbitals in a superposition diagram is usually written as a single line, but it is nevertheless an island.) The version of rule (1) applicable to superposition diagrams is:

> $\langle Y|\mathcal{H}|Z\rangle = 2^{x-n}\{Q + \frac{3}{2}[\Sigma$(single exchange integrals between orbitals which lie on an unbroken chain of lines (the "island") and are an odd number of links (lines) apart) $-\ \Sigma$(single exchange integrals between orbitals lying on an unbroken line chain and which are an even number of links apart)$]\ -\ \frac{1}{2}$(all single exchange integrals)$\}$.

The overlap coefficients of the canonical states are also given in

Table E below. This table is followed by Table F, which contains the overlap coefficients for the seven A-type symmetry functions of Section II. Both tables are symmetric across the diagonal.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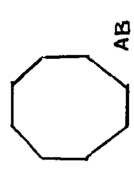
MM
AA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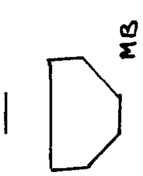
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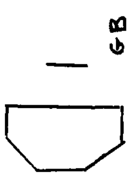
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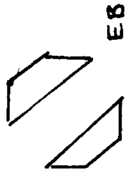
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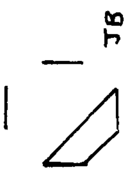
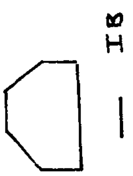

JB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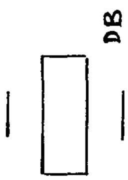
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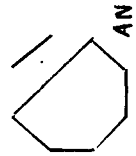
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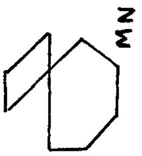
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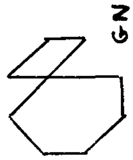
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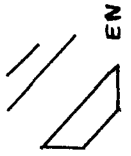
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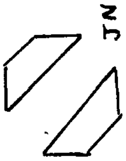
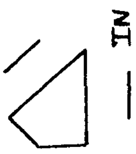

JN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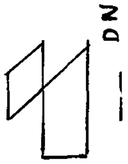
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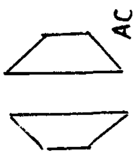
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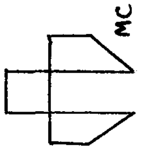
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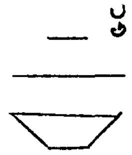
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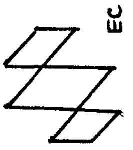
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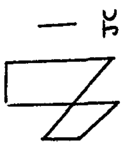
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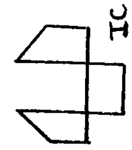
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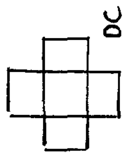
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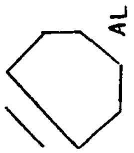
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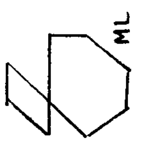
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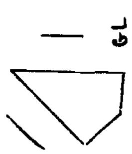
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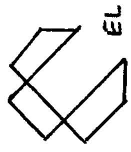
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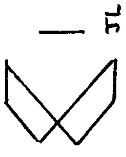
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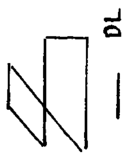
IL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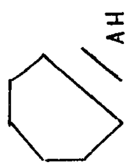
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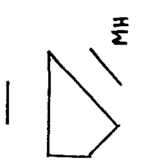
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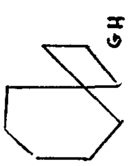
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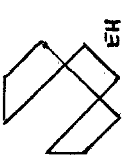
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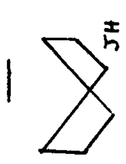
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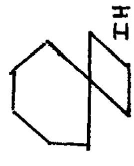
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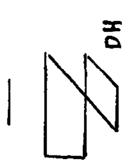
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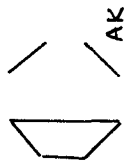
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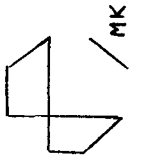
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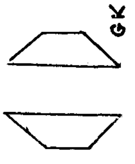
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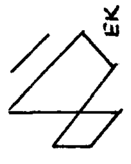
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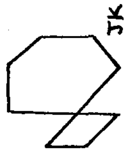
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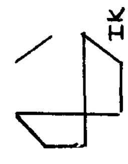
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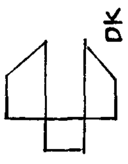
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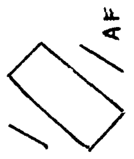
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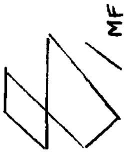
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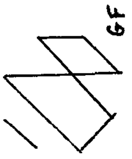
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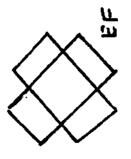
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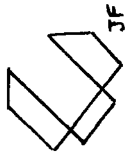
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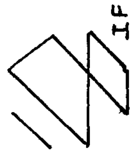
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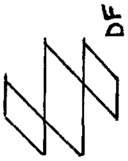
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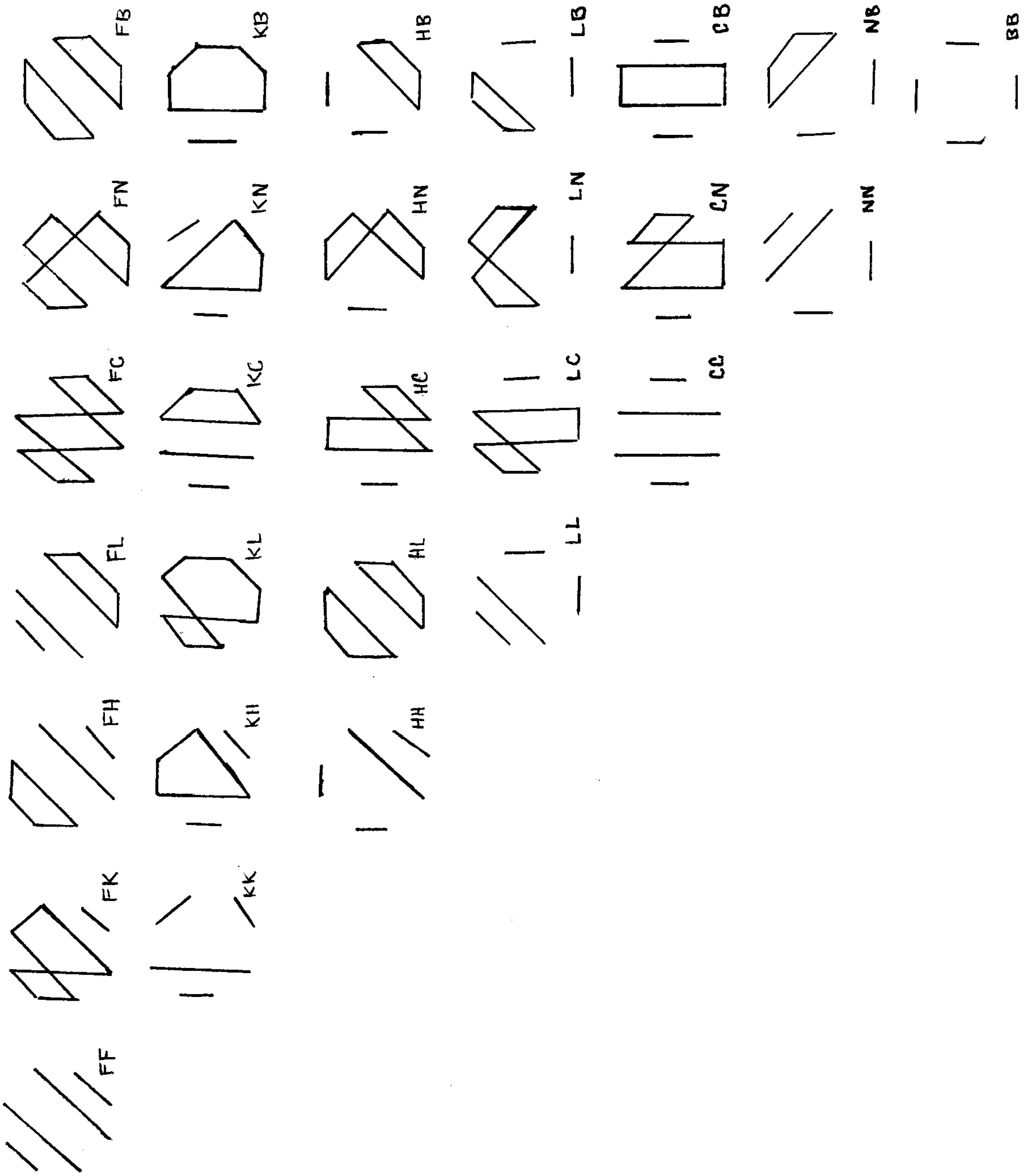
FB
KB
HB
LB
CB
NB
BB
FN
KN
HN
LN
CN
NN
FC
KC
HC
LC
CC
FL
KL
HL
LL
FH
KH
HH
FK
KK
FF

TABLE E

	A	M	G	E	J	I	D	F	K	H	L	C	N	B
A	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{8}$
M		1	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{4}$
G			1	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{8}$	$\frac{1}{4}$
E				1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{2}$	$\frac{1}{4}$
J					1	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$
I						1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{2}$	$\frac{1}{8}$	$\frac{1}{2}$	$\frac{1}{4}$
D							1	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$
F								1	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{4}$
K									1	$\frac{1}{2}$	$\frac{1}{8}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$
H										1	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$
L											1	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$
C												1	$\frac{1}{4}$	$\frac{1}{2}$
N													1	$\frac{1}{2}$
B														1

TABLE F

	A+B	G+H	J+M	C+F	K+L	D+E	I+N
A+B	$\frac{9}{4}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$
G+H		$\frac{9}{4}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{4}$	$\frac{3}{4}$
J+M			3	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{2}$	$\frac{3}{4}$
C+F				$\frac{9}{4}$	$\frac{3}{2}$	$\frac{3}{4}$	$\frac{3}{4}$
K+L					$\frac{9}{4}$	$\frac{3}{4}$	$\frac{3}{2}$
D+E						$\frac{9}{4}$	$\frac{3}{2}$
I+N							3

APPENDIX III. WELL-KNOWN EXPRESSIONS FOR STATES WHOSE TOTAL ANGULAR MOMENTUM J IS EQUAL TO THE VECTOR SUM OF ANGULAR MOMENTA J_1 AND J_2 IN TERMS OF STATES WHOSE TOTAL ANGULAR MOMENTUM IS J_1 AND J_2, RESPECTIVELY

The notation is $\left|\begin{smallmatrix} J \\ M_J \end{smallmatrix}\right\rangle$, $\left|\begin{smallmatrix} J_1 \\ M_{J_1} \end{smallmatrix}\right\rangle$, $\left|\begin{smallmatrix} J_2 \\ M_{J_2} \end{smallmatrix}\right\rangle$.

$J = \frac{5}{2}$, $J_1 = \frac{3}{2}$, $J_2 = 1$, for $\left|\begin{smallmatrix} \frac{5}{2} \\ \frac{5}{2} \end{smallmatrix}\right\rangle = \left|\begin{smallmatrix} \frac{3}{2} \\ \frac{3}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ 1 \end{smallmatrix}\right\rangle$. The expression for the $J=\frac{1}{2}$ state is found as follows:

$$\left|\begin{smallmatrix} \frac{5}{2} \\ \frac{5}{2} \end{smallmatrix}\right\rangle = \left|\begin{smallmatrix} \frac{3}{2} \\ \frac{3}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ 1 \end{smallmatrix}\right\rangle$$

$$\left|\begin{smallmatrix} \frac{5}{2} \\ \frac{3}{2} \end{smallmatrix}\right\rangle = \frac{1}{\sqrt{5}}\left[\sqrt{3}\left|\begin{smallmatrix} \frac{3}{2} \\ \frac{1}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ 1 \end{smallmatrix}\right\rangle + \sqrt{2}\left|\begin{smallmatrix} \frac{3}{2} \\ \frac{3}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}\right\rangle\right]$$

$$\left|\begin{smallmatrix} \frac{5}{2} \\ \frac{1}{2} \end{smallmatrix}\right\rangle = \frac{1}{\sqrt{10}}\left[\sqrt{3}\left|\begin{smallmatrix} \frac{3}{2} \\ -\frac{1}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ 1 \end{smallmatrix}\right\rangle + \sqrt{6}\left|\begin{smallmatrix} \frac{3}{2} \\ \frac{1}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}\right\rangle + \left|\begin{smallmatrix} \frac{3}{2} \\ \frac{3}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ -1 \end{smallmatrix}\right\rangle\right]$$

$$\left|\begin{smallmatrix} \frac{3}{2} \\ \frac{3}{2} \end{smallmatrix}\right\rangle = \frac{1}{\sqrt{5}}\left[\sqrt{3}\left|\begin{smallmatrix} \frac{3}{2} \\ \frac{3}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}\right\rangle - \sqrt{2}\left|\begin{smallmatrix} \frac{3}{2} \\ \frac{1}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ 1 \end{smallmatrix}\right\rangle\right]$$

$$\left|\begin{smallmatrix} \frac{3}{2} \\ \frac{1}{2} \end{smallmatrix}\right\rangle = \frac{1}{\sqrt{15}}\left[\left|\begin{smallmatrix} \frac{3}{2} \\ \frac{1}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}\right\rangle + \sqrt{6}\left|\begin{smallmatrix} \frac{3}{2} \\ \frac{3}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ -1 \end{smallmatrix}\right\rangle - 2\sqrt{2}\left|\begin{smallmatrix} \frac{3}{2} \\ -\frac{1}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ 1 \end{smallmatrix}\right\rangle\right]$$

$$\left|\begin{smallmatrix} \frac{1}{2} \\ \frac{1}{2} \end{smallmatrix}\right\rangle = \sqrt{\frac{1}{2}}\left[\left|\begin{smallmatrix} \frac{3}{2} \\ \frac{3}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ -1 \end{smallmatrix}\right\rangle - \sqrt{\frac{2}{3}}\left|\begin{smallmatrix} \frac{3}{2} \\ \frac{1}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}\right\rangle + \frac{1}{\sqrt{3}}\left|\begin{smallmatrix} \frac{3}{2} \\ -\frac{1}{2} \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} 1 \\ 1 \end{smallmatrix}\right\rangle\right]$$

The expression for the $J=\frac{1}{2}$ state for $J_1 = 1$, $J_2 = \frac{1}{2}$ is obtained as follows:

$$\left|\begin{smallmatrix} \frac{3}{2} \\ \frac{3}{2} \end{smallmatrix}\right\rangle = \left|\begin{smallmatrix} 1 \\ 1 \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} \frac{1}{2} \\ \frac{1}{2} \end{smallmatrix}\right\rangle$$

$$\left|\begin{smallmatrix} \frac{3}{2} \\ \frac{1}{2} \end{smallmatrix}\right\rangle = \frac{1}{\sqrt{3}}\left[\sqrt{2}\left|\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} \frac{1}{2} \\ \frac{1}{2} \end{smallmatrix}\right\rangle + \left|\begin{smallmatrix} 1 \\ 1 \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} \frac{1}{2} \\ -\frac{1}{2} \end{smallmatrix}\right\rangle\right]$$

$$\left|\begin{smallmatrix} \frac{1}{2} \\ \frac{1}{2} \end{smallmatrix}\right\rangle = \frac{1}{\sqrt{3}}\left[\left|\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} \frac{1}{2} \\ \frac{1}{2} \end{smallmatrix}\right\rangle - \sqrt{2}\left|\begin{smallmatrix} 1 \\ 1 \end{smallmatrix}\right\rangle \left|\begin{smallmatrix} \frac{1}{2} \\ -\frac{1}{2} \end{smallmatrix}\right\rangle\right]$$

The J = 4, $J_1 = J_2 = 2$ state is known; find an expression for the J = 0 state in terms of states whose total angular momentum is $J_1 = J_2 = 2$.

$$\left|{4 \atop 4}\right\rangle = \left|{2 \atop 2}\right\rangle\left|{2 \atop 2}\right\rangle$$

$$\left|{4 \atop 3}\right\rangle = \frac{1}{\sqrt{2}}\left[\left|{2 \atop 1}\right\rangle\left|{2 \atop 2}\right\rangle + \left|{2 \atop 2}\right\rangle\left|{2 \atop 1}\right\rangle\right]$$

$$\left|{4 \atop 2}\right\rangle = \frac{1}{\sqrt{14}}\left[\sqrt{3}\left|{2 \atop 0}\right\rangle\left|{2 \atop 2}\right\rangle + 2\sqrt{2}\left|{2 \atop 1}\right\rangle\left|{2 \atop 1}\right\rangle + \sqrt{3}\left|{2 \atop 2}\right\rangle\left|{2 \atop 0}\right\rangle\right]$$

$$\left|{4 \atop 1}\right\rangle = \frac{1}{\sqrt{14}}\left[\left|{2 \atop 2}\right\rangle\left|{2 \atop -1}\right\rangle + \sqrt{6}\left(\left|{2 \atop 0}\right\rangle\left|{2 \atop 1}\right\rangle + \left|{2 \atop 1}\right\rangle\left|{2 \atop 0}\right\rangle\right) + \left|{2 \atop -1}\right\rangle\left|{2 \atop 2}\right\rangle\right]$$

$$\left|{4 \atop 0}\right\rangle = \frac{1}{\sqrt{70}}\left[\left|{2 \atop 2}\right\rangle\left|{2 \atop -2}\right\rangle + \left|{2 \atop -2}\right\rangle\left|{2 \atop 2}\right\rangle + 4\left(\left|{2 \atop 1}\right\rangle\left|{2 \atop -1}\right\rangle + \left|{2 \atop -1}\right\rangle\left|{2 \atop 1}\right\rangle\right) + 6\left|{2 \atop 0}\right\rangle\left|{2 \atop 0}\right\rangle\right]$$

$$\left|{3 \atop 3}\right\rangle = \frac{1}{\sqrt{2}}\left[\left|{2 \atop 2}\right\rangle\left|{2 \atop 1}\right\rangle - \left|{2 \atop 1}\right\rangle\left|{2 \atop 2}\right\rangle\right]$$

$$\left|{3 \atop 2}\right\rangle = \frac{1}{\sqrt{2}}\left[\left|{2 \atop 2}\right\rangle\left|{2 \atop 0}\right\rangle - \left|{2 \atop 0}\right\rangle\left|{2 \atop 2}\right\rangle\right]$$

$$\left|{3 \atop 1}\right\rangle = \frac{1}{\sqrt{5}}\left[\left|{2 \atop 1}\right\rangle\left|{2 \atop 0}\right\rangle + \sqrt{\frac{3}{2}}\left(\left|{2 \atop 2}\right\rangle\left|{2 \atop -1}\right\rangle - \left|{2 \atop -1}\right\rangle\left|{2 \atop 2}\right\rangle\right) - \left|{2 \atop 0}\right\rangle\left|{2 \atop 1}\right\rangle\right]$$

$$\left|{3 \atop 0}\right\rangle = \frac{1}{\sqrt{10}}\left[2\left|{2 \atop 1}\right\rangle\left|{2 \atop -1}\right\rangle - 2\left|{2 \atop -1}\right\rangle\left|{2 \atop 1}\right\rangle + \left|{2 \atop 2}\right\rangle\left|{2 \atop -2}\right\rangle - \left|{2 \atop -2}\right\rangle\left|{2 \atop 2}\right\rangle\right]$$

$$\left|{2 \atop 2}\right\rangle = \sqrt{\frac{2}{7}}\left|{2 \atop 2}\right\rangle\left|{2 \atop 0}\right\rangle - \sqrt{\frac{3}{7}}\left|{2 \atop 1}\right\rangle\left|{2 \atop 1}\right\rangle + \sqrt{\frac{2}{7}}\left|{2 \atop 0}\right\rangle\left|{2 \atop 2}\right\rangle$$

$$\left|{2 \atop 1}\right\rangle = \frac{1}{2\sqrt{7}}\left[2\sqrt{3}\left(\left|{2 \atop 2}\right\rangle\left|{2 \atop -1}\right\rangle + \left|{2 \atop -1}\right\rangle\left|{2 \atop 2}\right\rangle\right) - \sqrt{2}\left(\left|{2 \atop 0}\right\rangle\left|{2 \atop 1}\right\rangle + \left|{2 \atop 1}\right\rangle\left|{2 \atop 0}\right\rangle\right)\right]$$

$$\left|{2 \atop 0}\right\rangle = \frac{1}{\sqrt{14}}\left[\left|{2 \atop 1}\right\rangle\left|{2 \atop -1}\right\rangle + \left|{2 \atop -1}\right\rangle\left|{2 \atop 1}\right\rangle + 2\left(\left|{2 \atop 2}\right\rangle\left|{2 \atop -2}\right\rangle + \left|{2 \atop -2}\right\rangle\left|{2 \atop 2}\right\rangle - \left|{2 \atop 0}\right\rangle\left|{2 \atop 0}\right\rangle\right)\right]$$

$$\left|{1 \atop 1}\right\rangle = \frac{1}{\sqrt{5}}\left[\left|{2 \atop 2}\right\rangle\left|{2 \atop -1}\right\rangle + \sqrt{\frac{3}{2}}\left(\left|{2 \atop 0}\right\rangle\left|{2 \atop 1}\right\rangle - \left|{2 \atop 1}\right\rangle\left|{2 \atop 0}\right\rangle\right) - \left|{2 \atop -1}\right\rangle\left|{2 \atop 2}\right\rangle\right]$$

$$\left|{1 \atop 0}\right\rangle = \frac{1}{\sqrt{10}}\left[\left|{2 \atop 1}\right\rangle\left|{2 \atop -1}\right\rangle - \left|{2 \atop -1}\right\rangle\left|{2 \atop 1}\right\rangle + 2\left(\left|{2 \atop -2}\right\rangle\left|{2 \atop 2}\right\rangle - \left|{2 \atop 2}\right\rangle\left|{2 \atop -2}\right\rangle\right)\right]$$

$$\left|{0 \atop 0}\right\rangle = \sqrt{\frac{1}{5}}\left[\left|{2 \atop 2}\right\rangle\left|{2 \atop -2}\right\rangle - \left|{2 \atop 1}\right\rangle\left|{2 \atop -1}\right\rangle + \left|{2 \atop 0}\right\rangle\left|{2 \atop 0}\right\rangle - \left|{2 \atop -1}\right\rangle\left|{2 \atop 1}\right\rangle + \left|{2 \atop -2}\right\rangle\left|{2 \atop 2}\right\rangle\right]$$

This $\left|{0 \atop 0}\right\rangle$ is applicable to vector-coupling state (1).

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