CALCULATIONS OF THE ANISOTROPIC HYPERFINE COUPLING CONSTANTS IN ORGANIC RADICALS

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STATEMENT BY AUTHOR

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ABSTRACT

The anisotropic hyperfine coupling constant (AHCC) from the electron spin resonance (ESR) spectra of a variety of atoms in organic radicals have been calculated by means of semiempirical molecular orbital wavefunctions in the INDO approximation. All integrals of the operator entering the electronic contributions have been evaluated over Slater type orbitals without approximation in their evaluation. The AHCC involving $^{13}$C, $^{19}$F and $^1$H nuclei are calculated for the radicals: CH, methyl, ethyl, t-butyl, malonic acid, CH₂F, CF₂H, CF₃ and β,β,β-trifluoroethyl. The geometry is predicted according to the information available in the literature and the computed results are compared with experimental values and with available nonempirical or empirical calculations. The concept of deorthogonalization of the wavefunctions is introduced and the resulting spin density matrices give values for the tensor components of $^{19}$F AHCC in good agreement with the observed values.
CHAPTER 1

INTRODUCTION

The electron spin resonance (ESR) experiment measures the magnitude, sign, and directional properties of the hyperfine interaction between electronic and nuclear magnetic moments. This interaction arises from the unpaired electron density at or near magnetic nuclei of a paramagnetic molecule. In favorable cases the information can be separated into isotropic and anisotropic contributions. Considering molecular electronic structure in terms of atomic orbitals of constituent atoms, the isotropic hyperfine coupling constant is essentially a measure of the unpaired electron populations of s-orbitals centered on the magnetic nucleus. The anisotropic hyperfine coupling constants reflect the unpaired electron populations of valence p(and d) orbitals centered on the magnetic nucleus and of all orbitals centered on neighboring atoms.

The analysis of ESR spectra and the interpretation of observed hyperfine coupling constants is facilitated by reference to quantum mechanical calculations. A knowledge of theoretically calculated hyperfine coupling constants and approximate geometry of the molecule being studied is helpful in explaining the magnitudes and signs of the observed values.
The major purpose of this study is the investigation of the applicability of semiempirical molecular orbital (MO) theory for the calculations of the anisotropy of the proton, carbon-13, and fluorine-19 hyperfine coupling constants in organic radicals. Semiempirical SCF-MO wavefunctions in the intermediate neglect of differential overlap (INDO) approximation are used to calculate the anisotropic hyperfine coupling constants (AHCC) including all electronic contributions to the dipolar interactions with no approximations in the evaluations of the relevant integrals. A related work of Barfield, Gottlieb, and Doddrell (1978) on semiempirical molecular orbital (MO) calculations of deuterium quadrupole coupling constants (DQCC) has been generally successful. The calculations of spin densities are based on the intermediate neglect of differential overlap (INDO) approximation (Pople, Beveridge, and Dobosh 1968) of unrestricted self consistent-field (SCF)-MO theory (Roothaan 1951).
The Dipolar Hamiltonian

The classical interaction between two magnetic moments can be derived by considering the energy of one in the magnetic field of the other. The scalar potential at a point defined by a vector \( \mathbf{r} \), due to a magnetic moment \( \mathbf{u}_1 \) at the origin, is (Atherton 1973).

\[
\phi = -\mathbf{u}_1 \cdot \text{grad} \left(\frac{1}{r}\right) \tag{1}
\]

The magnetic field derived from this potential is

\[
\mathbf{H} = -\text{grad} \left(\phi\right) \tag{2}
\]

Then, by straightforward calculation,

\[
\mathbf{H} = \frac{3(\mathbf{u}_1 \cdot \mathbf{r}) \mathbf{r}}{r^5} - \frac{\mathbf{u}}{r^3} \tag{3}
\]

The energy of a second magnetic moment in this field is

\[
E = -\mathbf{u}_2 \cdot \mathbf{H} = \frac{-3(\mathbf{u}_1 \cdot \mathbf{r})(\mathbf{u}_2 \cdot \mathbf{r})}{r^5} + \frac{\mathbf{u}_1 \cdot \mathbf{u}_2}{r^3} \tag{4}
\]

This formula is valid for point dipoles; it gives the energy of interaction of two bar moments if their size
is small compared to the distance between them. The Hamiltonian for the magnetic interaction of a nuclear and an electron spin can be obtained by replacing \( \mu_1 \) and \( \mu_2 \) by their operator equivalent. If we take the case of a nucleus with magnetogyric ratio \( \gamma_N \) situated at the origin, we can substitute

\[
\mu_1 = \gamma_N \hbar I_N \quad (5)
\]

\[
\mu_2 = -\gamma \beta S_κ \quad (6)
\]

where \( I_N \) is the nuclear spin operator, \( S_κ \) is the electron spin operator and \( \beta \) is the Bohr magneton. Thus, the total dipole-dipole interaction between the electrons and nuclei is given by

\[
H_d = \gamma \beta \hbar \sum_{κ,N} \gamma_N \left\{ \frac{3(I_N \cdot r_{κN})(S_κ \cdot r_{κN})}{r_{κN}^5} - \frac{I_N \cdot S_κ}{r_{κN}^3} \right\}
\]

\[
= \gamma \beta \hbar \sum_{κ,N} \gamma_N H_{d'} \quad (7)
\]

where \( r_{κN} \) is the vector between electron \( κ \) and nucleus \( N \).

For an electron at the site of nucleus \( N \)

\[
H_{d'} = r^{-5}(S_x I_x (r^2 - 3x^2) + S_y I_y (r^2 - 3y^2) + S_z I_z (r^2 - 3z^2) + 3xy - (S_y I_z + S_z I_y) 3yz - (S_z I_x + S_x I_z) 3zx)
\]

\[(8)\]
\[ H'_d = r^{-5} \begin{bmatrix} S_x, S_y, S_z \end{bmatrix} \begin{bmatrix} (r^2 - 3x^2) - 3xy - 3xz \\ -3xy (r^2 - 3y^2) - 3yz \\ -3xz - 3yz (r^2 - 3z^2) \end{bmatrix} \begin{bmatrix} I_x \\ I_y \\ I_z \end{bmatrix} \]  

(9)

\[ H'_d = S \cdot \mathbf{t}_N \cdot \mathbf{I}_N \]  

(10)

and \( H_d \) for the system is

\[ H_d = g_\beta \hbar \gamma_N \sum_{\mathbf{S}, \mathbf{t}_N} \mathbf{S} \cdot \mathbf{t}_N \cdot \mathbf{I}_N \]  

(11)

### Spin Density Matrix Formalism

The calculation of most properties of an \( N \) electron system does not require all of the information contained in the total wavefunction, but only the first and second order density matrices. This is a consequence of the fact that the quantum mechanical operators associated with most physical properties are generally sums of one or two electron operators. In this section a brief discussion of the spin density matrix is presented in terms of the notation of McWeeny and Mizuno (1961).

The wavefunction is given by \( \psi(x_1, x_2, \ldots x_n) \) where \( x_i \) denotes the space and spin coordinates of electron \( i \) and \( r_i, s_i \) denote the space and spin coordinates, respectively. The probability of finding electron 1 in volume element
dx_1, electron 2 simultaneously in volume element dx_2, etc. is given by

$$\psi(x_1, x_2, \ldots x_n)\psi^*(x_1, x_2, \ldots x_n)dx_1dx_2\ldots dx_N$$  (12)

The system density matrix is defined by

$$\rho(x_1, x_2, \ldots x_N; x_1', x_2', \ldots x_N') =$$

$$\psi(x_1, x_2, \ldots x_N)\psi^*(x_1', x_2', \ldots x_N')$$  (13)

Since we are only concerned with one electron operator, it is sufficient to consider only the one electron density matrix. The normalization of McWeeny (1959) thus is given by

$$\rho_1(x_1; x_1') = N\int \psi(x_1, x_2, \ldots x_N)\psi^*(x_1', x_2, \ldots x_N)$$

$$dx_2\ldots dx_N$$  (14)

where it is understood that the primes are removed before integration.

A physical quantity \( \tilde{F} \) associated with a system is represented by a Hermitian operator \( \tilde{F} \) which is expressed as

$$\tilde{F} = \tilde{F} (0) + \tilde{F} (1) + \tilde{F} (2) + \ldots$$  (15)

Let us take, for example, the Hamiltonian for a many electron system:
\[ H = \sum_i h(i) + \frac{1}{2} \sum_{i,j} g(i,j) \]  

(16)

where \( H(i) \) is the one-electron Hamiltonian for electron \( i \) in the field of the nuclei, and the \( g(i,j) \) are Coulomb repulsion terms. The expectation value of the one-electron part of the energy is

\[ \langle \psi | \sum_i h(i) | \psi \rangle = N \int \psi^*(x_1', x_2', \ldots x_N) h(1) \psi(x_1, x_2, \ldots x_N) \]

\[ dx_1 \ldots dx_N = \int h(1) \rho_1(x_1; x_1') dx_1 \]

(17)

The spinless density matrix is obtained on integrating over the spin,

\[ p_1(r_1; r_1') = \int_{s_1'=s_1} \rho_1(x_1, x_1') ds_1 \]

(18)

A one-electron transition density matrix can be defined by considering two wavefunctions \( \psi_\kappa \) and \( \psi_\lambda \) where

\[ \rho_1(\kappa\lambda | x_1; x_1') = N \int \psi_\kappa(x_1, x_2, \ldots x_N) \psi_\lambda^*(x_1', x_2', \ldots x_N') \]

\[ dx_2 \ldots dx_N \]

(19)

and the matrix element expression of a one-electron symmetrical operator between the two states \( \psi_\kappa \) and \( \psi_\lambda \) is given by

\[ \langle \psi_\kappa | \sum_i h(i) | \psi_\lambda \rangle = \int h(1) \rho_1(\kappa\lambda | x; x_1') dx_1 \]

(20)
This can always be specialized to our case of $\kappa = \lambda$. The density matrix can be expanded in terms of the dyads of spin space

$$
\rho_1(\kappa \kappa | x_1', x_1') = P_1(\kappa \kappa | r_1', r_1') \alpha(s_1) \alpha^*(s_1') + P_1(\kappa \kappa | r_1, r_1') \alpha(s_1) \beta^*(s_1') + P_1(\kappa \kappa | r_1, r_1') \beta(s_1) \alpha^*(s_1') + P_1(\kappa \kappa | r_1; r_1') \beta(s_1) \beta^*(s_1')
$$

Bingel (1961) showed that in the case of $\kappa = \lambda$ the coefficients $P_1(\kappa \kappa | r_1; r_1')$ and $P_1(\kappa \kappa | r_1; r_1')$ are zero.

$P_1(\kappa \kappa | r_1; r_1')$ can be related to a matrix element involving the product of spatial and spin portions of $\mathcal{F}$.

$$
P_1(\kappa \kappa | r_1; r_1') = \frac{N}{2} \int \psi^*(x_1', x_2, \ldots x_N) \mathcal{I} \psi(x_1, x_2, \ldots x_N) ds_1 dr_2 dr_3 \ldots dr_N + N \int \psi^*(x_1', x_2, \ldots x_N) \mathcal{Z}(s_1) x \psi(x_1, x_2, \ldots x_N) ds_1 dr_2 \ldots dr_N.
$$

The spin operator and their corresponding elements of the dyads expansion are given in Table 1. These operators can be expressed as standard components of an irreducible tensor operator $T_q^{(k)}$ of order $2k + 1$. The commutation relations with the angular momentum operators
Table 1. Spin density operators and corresponding matrix elements.—McWeeny and Mizuno 1961

| $F(s)$            | Component of $\rho_1 (\kappa \lambda | x_1; x'_1)$ |
|------------------|---------------------------------|
| $S_+$            | $\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$ $P_1 (\kappa \lambda | r_1; r'_1)$ |
| $S_-$            | $\begin{pmatrix} \beta & \alpha \\ \alpha & \beta \end{pmatrix}$ $P_1 (\kappa \lambda | r_1; r'_1)$ |
| $\frac{1}{2}I+S_z$ | $\begin{pmatrix} \alpha & \alpha \\ \alpha & \alpha \end{pmatrix}$ $P_1 (\kappa \lambda | r_1; r'_1)$ |
| $\frac{1}{2}I-S_z$ | $\begin{pmatrix} \beta & \beta \\ \beta & \beta \end{pmatrix}$ $P_1 (\kappa \lambda | r_1; r'_1)$ |
given by Racah (1942) are as follows:

\[
\begin{align*}
    [J_+, T_q^{(k)}] &= \sqrt{k(k-1)} - (q + 1) T_q^{(k)+ 1} \\
    [J_-, T_q^{(k)}] &= \sqrt{k(k+1)} - (q + 1) T_q^{(k)- 1} \\
    [J_z, T_q^{(k)}] &= T_q^{(k)}
\end{align*}
\]  

(23)  

(24)  

(25)  

Using this definition the spin operators can be expressed as the following components:

\[
\begin{align*}
    T_0^o &= I \\
    T_{-1}^1 &= -\frac{1}{\sqrt{2}} S_z \\
    T_{+1}^1 &= \frac{1}{\sqrt{2}} S_z \\
    T_{-1}^1 &= \frac{1}{\sqrt{2}} S_z
\end{align*}
\]  

(26)  

(27)  

(28)  

(29)  

Thus

\[
\begin{align*}
    P_1(\kappa \lambda | r_1; r_1'') &= (1/2) T_0^o + T_0^1 \\
    P_1(\kappa \lambda | r_1, r_1'') &= (1/2) T_0^o - T_0^1
\end{align*}
\]  

(30)  

(31)  

where

\[
T_{\lambda}^{i} = \int_{x_1', x_2', \ldots x_N} \psi_\lambda^* (x_1', x_2', \ldots x_N) T_j^{(i)} \psi_\kappa (x_1, x_2, \ldots x_N) ds_1 dr_2 \ldots dr_N
\]  

(32)
suppose \( \psi_\lambda \) has spin quantum numbers \( S', M' \) and \( \psi_\kappa \) has spin quantum numbers \( S, M \) corresponding to the operators \( S^2 \) and \( S_z \). The matrix elements of \( \psi_\lambda \) and \( \psi_\kappa \) with the irreducible tensor operators are given in the Wigner-Eckert theorem by

\[
\langle S'M'|T^k_q|S\rangle = (S'k'M'|SM)(S'|T^{(k)}q|S) \tag{33}
\]

where \( (S'k'M'|SM) \) is the Clebsch-Gordon coefficient obtained from coupling the angular momentum \( S,M \) to \( S', M' \) and \( \langle S'|T^{(k)}q|S> \) is the matrix element which depends on \( S \) and \( S' \).

The real use of this result is that if the spinless components of \( \rho_1(\kappa; 1,1') \) are known for one pair of \( M \) and \( M' \) values, they can be obtained for all other values of \( M \) and \( M' \) through the use of Clebsch-Gordon coefficients.

The spin density \( Q_1(\kappa; r_1; r_1') \) is defined by

\[
Q_1(\kappa; r_1; r_1') = P_1(\kappa; r_1; r_1) - P_1(\kappa; r_1; r_1')
\]

\[
= 2\int S^z(1)\rho_1(\kappa; x_1; x_1')ds_1 \tag{34}
\]

For the case which we are discussing \( \kappa = \lambda \) and if the standard state is taken for \( M = S \)

\[
Q_1(\kappa\kappa; 1; 1) = \frac{M}{S} Q_1(\kappa\kappa; 1; 1)
\]

where \( Q_1(\kappa\kappa; 1; 1) \) is the spin density for the standard state \( M = S \) and \( r_1 \) is abbreviated \( (r_1 \rightarrow 1) \).
The approximate wavefunctions used here are the unrestricted ones proposed by Pople, Beveridge, and Dobosh (1967). For a system with $p$ electrons of $\alpha$-spin and $q$ electrons of $\beta$-spin

$$\psi = \psi_1^\alpha (1) \psi_2^\alpha (2) \ldots \psi_p^\alpha (p) \psi_1^\beta (p+1) \ldots \psi_{p+1}^\beta (p+q)$$  \hspace{1cm} (36)

where $\psi_1^\alpha$ and $\psi_1^\beta$ are taken as linear combinations of atomic orbitals $\phi_\mu$,

$$\psi_1^\alpha = \sum_\mu C_{\mu i}^\alpha \phi_\mu$$  \hspace{1cm} (37)

$$\psi_1^\beta = \sum_\mu C_{\mu i}^\beta \phi_\mu$$  \hspace{1cm} (38)

The linear expansion coefficients $C_{\mu i}^\alpha$ and $C_{\mu i}^\beta$ are determined by solving a set of coupled algebraic equations in the standard self-consistent field manner (Roothaan 1951), with approximations introduced in the evaluation of the atomic and molecular integrals involved.

The densities $P^\alpha$ and $P^\beta$ for electrons of $\alpha$- and $\beta$-spin, respectively, are defined as:

$$P_{\mu \nu}^\alpha = \sum_i C_{\mu i}^\alpha C_{\nu i}^{*\alpha}$$  \hspace{1cm} (39)

$$P_{\mu \nu}^\beta = \sum_i C_{\mu i}^\beta C_{\nu i}^{*\beta}$$  \hspace{1cm} (40)
\[ Q_1(\kappa \bar{\kappa}|1; 1) = P_1(\kappa \bar{\kappa}|1; 1) - P_1(\kappa \bar{\kappa}|1; 1') \] (41)

\[ P_1(\kappa \bar{\kappa}|1; 1) = \sum_{\mu \nu} P_{\mu \nu}^\alpha \phi^\mu(1) \phi^\nu_\nu(1') \] (42)

\[ P_1(\kappa \bar{\kappa}|1; 1) = \sum_{\mu \nu} P_{\mu \nu}^\beta \phi^\mu_\mu(1) \phi^\nu\nu(1') \] (43)

\[ Q_1(\kappa \bar{\kappa}|1; 1') = \sum_{\mu \nu} \rho_{\mu \nu} \phi^\mu_\mu(1) \phi^\nu\nu(1') \] (44)

where \( \rho_{\mu \nu} = P_{\mu \nu}^\alpha - P_{\mu \nu}^\beta \) (44)

All of the above discussion will be useful for considering the interaction energy at nucleus \( N \),

\[ E_N = g^2 h \gamma_N \langle \psi | \sum_\kappa S_{\kappa} \cdot t_{N} \cdot I_N | \psi \rangle \]

\[ = h \sum_{i,j} t_{N ij} I_{N j} \quad i,j = x,y,z \] (45)

where \( t_{N ij} = \frac{g^2}{4\pi} \gamma_N S^{-1} \langle \psi | \sum_\kappa S_{\kappa} T_{ij N} | \psi \rangle \) (46)

where

\[ T_{ij N} = r^{-5}_{\kappa N} \{ 3r_{\kappa N} r_{j N} - r_{N}^2 \delta_{ij} \} \] (47)

from the definition of the spin density \( Q_1(\kappa \bar{\kappa}|1; 1') \)

\[ t_{N ij} = \frac{g^2}{4\pi} \gamma_N S^{-1} \int T_{ij N} Q_1(\kappa \bar{\kappa}|1; 1') \, d\tau \] (48)
Where $Q_1(\kappa \kappa |1_N; 1_N)$ is the spin density for the standard state ($M = S$) evaluated at the nuclear site $N$. In many applications it is convenient to introduce a spin density which is normalized to unity:

$$D_S(\kappa \kappa |1; 1) = S^{-1}Q_1(\kappa \kappa |1; 1)$$

so that $t_{Ni,j}$ becomes

$$t_{Ni,j} = (2\hbar)^{-1}g_\beta g_\kappa n p \int \tau_{i,j}N D_S(\kappa \kappa |1; 1) d\tau_1$$

or

$$t_{Ni,j} = (4\pi)^{-1}g_\beta y_N S^{-1} \sum_{\mu \nu} \rho_{\mu \nu} \int \tau^{-5} (3r_{1i} r_{1j} - r_1^2 \delta_{ij})$$

$$\times \phi_\mu(1) \phi^*_\nu(1) d\tau_1$$

Equation (51) is used for all the calculations in this study; the next sections are concerned with calculations of the various integrals entering Equation (51).
Dipolar Integrals

For the electron-nuclear magnetic dipole-dipole interaction integrals entering the calculations of the anisotropic hyperfine coupling constants, one-, two-, and three-center integrals arise. They are represented as follows:

(1) \( <\mu_A | T_{ij} | \nu_A> \) one-center integrals

(2) \( <\mu_B | T_A | \nu_B> \) two-center-type I integrals

(3) \( <\mu_A | T_A | \nu_B> \) two-center-type II integrals

(4) \( <\mu_B | T_A | \nu_C> \) three-center integrals

where the dipolar operator \( T_{ij} \) in Equation (1) is centered at A, and the \( \nu_i \) and \( \mu_j \) denote Slater type orbitals (STO's) centered on i and j respectfully. For analytical expressions for integrals 1, 2, and 3 see the Appendix.

The two-center type I integrals have been evaluated by McConnell and Strathdee (1959), Barfield (1970), and Pitzer, Kern and Lipscomb (1969). Certain two-center type II integrals have been evaluated by Barfield, Gottlieb and Doddrell (1978) in the course of their study of deuterium quadrupole coupling constants (DQCC). The three-center
integrals are evaluated numerically since to our knowledge analytical expressions are not available.

All of these four types of integrals are included in this work to calculate the anisotropic hyperfine coupling constants of organic radicals. Their importance will be discussed in the following chapters with specific examples. The one-center and two-center integrals are checked by numerical integration techniques (Shavitt and Karplus 1965). The values obtained for the AHCC for many radicals indicate that the analytical expressions are reliable and less expensive to evaluate.

**Transformation from the Diatomic to Molecular Frame**

The dipolar tensor is first evaluated in the diatomic frame with the z-axis taken along the interatomic axis, and then transformed to the molecular frame via a similarity transformation (McConnell and Strathdee 1959; Barfield et al. 1978).

\[ T = L \tilde{T} L^{-1} \quad (52) \]

where

\[ L = \begin{bmatrix}
\cos \theta & \cos \phi & -\sin \phi & \sin \theta \cos \phi \\
\cos \theta & \sin \phi & \cos \phi & \sin \theta \sin \phi \\
-\sin \theta & 0 & \cos \theta & 0 \\
\end{bmatrix} \quad (53) \]

where the angles \( \theta \) and \( \phi \), which relate the diatomic axis system to the molecular axis system, are determined from
the unit vectors relating the two frames. This transformation only applies to the operator; to ensure that the transformed matrix element is multiplied by the correct spin density matrix element, the orbitals in the diatomic reference frame must also be transformed to the molecular frame as it is this frame in which \( \rho_{\mu\nu} \) is specified. The full transformation for a matrix element \( \langle \kappa' | T_{\sigma\delta} | \lambda' \rangle \) in the diatomic frame according to Pople and Beveridge (1970) is thus

\[
\langle \mu | T_{\alpha\beta} | \nu \rangle = \sum_{\kappa\sigma\delta\lambda} \ell'_{\mu\kappa} \ell_{\alpha\sigma} \ell_{\beta\delta} \ell_{\nu\lambda} \langle \kappa' | T'_{\sigma\delta} | \lambda' \rangle
\]  
(54)

where \( \ell'_{\mu\kappa} \) and \( \ell_{\alpha\sigma} \) are elements of the transformation matrices for the orbitals and the operator, respectively.

**Deorthogonalization**

All polycenter electron repulsion integrals involving overlap distributions (e.g., \( \phi_{\mu} \phi_{\nu}^* \), on atom A, \( \nu \) on atom B) are neglected in the generation of the wavefunctions, in semiempirical MO methods (such as INDO) which invoke the zero differential overlap (ZDO) approximation. However, introducing integrals of the type \( \langle \mu_A | T_A | \nu_B \rangle \) and \( \langle \nu_B | T_A | \nu_C \rangle \) requires a recomputation of the spin density matrix from the coefficient matrices \( \Sigma' \), with the requirement, (Pople and Beveridge 1970, Löwdin 1950).

\[
\Sigma' + \Sigma = I
\]  
(55)
where $\mathbf{I}$ denotes the identity matrix, $\mathbf{S}$ the overlap matrix, and

$$
\mathbf{C}' = \mathbf{S}^{-1/2} \mathbf{C}
$$

where $\mathbf{C}$ is the matrix of eigenvectors obtained in the semi-empirical ZDO scheme and

$$
\mathbf{S}^{-1/2} = \mathbf{Q} \mathbf{d}^{-1/2} \mathbf{Q}
$$

where $\mathbf{Q}$ denotes the matrix of eigenvectors of $\mathbf{S}$, and $\mathbf{d}^{1/2}$ is the diagonal array of the reciprocals of the square roots of the eigenvalues of $\mathbf{S}$. This procedure was called "deorthogonalization" of the wavefunction (Shillady, Billingsley, and Bloor 1971).

To find the new spin density matrix $\rho_{\mu\nu}'$, the density matrices $P'_{\mu\nu}^{\alpha}$ and $P'_{\mu\nu}^{\beta}$ have to be recomputed; where

$$
P'_{\mu\nu}^{\alpha} = \sum_{i} P_{\mu\nu}^{\alpha} C'_{\mu i} C'_{\mu i}
$$

$$
P'_{\mu\nu}^{\beta} = \sum_{i} P_{\mu\nu}^{\beta} C'_{\mu i} C'_{\nu i}
$$

and

$$
\rho_{\mu\nu}' = P'_{\mu\nu}^{\alpha} - P'_{\mu\nu}^{\beta}
$$
CHAPTER 3

RESULTS AND DISCUSSION

Computational Methods

All calculations were performed by means of the INDO approximation of SCF-MO theory on a Control Data Corporation CYBER 175 digital computer. The radical geometries for the computation were based on literature values or were estimated from structural data for related compounds. The calculated values were compared with available experimental data or with independent calculated results.

The steps and schemes for the calculations were as follow:

(1) Overlap integrals, wavefunctions for alpha and beta spins, energies, and spin densities, isotropic hyperfine coupling constant values, and dipole moments were obtained in the INDO-MO approximation (Dobosh 1967).

(2) In order to calculate AHCC according to procedure described in previous sections, a number of modifications were made in the computer program which was developed to calculate deuterium QCC (Barfield et al. 1978). This program made use of all the dipolar integrals tabulated in Appendix A. In the scheme designated AHF1, STO exponents were used in the calculations of wavefunctions as well as
integrals. Because no three-center integrals enter these
calculations, the results will be useful in determination
of their importance for AHCC. A subroutine was added in
this program to calculate spin density matrices that arise
after deorthogonalization of the wavefunctions. This
scheme is designated NSD.

(3) In the computational scheme designated NHF2 all
integrals (including the three-center ones) were based on
the numerical Gaussian transform method (Shavitt and Karplus
1965, Kern and Kleinman 1967) and INDO wavefunctions with
STO exponents.

Because IS inner shell electrons are not implicit in
the INDO scheme, contributions of IS-electrons to the AHCC
were based on Equations A4 and A5 in the Appendix, with the
simple assumption of double occupation of these orbitals.
The implications for these calculations of the lack of
orthogonality of the IS to the 2S atomic orbitals has not
yet been investigated.

The calculations were carried out for several
organic radicals. The results of the computations are
discussed in the subsequent sections. The following section
deals with CH, methyl, ethyl, and t-butyl hydrocarbon
radicals. The results for the malonic acid radical are
also included and discussed here because of certain simila-
rities which will subsequently be discussed. Section III
presents results for α-fluoro substituted methyl radicals.
These are discussed and compared with the hydrocarbon radicals. The last section presents the results for the $\beta$-substituted ethyl radical.

**Anisotropy of the Hyperfine in Hydrocarbon Radicals and Malonic Acid Radical**

Theoretical results are presented for CH, CH$_3$, ethyl CH$_3$CH$_2$ radical, t-butyl radical, and malonic acid radical. The structure of each radical is discussed first and then the computed tensor components are compared with other available experimental or other previous theoretical results. The changes due to the new generated spin density matrix from deorthogonalization of the wavefunction are also discussed. At the end of the section a comparison is made between the tensor components of $^{13}$C and $^1$H in the five radicals.

**CH Radical**

This molecule is used because it is the simplest radicaloid fragment containing a carbon-hydrogen bond. As a consequence three-center integrals do not appear, the one-center and two-center dipolar integrals are evaluated both numerically and analytically; so that the values of the tensor components for the proton should be identical in both Schemes AHF1 and NHF2. The C-H bond distance is assumed to be 1.09 Å, although this bond is slightly different from the 1.10 Å value which corresponds to the lowest total
calculated energy in the INDO-MO method. These results are
given in Table 2. This choice of the bond length (1.09 Å)
permits comparison with the tensor components obtained in
previous studies (Beveridge and McIver 1971). The z-axis
is taken along the C-H bond.

The calculated spin density matrix for C-H is given
in Table 3. Note that the carbon 2P_y orbital has unit spin
density; i.e., the spin density is concentrated in the 2P_y
orbital perpendicular to the radical plane. Therefore most
of the contributions to AHFCC for ^13_C arise from the one-
center integrals <2P_yC|2P_yC>. For the ^1H AHCC most of the
contributions come from the two-center type I integrals
<2P_yC|T_H|2P_yC>. Contributions from different types of
dipolar integrals for both ^13_C and ^1H are tabulated in
Tables 4 and 5 respectively. The values of the tensor
components for ^1H AHCC computed from both schemes AHF1 and
NHF2 are identical because the dipolar integrals required
are present in both schemes. There are small differences
in the values of the ^13_C AHCC tensor components due to the
fact that AHF1 does not include two-center type II integrals
for ^13_C.

The tensor components for both ^1_H and ^13_C computed
in this work are compared in Table 6 with those obtained by
Beveridge and McIver (1971), as well as to those obtained
by McConnell and Strathdee (1959). The experimental results
with which these values can be compared are those obtained
Table 2. Calculated total energy for different $r$(C-H) for CH radical (INDO).

<table>
<thead>
<tr>
<th>$r$(C-H), Å</th>
<th>Total energy (a.u.) x10^5$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.07</td>
<td>281</td>
</tr>
<tr>
<td>1.08</td>
<td>157</td>
</tr>
<tr>
<td>1.09</td>
<td>63</td>
</tr>
<tr>
<td>1.10</td>
<td>0</td>
</tr>
<tr>
<td>1.11</td>
<td>91</td>
</tr>
<tr>
<td>1.12</td>
<td>88</td>
</tr>
</tbody>
</table>

$^a$The values are the result of subtracting the total energy corresponding to $r$(C-H) = 1.10 (-6.88994 a.u.) from other energies.
Table 3. Spin density matrix for the CH radical.

<table>
<thead>
<tr>
<th>Atomic Orbital</th>
<th>1S&lt;sub&gt;H&lt;/sub&gt;</th>
<th>2S&lt;sub&gt;C&lt;/sub&gt;</th>
<th>2P&lt;sub&gt;xC&lt;/sub&gt;</th>
<th>2P&lt;sub&gt;yC&lt;/sub&gt;</th>
<th>2P&lt;sub&gt;zC&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1S&lt;sub&gt;H&lt;/sub&gt;</td>
<td>-0.0239</td>
<td>-0.0176</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-0.0076</td>
</tr>
<tr>
<td>2S&lt;sub&gt;C&lt;/sub&gt;</td>
<td>-0.0176</td>
<td>0.0183</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-0.0215</td>
</tr>
<tr>
<td>2P&lt;sub&gt;xC&lt;/sub&gt;</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>2P&lt;sub&gt;yC&lt;/sub&gt;</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>1.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>2P&lt;sub&gt;zC&lt;/sub&gt;</td>
<td>-0.0076</td>
<td>-0.0215</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0056</td>
</tr>
</tbody>
</table>
Table 4. Non-zero contributions to the AHCC for $^{13}$C in CH radical (values in MHz).

<table>
<thead>
<tr>
<th>Type of Integral</th>
<th>AMF1</th>
<th>NHF2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt; 1S_H \mid T_{zz}^C \mid 1S_H &gt;$</td>
<td>-0.533</td>
<td>-0.533</td>
</tr>
<tr>
<td>$&lt; 2S_C \mid T_{zz}^C \mid 1S_H &gt;$</td>
<td>(a)</td>
<td>-0.327</td>
</tr>
<tr>
<td>$&lt; 2P_{yc} \mid T_{zz}^C \mid 2P_{yc} &gt;$</td>
<td>-76.750</td>
<td>-76.770</td>
</tr>
<tr>
<td>$&lt; 2P_{zc} \mid T_{zz}^C \mid 1S_H &gt;$</td>
<td>(a)</td>
<td>-0.377</td>
</tr>
<tr>
<td>$&lt; 2P_{zc} \mid T_{zz}^C \mid 2P_{zc} &gt;$</td>
<td>0.860</td>
<td>0.860</td>
</tr>
</tbody>
</table>

*aNot calculated in this scheme.*
Table 5. Non-zero contributions to AHCC for $^1$H in CH radical.

<table>
<thead>
<tr>
<th>Type of Integral</th>
<th>AHF1(MHz)</th>
<th>NHF2(MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt; 2S_C</td>
<td>T^H_{zz}</td>
<td>2S_C &gt;$</td>
</tr>
<tr>
<td>$&lt; 2P_{yC}</td>
<td>T^H_{zz}</td>
<td>2P_{yC} &gt;$</td>
</tr>
<tr>
<td>$&lt; 2P_{zC}</td>
<td>T^H_{zz}</td>
<td>2P_{zC} &gt;$</td>
</tr>
<tr>
<td>$&lt; 1S_H</td>
<td>T^H_{zz}</td>
<td>2S_C &gt;$</td>
</tr>
<tr>
<td>$&lt; 1S_H</td>
<td>T^H_{zz}</td>
<td>2P_{zC} &gt;$</td>
</tr>
<tr>
<td>$&lt; 2S_C</td>
<td>T^H_{zz}</td>
<td>2P_{zC} &gt;$</td>
</tr>
</tbody>
</table>
Table 6. Anisotropic hyperfine coupling constants for $\dot{\text{CH}}$ radical (MHz).

<table>
<thead>
<tr>
<th></th>
<th>$^1\text{H}$</th>
<th>$\text{NHF}_2$</th>
<th>(a)</th>
<th>(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{xx}$</td>
<td>-41.1</td>
<td>-41.1</td>
<td>-39.8</td>
<td>-39</td>
</tr>
<tr>
<td>$t_{yy}$</td>
<td>-7.7</td>
<td>-7.7</td>
<td>-5.1</td>
<td>-5</td>
</tr>
<tr>
<td>$t_{zz}$</td>
<td>48.8</td>
<td>48.8</td>
<td>44.9</td>
<td>43</td>
</tr>
<tr>
<td>$t_{xx}$</td>
<td>-76.7</td>
<td>-77.0</td>
<td>-77.0</td>
<td></td>
</tr>
<tr>
<td>$^{13}\text{C}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{yy}$</td>
<td>153.5</td>
<td>153.3</td>
<td>152.0</td>
<td></td>
</tr>
<tr>
<td>$t_{zz}$</td>
<td>-76.8</td>
<td>-76.4</td>
<td>-75.8</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Beveridge and McIver (1971).

$^b$McConnell and Strathdee (1959).
for malonic acid radical (see discussion on malonic acid radical section).

**Methyl Radical, CH₃**

Experimental studies, analysis of the electronic spectrum by Herzberg and Shoosmith (1956), electron spin resonance studies by Rogers and Kispert (1967), and photoionization studies by Lifshitz and Chupka (1967) have shown that the methyl radical is planar, or nearly so.

Ab initio MO calculations, carried out by Morokuma, Pedersen, and Karplus (1968), showed that the minimum in the total energy for CH₃ occurred when the radical was considered to be planar. Pauling (1969) argued on the basis of electronegativity differences of C and H that CH₃ should be planar (for more detail see discussion on the structure of fluorinated methyl radicals).

In this study the structure of methyl is assumed to be planar and the C-H bond length is taken to be 1.08 Å (Herzberg 1961). The spin density is unity for the carbon atom 2Pᵥ orbital which is perpendicular to the plane of the radical. The spin density of 1Sᵥ is more negative than that in the CH radical. Also, the spin densities of 2Sᵥ and 2Pᵥ have increased while that of 2Pₓ did not change from zero.

The results computed in this study for the AHCC tensors for both ¹³C and ¹H are compared to previous
results, and to experimental data in Table 7. The computations of AHCC by Barfield (1970) and Beveridge and McIver (1971) did not include two-center type II integrals nor three-center integrals. Although the integrals are appreciable, their contribution to the calculated AHCC is small because of the very small values of the associated spin densities. In Table 8 are entered the values of the dipolar integrals and their contributions to AHCC after being multiplied by the appropriate constant and the spin density matrix element. Three-center integrals are computed in the scheme NHF2. When the operator $τ_{yy}$ is on the hydrogen atom $H_1$ (see Figure 1), it can be seen from the table that the greatest contribution to the $^1$H AHCC tensors are due to the two-center type I integrals. For $^{13}$C most of the contributions come from the diagonal one-center integrals.

When deorthogonalization was performed, the changes in the tensor components are not large as can be seen from Table 9.
Table 7. Anisotropic hyperfine constants for $\text{CH}_3$(MHz).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Valence</th>
<th>A HF1</th>
<th>NHF2</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(a)</td>
<td>(b)</td>
<td>(c)</td>
<td>(d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^1\text{H}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{xx}$</td>
<td>-43.7</td>
<td>-43.50</td>
<td>-44.2</td>
<td>-43.3</td>
<td>-42.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{yy}$</td>
<td>-9.5</td>
<td>-9.21</td>
<td>-9.7</td>
<td>-10.4</td>
<td>-6.5</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>$t_{zz}$</td>
<td>53.2</td>
<td>52.71</td>
<td>53.9</td>
<td>53.7</td>
<td>49.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{xx}+t_{zz}$</td>
<td>4.75</td>
<td>4.60</td>
<td>4.8</td>
<td>5.2</td>
<td>3.9</td>
<td>-0.6 ± 0.8</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond</th>
<th>Valence</th>
<th>A HF1</th>
<th>NHF2</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{13}\text{C}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{xx}$</td>
<td>-74.9</td>
<td>-74.94</td>
<td>-63.6</td>
<td>-74.3</td>
<td>-51.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{yy}$</td>
<td>149.7</td>
<td>149.80</td>
<td>127.3</td>
<td>148.6</td>
<td>103.1</td>
<td>126.1</td>
<td></td>
</tr>
<tr>
<td>$t_{zz}$</td>
<td>-74.9</td>
<td>-74.94</td>
<td>-63.6</td>
<td>-74.3</td>
<td>-51.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{xx}+t_{zz}$</td>
<td>-74.9</td>
<td>-74.94</td>
<td>-63.6</td>
<td>-74.3</td>
<td>-51.6</td>
<td>-63.5</td>
<td></td>
</tr>
</tbody>
</table>


$^b$Beveridge and McIver (1971).

$^c$Vincow, Chang, and Davidson (1971).

$^d$Rogers and Kispert (1967).
Table 8. Non-zero integrals and their contributions to $t_{yy}$ of $^1H_1$ in $CH_3$ radical.

<table>
<thead>
<tr>
<th>Type of Integral</th>
<th>AHF1 Integral (a.u.)</th>
<th>AHF1 Contribution (MHz)</th>
<th>NHF2 Integral (a.u.)</th>
<th>NHF2 Contribution (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt; 2S_C</td>
<td>T_{yy}</td>
<td>2S_C &gt;$</td>
<td>-0.065</td>
<td>-1.915</td>
</tr>
<tr>
<td>$&lt; 2S_C</td>
<td>T_{yy}</td>
<td>1S_{H_1} &gt;$</td>
<td>-0.033</td>
<td>0.178</td>
</tr>
<tr>
<td>$&lt; 2S_C</td>
<td>T_{yy}</td>
<td>1S_{H_2} &gt;$</td>
<td>(a)</td>
<td>(a)</td>
</tr>
<tr>
<td>$&lt; 2S_C</td>
<td>T_{yy}</td>
<td>1S_{H_3} &gt;$</td>
<td>(a)</td>
<td>(a)</td>
</tr>
<tr>
<td>$&lt; 2P_{xC}</td>
<td>T_{yy}</td>
<td>2P_{xC} &gt;$</td>
<td>-0.075</td>
<td>-1.386</td>
</tr>
<tr>
<td>$&lt; 2P_{zC}</td>
<td>T_{yy}</td>
<td>2P_{xC} &gt;$</td>
<td>-0.111</td>
<td>-2.053</td>
</tr>
<tr>
<td>$&lt; 2P_{yC}</td>
<td>T_{yy}</td>
<td>2P_{yC} &gt;$</td>
<td>-0.010</td>
<td>-5.423</td>
</tr>
<tr>
<td>$&lt; 2S_C</td>
<td>T_{yy}</td>
<td>2P_{xC} &gt;$</td>
<td>-0.052</td>
<td>(b)</td>
</tr>
<tr>
<td>$&lt; 2P_{zC}</td>
<td>T_{yy}</td>
<td>1S_{H_1} &gt;$</td>
<td>-0.046</td>
<td>-0.037</td>
</tr>
<tr>
<td>$&lt; 1S_{H_2}</td>
<td>T_{yy}</td>
<td>1S_{H_2} &gt;$</td>
<td>-0.022</td>
<td>0.484</td>
</tr>
<tr>
<td>$&lt; 2P_{xC}</td>
<td>T_{yy}</td>
<td>1S_{H_3} &gt;$</td>
<td>(a)</td>
<td>(a)</td>
</tr>
</tbody>
</table>

aNot calculated in this scheme.

bThe value is zero because of zero spin densities.
Figure 1. The structure of $\cdot$CH$_3$ radical.---The three hydrogens are in the xz plane and y-axis is perpendicular to the radical plane.
Table 9. The AHCC for $^1$H and $^{13}$C for methyl radical using spin densities after deorthogonalization (MHz).

<table>
<thead>
<tr>
<th></th>
<th>$^{13}$C</th>
<th>$^1$H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{xx}$</td>
<td>-74.66</td>
<td>-45.74</td>
</tr>
<tr>
<td>$t_{yy}$</td>
<td>149.35</td>
<td>-11.71</td>
</tr>
<tr>
<td>$t_{zz}$</td>
<td>-74.66</td>
<td>57.45</td>
</tr>
</tbody>
</table>
Ethyl Radical ($\hat{\text{CH}}_2\text{CH}_3$)

The geometry assumed for the radical is one in which the methylene group ($\hat{\text{CH}}_2$) is planar, $r(\text{C-H}) = 1.08 \text{ Å}$, $\angle \text{HCH} = 120^\circ$; for the methyl group $r(\text{C-H}) = 1.09 \text{ Å}$ with tetrahedral angle, the C-C bond is taken to be 1.46 Å.

The only theoretical work for AHCC in the literature appears to be that of Barfield (1970). Subsequently, McDowell, Raghunathan and Shimokoshi (1973) reported the experimental data for alpha and beta hydrogens in the $\hat{\text{CH}}_2\text{CH}_3$ radical.

Values calculated in this study, which were based on the techniques described in previous sections, are compared with the experimental data. In Table 10 the AHCC for the ethyl radical computed by both schemes AHF1 and NHF2 are compared with the MO and VB results of Barfield (1970) and with the experimental values reported by McDowell et al. (1973). Barfield's values, which were based on the UHF-INDO method did not include the two-center type II or three-center integral contributions. However, the values obtained in this work do not show drastic differences due to the fact that the contributions from the two-center type II and three-center integral are small. Also it can be seen that there is a great disparity between the experimental values and those computed for alpha hydrogens. The experimental results of McDowell et al. (1973) were treated so that there is correspondence in the
Table 10. AHCC tensor components for ethyl radical (MHz).

<table>
<thead>
<tr>
<th></th>
<th>AHF1</th>
<th>NHF2</th>
<th>VB</th>
<th>(b) UHF-</th>
<th>(c) Expt'1.</th>
<th>(d) Expt'1.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>INDO</td>
<td>CH₃CH(CH₂CO₂H)</td>
<td></td>
</tr>
<tr>
<td>(CH₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>¹³C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tₓₓ</td>
<td>47.76</td>
<td>46.57</td>
<td>50.9</td>
<td>44.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tᵧᵧ</td>
<td>-8.60</td>
<td>-8.15</td>
<td>-8.3</td>
<td>-6.0</td>
<td>9.54 ± 1.4</td>
<td></td>
</tr>
<tr>
<td>tₗₗ</td>
<td>-39.20</td>
<td>-38.42</td>
<td>-42.5</td>
<td>-38.3</td>
<td>19.01 ± 1.4</td>
<td></td>
</tr>
<tr>
<td>¹H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tₓₓ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tᵧᵧ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tₗₗ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH₃)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>¹³C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tₓₓ</td>
<td>-1.01</td>
<td>-0.63</td>
<td>-2.9</td>
<td>-1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tᵧᵧ</td>
<td>-5.60</td>
<td>-6.05</td>
<td>-9.3</td>
<td>-4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tₗₗ</td>
<td>6.61</td>
<td>6.68</td>
<td>10.1</td>
<td>6.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 10. AHCC tensor components for ethyl radical (MHz). --Continued

<table>
<thead>
<tr>
<th></th>
<th>AHF1</th>
<th>NHF2</th>
<th>VB</th>
<th>(b) UHF-INDO</th>
<th>(c) Expt'1.</th>
<th>(d) Expt'1.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>¹H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tₚₓₓ</td>
<td>-8.53</td>
<td>-8.5</td>
<td>-10.2</td>
<td>-6.9</td>
<td></td>
<td>-3.3 ± 2</td>
</tr>
<tr>
<td>tᵧᵧ</td>
<td>-2.60</td>
<td>-2.01</td>
<td>2.4</td>
<td>-4.6</td>
<td></td>
<td>2.5 ± 1.4</td>
</tr>
<tr>
<td>tₓᵧz</td>
<td>11.13</td>
<td>10.51</td>
<td>12.6</td>
<td>11.4</td>
<td></td>
<td>5.3 ± 1.4</td>
</tr>
</tbody>
</table>


*c McDowell et al. (1973).


*e This is (tₓₓ + tᵧᵧ)/2.
For beta hydrogens the disparity is not as great as that in the \( \alpha \)-hydrogen, also the values obtained by Morton and Horsfield (1961) for the methyl group hydrogens in \( \text{CH}_3\text{CH(CO}_2\text{H)} \) can be used for comparison and these are in better agreement with the computed values.

An investigation of the dihedral angle dependence for the AHCC for the methyl group protons of the ethyl radical was carried out. The computations are taken for 30° intervals of the dihedral angle. The angle \( \theta \) is defined as shown in Figure 2. So that if \( H_\beta(1) \) angle is \( \theta \) the angle for \( H_\beta(2) = \theta + 120° \).

In the Table 11 the values calculated in this study by using the NHF2 scheme are compared with those computed for a simple C-C-H radical fragment by Derbyshire (1962). Also the values obtained here are plotted in Figure 3. It can be noticed that the x- and y-axes exchange for \( \theta = 60° \). The symmetry about \( \theta^0 = 90° \) is predicted from the symmetry of the three methyl hydrogens.

There are some mathematical errors in the expressions of Derbyshire and the results reported by him are in error (Derbyshire 1962).
Figure 2. Definition of the dihedral angle for \( \beta \)-hydrogens in ethyl radical.
Table 11. AHCC for β-hydrogens in ethyl radical (MHz) and their angle dependence.

<table>
<thead>
<tr>
<th>θ (°)</th>
<th>AHCC in XYZ&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Directional Cosines</th>
<th>(b)</th>
<th>θ</th>
<th>Derbyshire (1962)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>-4.67 0.00 4.93</td>
<td>-0.9449 0.0000 .3274</td>
<td>-6.38</td>
<td>-6.25</td>
<td>-4.44 0.91 -8.95</td>
</tr>
<tr>
<td>180°</td>
<td>0.0 -3.18 0.00</td>
<td>0.0000 1.0000 .0000</td>
<td>-3.18</td>
<td>-4.44</td>
<td>1.52 -0.11 1.10</td>
</tr>
<tr>
<td></td>
<td>4.93 0.00 7.85</td>
<td>.3274 .0000 .9449</td>
<td>9.56</td>
<td>0.91</td>
<td>-0.11 7.77 7.85</td>
</tr>
<tr>
<td>30°</td>
<td>-6.24 -1.06 -3.67</td>
<td>-.92739 .3078 .2126</td>
<td>-7.52</td>
<td>-3.79</td>
<td>-3.91 1.61 -7.61</td>
</tr>
<tr>
<td>150°</td>
<td>-1.06 -2.65 -1.77</td>
<td>.2882 .9502 -.1182</td>
<td>-2.40</td>
<td>-3.91</td>
<td>-3.31 0.46 0.28</td>
</tr>
<tr>
<td></td>
<td>-3.67 -1.77 8.9</td>
<td>.2384 .04838 .9699</td>
<td>9.92</td>
<td>1.61</td>
<td>0.46 7.09 7.33</td>
</tr>
<tr>
<td>60°</td>
<td>-4.34 3.87 -1.42</td>
<td>.7991 .5972 .0689</td>
<td>-1.43</td>
<td>-2.62</td>
<td>0.52 1.19 -4.16</td>
</tr>
<tr>
<td>120°</td>
<td>3.87 -6.58 1.86</td>
<td>.6011 -.7941 -.0892</td>
<td>-9.76</td>
<td>0.52</td>
<td>-1.98 4.37 -2.79</td>
</tr>
<tr>
<td></td>
<td>-1.42 1.86 10.92</td>
<td>.0014 .1127 -.9936</td>
<td>11.19</td>
<td>1.19</td>
<td>4.37 4.60 6.95</td>
</tr>
<tr>
<td>90°</td>
<td>-1.01 1.46 0.0</td>
<td>1.000 .0000 .0000</td>
<td>-1.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0 -10.97 0.0</td>
<td>.0000 -.9979 .0637</td>
<td>10.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0 1.46 11.99</td>
<td>.0000 .06378 .9979</td>
<td>11.99</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>This work; <sup>b</sup>Principle components.
Figure 3. The tensor components of β-hydrogen vs. the dihedral angle (°).
t-Butyl Radical \((\text{CH}_2)_3\text{C}\)

There are two viewpoints concerning the structure of the t-butyl radical in the literature:

(a) Rincon (1967) observed two sets of \(^{13}\text{C}\) lines assignable to t-butyl radicals in an irradiated t-butyl chloride. This led him to propose two types of t-butyl radicals, one planar, and one pyramidal.

(b) Wood and his associates (Wood et al.1972; Wood and Sprecher 1973), who detected narrowlined, isotropic features for the t-butyl radical in a perdeuterated adamantane matrix used the isotropic \(^{13}\text{C}\) coupling constant of 46G(128.8MHz). From this data and Coulson's (1948) equation\(^1\) they estimated that the radical was pyramidal.

The ab initio MO results of Lathan, Hehre, and Pople (1971) predicted the C-C-C angle to be 117.6°, in apparent agreement with experiment. The temperature changes in the \(^{13}\text{C}\) isotropic value were opposite to those expected for planar radicals. Schrader and Karplus (1964) attributed this to population of low-lying vibrational states which leads to an increased population of the 2S-orbital on carbon. Wood and Sprecher (1973) argued that the pyramidal molecules on heating tend to become more nearly planar, which would account for the decrease in the coupling

\(^1\) For C\(_2\)v symmetry and two hybrid orbitals the equation used to evaluate the bond angle \(\phi\) for the radical is found to be \(\phi = 2 \cos^{-1}(\lambda^2 + 2)^{-1/2}\) where \(\lambda\) is the hybridization ratio for sp\(_n\), Atkins and Symons (1967).
constant value of $^{13}\text{C}$ and the increase in isotropic coupling constants value of $^1\text{H}$.

The argument for planarity of the t-butyl radical (Symons 1973; Claxton, Platt and Symons 1976) is as follows:

(1) The isotropic coupling constant for the central carbon is 46G (Wood et al. 1972); according to Symons (1969) this coupling arises from a spin-polarization, which occurs in a planar system (ca. 27G, based on CH$_3$ radical at low temperatures), and the admixture of 2S character into the wavefunction which occurs only where there is deviation from planarity. This gives 1.7% deviation in the 2S character for the carbon from Coulson's (1948) relationship and gives a bond angle of 119.5° ($\lambda$ here = 2/1.017).

(2) Hehre, Stewart and Pople (1969) in their INDO calculations for the t-butyl radical found a minimum energy with a C-C-C-bond angle of 120 degrees.

(3) If the electronegativity difference ($\chi_A - \chi_B$) for an AB$_3$ radical increases, the tendency to become pyramidal increases (Pauling 1969). Changes $\Delta\chi$ need not lead to a change in bond angle, since once planarity is achieved, all that will result as $\Delta\chi$ decreases is a greater resistance to bending. On the criterion of the isotropic coupling to boron, BH$_3$ is taken to be planar (Cotton, Symons and Wardale 1969). Since $\Delta\chi$ for CMe$_3$ falls between that for BH$_3$ and CH$_3$, the radical should certainly be planar (Symons 1973).
(4) An ab initio study of the geometry of the t-butyl radical by Claxton, Platt, and Symons (1976) indicated that the radical is planar. In that study they also calculated the anisotropic coupling constant for the central carbon.

In this study computations of AHCC were performed for the planar structure. The C-C and C-H bond lengths were 1.54 Å and 1.09 Å, respectively, and the symmetry is $C_{3h}$.

In Table 12 the AHCC tensor for the central $^{13}$C atom is compared with the ab initio results. It can be seen from the table that when using the spin densities based on orthogonalized wavefunctions the values of the tensor components are in better agreement with the ab initio ones.
Table 12. Calculated AHCC for the central carbon atom in the t-butyl radical (MHz).

<table>
<thead>
<tr>
<th></th>
<th>AHF1</th>
<th>AHF1-NSD</th>
<th>Ab initio (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(t_{xx})</td>
<td>-60.5</td>
<td>-66.6</td>
<td>-89.5</td>
</tr>
<tr>
<td>(t_{yy})</td>
<td>121.1</td>
<td>133.3</td>
<td>179.0</td>
</tr>
<tr>
<td>(t_{zz})</td>
<td>-60.5</td>
<td>-66.6</td>
<td>-89.5</td>
</tr>
</tbody>
</table>

\(^a\text{Claxton et al. (1976).}\)
Malonic Acid Radical \( \{\text{CH(COOH)}_2\} \)

Guedkoop and MacGillavry (1957) reported the x-ray structure of malonic acid crystals. The crystals are triclinic and have two molecules per unit cell. The plane of the carboxyl group nearest the center of the unit cell is twisted 14.7 deg. with respect to the plane of the three carbon atoms (CCC plane). The plane of the other carboxyl group makes a dihedral angle of 85.8° with the CCC plane. The radical for which the calculations were carried out is \( \text{CH(COOH)}_2 \). All bond angles about the central carbon were taken to be 120°, placing the α-hydrogen in the C-C-C plane and taking C-H bond length to be 1.08 Å. The other bond lengths and bond angles were taken as reported by Guedkoop and MacGillavry (1957) except for the O-H bond length which was taken to be 0.95 Å and the C-O-H angle was taken to be 107.8°.

The ESR spectra of radiation-damaged malonic acid crystals have been reported and analyzed by McConnell et al. (1960) as well as by Horsfield, Morton, and Whiffen (1961). The INDO-MO calculations were carried out by Beveridge and McIver (1971). The results of this study and the above mentioned studies are listed in Table 13. It can be seen from the table that this study gives nearly the same tensor components as reported by Beveridge and McIver (1971), although they did not include the two-center type II and three-center dipolar integrals and some of their
Table 13. Calculated and observed AHCC for CH(COOH)₂ (MHz).

<table>
<thead>
<tr>
<th></th>
<th>AHF1</th>
<th>NHF2</th>
<th>INDO(^a)</th>
<th>Observed(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1)H</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(t_{xx})</td>
<td>-32.65</td>
<td>-32.90</td>
<td>-36</td>
<td>-32</td>
</tr>
<tr>
<td>(t_{yy})</td>
<td>-8.07</td>
<td>-7.67</td>
<td>-8</td>
<td>1</td>
</tr>
<tr>
<td>(t_{zz})</td>
<td>40.72</td>
<td>40.57</td>
<td>44</td>
<td>31</td>
</tr>
<tr>
<td>(^13)C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(t_{xx})</td>
<td>-59.14</td>
<td>-59.70</td>
<td>-60</td>
<td>-70</td>
</tr>
<tr>
<td>(t_{yy})</td>
<td>120.22</td>
<td>120.52</td>
<td>122</td>
<td>120</td>
</tr>
<tr>
<td>(t_{zz})</td>
<td>-61.10</td>
<td>-60.83</td>
<td>-62</td>
<td>-50</td>
</tr>
</tbody>
</table>

\(^a\)Beveridge and McIver (1971).

\(^b\)McConnell et al. (1960) and Horsfield, Morton, and Whiffen (1961).
integral expressions were in error. The calculated results in Table 13 are generally in good agreement with the experimental values.

**Fluorinated Methyl Radicals**

$\text{CH}_2\text{F}, \text{CHF}_2, \text{CF}_3$

It was found from the single crystal analysis of some fluorine-containing compounds that the hyperfine tensors of fluorine coupling constants are entirely different from those of hydrogen (Iwasaki 1971). Both the isotropic and anisotropic coupling constants of $\alpha$-fluorine are very much larger than those of $\alpha$-hydrogen. The predominant contribution to the anisotropic fluorine coupling, which arises from the spin density in the fluorine $2p_\pi$ of fluorine, is attributed to the mixing of the excited spin configuration (II) in the configuration (I).
This spin density does not play any role in the case of hydrogen hyperfine coupling. Also, since the major contribution to anisotropic coupling is due to the spin configuration II, the sign of the maximum element of the anisotropic hyperfine tensor should be positive.

For the three radicals there are common features in the discussion of their structure which suggest that they are non-planar; i.e., pyramidal:

(a) In their ESR studies of $\cdot$CF$_3$, $\cdot$CHF$_2$ and $\cdot$CH$_2$F Fessenden and Schuler (1965) provided evidence that these radicals are non-planar. For example, in $\cdot$CF$_3$ the out of plane angle $\theta$ equals 17.8° from the relation between $\theta$ and the observed isotropic hyperfine coupling for $^{13}$C (Fessenden and Schuler 1965):

$$a_{c}(G) = 30 + 1190 \cdot (2\tan^{2} \theta)$$

when $$a(^{13}C) = 271G, \theta = 17.8^\circ$$ and $$<\text{FCF} > = 111.1^\circ.$$

The value of $\theta$ obtained from the above equation gives the percent s-character, so that the partial substitutions with hydrogen decrease the s-character and the radical geometry approaches planarity.

(b) Beveridge, Dobosh, and Pople (1968) carried out INDO-MO calculations of the geometry of the radicals. In spite of the approximations involved, Pople et al. (1967) have shown that INDO-MO method often gives reliable
results for molecular geometries. The computed angles are for $\text{CF}_3 (<\text{F-C-F} = 112^\circ)$, $\text{CH}_2\text{F} (<\text{H-C-H} = 121^\circ, <\text{F-C-F} = 109^\circ$ and $<\text{F-C-H} = 116^\circ$).

(c) The above structures are also supported by Pauling's (1969) argument based on electronegativity differences, the double-bond character of a C-F bond induced by partial ionic character, and the steric repulsion of fluorine atoms.

(d) The ab initio calculations of Morokuma et al. (1968) showed that an angle of $16.8^\circ (<\text{F-C-F} = 112^\circ)$ for $\text{CF}_3$ radical corresponded to the minimum total energy.

In addition to these considerations the C-H and C-F bond lengths were taken to be $1.08 \, \text{Å}$ and $1.33 \, \text{Å}$ respectively (Pople and Gordon 1967). For the $\text{CF}_3$ radical the F-C-F angle was taken to be $111.1^\circ$.

The spin density matrix elements for $^{19}\text{F}$ in these radicals show large off-diagonal elements. As a consequence the off-diagonal contributions from one-center, two-center, and three-center integrals will be large (see Tables 14 and 15).

It appears that there are no experimental studies of the anisotropic hyperfine coupling for $\text{CH}_2\text{F}$ and $\text{CHF}_2$ radicals. However, the $^{19}\text{F}$ in these two radicals is in an alpha position, and it should be of interest to compare the calculated tensor components with those of $^{19}\text{F}$ in similar radicals such as $\text{CHFCONH}_2$, $\text{CF}_2\text{CONH}_2$ and $\text{CF}$(CONH)$_2$. The ESR
Table 14. Spin density matrix for \( \text{CFH}_2 \) radical.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>(2S_C)</th>
<th>(2P_{xC})</th>
<th>(2P_{yC})</th>
<th>(2P_{zC})</th>
<th>(2S_F)</th>
<th>(2P_{xF})</th>
<th>(2P_{yF})</th>
<th>(2P_{zF})</th>
<th>(1S_{H_1})</th>
<th>(1S_{H_2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2S_C)</td>
<td>(0.1134)</td>
<td>(0.0080)</td>
<td>(0.0000)</td>
<td>(0.2507)</td>
<td>(-0.0108)</td>
<td>(0.0055)</td>
<td>(0.0000)</td>
<td>(-0.0881)</td>
<td>(0.0366)</td>
<td>(-0.0366)</td>
</tr>
<tr>
<td>(2P_{xC})</td>
<td>(0.0080)</td>
<td>(0.0189)</td>
<td>(0.0000)</td>
<td>(0.0308)</td>
<td>(-0.0038)</td>
<td>(-0.0100)</td>
<td>(0.0000)</td>
<td>(-0.0219)</td>
<td>(-0.0035)</td>
<td>(-0.0035)</td>
</tr>
<tr>
<td>(2P_{yC})</td>
<td>(0.0000)</td>
<td>(0.0000)</td>
<td>(0.0250)</td>
<td>(0.0000)</td>
<td>(-0.0000)</td>
<td>(-0.0039)</td>
<td>(0.0000)</td>
<td>(-0.0017)</td>
<td>(-0.0017)</td>
<td>(0.0000)</td>
</tr>
<tr>
<td>(2P_{zC})</td>
<td>(0.2507)</td>
<td>(0.0308)</td>
<td>(0.0000)</td>
<td>(0.7953)</td>
<td>(-0.0186)</td>
<td>(0.0235)</td>
<td>(0.0000)</td>
<td>(-0.2709)</td>
<td>(-1.059)</td>
<td>(-1.059)</td>
</tr>
<tr>
<td>(2S_F)</td>
<td>(-0.0108)</td>
<td>(-0.0038)</td>
<td>(-0.0000)</td>
<td>(-0.0186)</td>
<td>(0.0016)</td>
<td>(0.0040)</td>
<td>(0.0000)</td>
<td>(0.0099)</td>
<td>(0.0033)</td>
<td>(0.0033)</td>
</tr>
<tr>
<td>(2P_{xF})</td>
<td>(0.0055)</td>
<td>(-0.0100)</td>
<td>(-0.0000)</td>
<td>(0.0235)</td>
<td>(0.0040)</td>
<td>(-0.2209)</td>
<td>(0.0000)</td>
<td>(-0.0110)</td>
<td>(-0.0006)</td>
<td>(-0.0006)</td>
</tr>
<tr>
<td>(2P_{yF})</td>
<td>(0.0000)</td>
<td>(0.0000)</td>
<td>(0.0039)</td>
<td>(0.0000)</td>
<td>(0.0000)</td>
<td>(0.0000)</td>
<td>(0.0000)</td>
<td>(0.0000)</td>
<td>(-0.0002)</td>
<td>(0.0002)</td>
</tr>
<tr>
<td>(2P_{zF})</td>
<td>(-0.0881)</td>
<td>(-0.0219)</td>
<td>(0.0000)</td>
<td>(-0.2709)</td>
<td>(0.0099)</td>
<td>(0.0110)</td>
<td>(-0.0000)</td>
<td>(0.0948)</td>
<td>(0.0323)</td>
<td>(0.0323)</td>
</tr>
<tr>
<td>(1S_{H_1})</td>
<td>(-0.0366)</td>
<td>(-0.0035)</td>
<td>(-0.0017)</td>
<td>(-1.059)</td>
<td>(0.0033)</td>
<td>(-0.0006)</td>
<td>(-0.0002)</td>
<td>(0.0323)</td>
<td>(-0.0143)</td>
<td>(0.0112)</td>
</tr>
<tr>
<td>(1S_{H_2})</td>
<td>(-0.0366)</td>
<td>(-0.0035)</td>
<td>(-0.0017)</td>
<td>(-1.059)</td>
<td>(0.0033)</td>
<td>(-0.0006)</td>
<td>(-0.0002)</td>
<td>(0.0323)</td>
<td>(-0.0112)</td>
<td>(-0.0143)</td>
</tr>
</tbody>
</table>

\(^a\)Notice the large off diagonal elements.
Table 15. Non-zero dipolar integrals and their contributions in AHCC for $^{19}$F in $\text{CH}_2^-$ radical.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Type of integral</th>
<th>Integral (a.u.$^{-3}$)</th>
<th>Contributions (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt; 2\text{Px}_F</td>
<td>T_{yy}</td>
<td>2\text{Px}_F &gt;$</td>
</tr>
<tr>
<td>$&lt; 2\text{Py}_F</td>
<td>T_{yy}</td>
<td>2\text{Py}_F &gt;$</td>
</tr>
<tr>
<td>$&lt; 2\text{Pz}_F</td>
<td>T_{yy}</td>
<td>2\text{Pz}_F &gt;$</td>
</tr>
<tr>
<td>$&lt; 2S_C</td>
<td>T_{yy}</td>
<td>2S_C &gt;$</td>
</tr>
<tr>
<td>$&lt; 2\text{Px}_C</td>
<td>T_{yy}</td>
<td>2\text{Px}_C &gt;$</td>
</tr>
<tr>
<td>$&lt; 2\text{Py}_C</td>
<td>T_{yy}</td>
<td>2\text{Py}_C &gt;$</td>
</tr>
<tr>
<td>$&lt; 2\text{Pz}_C</td>
<td>T_{yy}</td>
<td>2\text{Pz}_C &gt;$</td>
</tr>
<tr>
<td>$&lt; 2\text{Pz}_F</td>
<td>T_{yy}</td>
<td>2\text{Pz}_C &gt;$</td>
</tr>
<tr>
<td>$&lt; 2\text{Py}_F</td>
<td>T_{yy}</td>
<td>2\text{Py}_C &gt;$</td>
</tr>
<tr>
<td>$&lt; 2\text{Px}_F</td>
<td>T_{yy}</td>
<td>2\text{Px}_C &gt;$</td>
</tr>
<tr>
<td>$&lt; 2S_F</td>
<td>T_{yy}</td>
<td>2S_C &gt;$</td>
</tr>
<tr>
<td>$&lt; 2\text{Pz}_F</td>
<td>T_{yy}</td>
<td>2S_C &gt;$</td>
</tr>
<tr>
<td>$&lt; 2S_C</td>
<td>T_{yy}</td>
<td>1S_H &gt;$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}These contributions are in $T_{yy}$ tensor component using spin densities after deorthogonalization.
spectra for $\cdot{\text{CF}}_3$ radical, in xenon, krypton, and argon matrices have been reported and analyzed by two independent research groups (Charles, Fischer, and McDowell 1967 and Fessenden and Schuler 1965). Maruani et al. (1968) were able to explain the main features of this spectrum by a simulation method.

A semiempirical MO study of the anisotropic hyperfine coupling of $\cdot{\text{CF}}_3$ was given by Edlund et al. (1976). The dipolar integrals which they adapted did not include two-center type II integrals and three-center integrals. These authors compiled in an appendix the available analytical expressions for dipolar integrals from the literature. However, it should be noted that several of these are incorrect (see Appendix). To achieve calculated results similar to the experimental values it was necessary for them to make empirical changes in the effective nuclear charges.

In this study results which are in good agreement with the experimental came from using spin densities generated from deorthogonalized wavefunctions as can be seen from Table 16. Furthermore, it was not necessary to change the orbital exponents or other parameters to achieve these results.
Table 16. AHCC tensor components for α-fluorines in different radicals.

<table>
<thead>
<tr>
<th></th>
<th>CH₂F</th>
<th></th>
<th>CHF₂</th>
<th></th>
<th>CF₃</th>
<th></th>
<th>CF₃</th>
<th></th>
<th>CHF-CONH₂</th>
<th>CF₂-CONH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OSD</td>
<td>NSD</td>
<td>OSD</td>
<td>NSD</td>
<td>OSD</td>
<td>NSD</td>
<td>c</td>
<td>d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tₓₓ</td>
<td>-128.6</td>
<td>-182.1</td>
<td>-89.1</td>
<td>-129.5</td>
<td>-114.7</td>
<td>-167.3</td>
<td>-155.4</td>
<td>-158.0</td>
<td>-168</td>
<td>-171</td>
</tr>
<tr>
<td>tᵧᵧ</td>
<td>-93.7</td>
<td>-133.8</td>
<td>-122.2</td>
<td>-185.0</td>
<td>-133.6</td>
<td>-200.74</td>
<td>-186.8</td>
<td>-177.8</td>
<td>-201</td>
<td>-177</td>
</tr>
<tr>
<td>tₓᵧ</td>
<td>222.4</td>
<td>315.9</td>
<td>211.4</td>
<td>314.5</td>
<td>248.4</td>
<td>368.1</td>
<td>342.2</td>
<td>336.0</td>
<td>372</td>
<td>350</td>
</tr>
</tbody>
</table>

\( a \) OSD stands for computations of AHCC using spin densities before deorthogonalizations.

\( b \) NSD stands for computations of AHCC using spin densities after deorthogonalization.

\( c \) Edlund et al. (1976) -- INDO method.

\( d \) Maruani et al. (1968), Maruani, Coope, and McDowell (1970) -- Simulation method.

\( e \) Cook, Rowlands, and Whiffen (1963) -- Experimental.

\( f \) Rogers and Kispert (1967) -- Experimental.
Fluorinated Ethyl Radical

The $\beta$- fluorine hyperfine coupling tensors exhibit large anisotropies which are attributable to the spin density in the fluorine $2p_\pi$ orbital as was the case for $\alpha$-fluorine coupling tensors. Iwasaki (1971) and Jinguji et al. (1976) suggested that overlap integrals of alpha carbon $2p_\pi$ orbital with the lone-pair fluorine orbitals give rise to spin densities on the $2p_\pi$ fluorine orbitals. These spin densities due to the overlap are more important than those which arise from spin polarization in the sigma bonds.

$\beta,\beta,\beta$-Trifluoroethyl Radical ($\text{CF}_3\text{CH}_2$)

The radical geometry is assumed to be one in which $\text{CF}_3$ group has tetrahedral angles with C-F bond length = 1.08 Å. The z-axis, along the C-C bond and the x-and y-axes, are then chosen along two mutually orthogonal directions to it, one along the half filled $C_\alpha^{2p_\pi}$ orbital direction and the other perpendicular to the C-C bond.

In Table 17 the values for the spin density elements corresponding to the off-diagonal elements with the hydrogen atoms, carbon atoms and other fluorine atoms are not listed. The computed values for the AHCC tensor components for $^{19}F$ are compared with the experimental values obtained by Jinguji et al. (1976) (Table 18). The correspondence between the absolute value of $^{19}F_{2,3}$ (see Figure 4) are in good agreement if the $t_{xx}$ and $t_{zz}$ are exchanged.
Table 17. Spin density matrix for $^{19}\text{F}$ in CF$_3$CH$_2$.\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>2S</th>
<th>2P$_x$</th>
<th>2P$_y$</th>
<th>2P$_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2S</td>
<td>0.0011</td>
<td>0.0047</td>
<td>-0.0001</td>
<td>0.0034</td>
</tr>
<tr>
<td>2P$_x$</td>
<td>-0.0047</td>
<td>0.0129</td>
<td>-0.0015</td>
<td>-0.0086</td>
</tr>
<tr>
<td>2P$_y$</td>
<td>-0.0001</td>
<td>-0.0015</td>
<td>-0.0015</td>
<td>0.0015</td>
</tr>
<tr>
<td>2P$_z$</td>
<td>0.0034</td>
<td>-0.0086</td>
<td>0.0015</td>
<td>0.0040</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The whole spin density matrix is not written although there are appreciable off-diagonal elements.
Table 18. AHCC for $^{19}F$ in CF$_3$CH$_2$, radical in scheme NHF$_2$ - NSD.

<table>
<thead>
<tr>
<th>(MHz)</th>
<th>$F_1^a$</th>
<th>$F_2^a$</th>
<th>$F_3^a$</th>
<th>Three equivalent fluorines$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{xx}$</td>
<td>-94.7</td>
<td>61.6</td>
<td>61.6</td>
<td>-30.8</td>
</tr>
<tr>
<td>$t_{yy}$</td>
<td>195.1</td>
<td>-34.6</td>
<td>-34.6</td>
<td>-24.4</td>
</tr>
<tr>
<td>$t_{zz}$</td>
<td>-100.4</td>
<td>-27.0</td>
<td>-27.0</td>
<td>54.0</td>
</tr>
</tbody>
</table>

$^a$For the subscripts, see Figure 4 for the structure.

Figure 4. The structure of $\beta,\beta,\beta$-trifluoroethyl radical.
CHAPTER 4

SUMMARY AND CONCLUSION

From all the results reported in this study it can be seen that the INDO-MO method provides a satisfactory tool to calculate the anisotropic hyperfine coupling constants for a variety of organic radicals. The inclusion of the two-center type II integrals and three-center integrals make some contribution in the final values although this contribution is small because of the low spin density matrix elements corresponding to these integrals.

There are apparent disagreements between the theoretical and experimental values of the AHCC in some radicals (CF₃CH₂, CH₂CH₃) which are noteworthy, and this raises the question of how the axes system is defined in both theoretical and experimental studies, because the disagreement may be due to this reason, especially for non-crystalline radicals. Alternatively, the importance of the \( r^{-3} L \) terms in the Hamiltonian should be investigated in organic radicals, as these are known to be important for AHCC of transition metal compounds (Golding and Stubbs 1978).

Some of the results for \(^{19}\text{F}\) in methyl fluorinated radicals were in good agreement with the experimental when deorthogonalized wavefunctions are introduced and spin
density matrix elements generated from these. However, the
effect of deorthogonalization was nearly negligible for \(^1\text{H}\) and \(^{13}\text{C}\) AHCC except for central carbon atom in the \(\text{t-butyl}\) radical.

In all cases the greatest contribution comes from
one-center integrals and two-center type I dipolar integrals. This study also proves that using analytical expressions computationally is far less expensive than using numerical methods and that the final results are in good correspondence.

In Table 19 the tensor components for AHCC for \(^1\text{H}\) and \(^{13}\text{C}\) in the alpha position are compared in all the radicals. It can be seen from the table that for \(^{13}\text{C}\) the \(t_{yy}\) has its highest value for \(\text{C-H}\) and the lowest values for \(\text{CF}_3\). The fluorinated methyl radicals have lower values due to the substitution by \(^{19}\text{F}\) in place of the protons. For \(^1\text{H}\) the \(t_{zz}\) highest value for methyl radical and \(\text{C-H}\) whereas \(\text{CHF}_2\) has the lowest value. For \(^{19}\text{F}\) in fluorinated methyl radical where the tensor components are compared in Table 16, the values of \(t_{zz}\) are within the same order of magnitude although \(^{19}\text{F}\) in \(\text{CF}_3\) has the highest value while \(\text{CH}_2\text{F}\) and \(\text{CHF}_2\) have nearly the same value.
Table 19. Comparison of the tensor components of AHCC for $\alpha^{-1}H$ and $\alpha^{-13}C$ in all radicals computed in this work (MHz).

<table>
<thead>
<tr>
<th></th>
<th>C-H</th>
<th>H-C</th>
<th>CH$_2$</th>
<th>CH$_3$</th>
<th>C(CH$_3$)$_3$</th>
<th>CH(COOH)$_2$</th>
<th>CH$_2$CF$_3$</th>
<th>CH$_2$F</th>
<th>CHF$_2$</th>
<th>CF$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha^{-13}C$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{xx}$</td>
<td>-76.7</td>
<td>-75.0</td>
<td>-67.0</td>
<td>-60.5</td>
<td>-59.1</td>
<td>-70.6</td>
<td>-60.6</td>
<td>-47.9</td>
<td>-37.3</td>
<td></td>
</tr>
<tr>
<td>$t_{yy}$</td>
<td>153.5</td>
<td>150.0</td>
<td>134.6</td>
<td>121.1</td>
<td>120.2</td>
<td>142.3</td>
<td>120.9</td>
<td>95.2</td>
<td>74.0</td>
<td></td>
</tr>
<tr>
<td>$t_{zz}$</td>
<td>-76.8</td>
<td>-75.0</td>
<td>-67.7</td>
<td>-60.5</td>
<td>-61.1</td>
<td>-71.7</td>
<td>-59.3</td>
<td>-47.6</td>
<td>-37.3</td>
<td></td>
</tr>
<tr>
<td>$\alpha^{-1}H$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{xx}$</td>
<td>-41.1</td>
<td>-43.7</td>
<td>-39.2</td>
<td>-32.7</td>
<td>-43.3</td>
<td>-34.5</td>
<td>-25.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{yy}$</td>
<td>-7.7</td>
<td>-9.5</td>
<td>-8.2</td>
<td>-8.1</td>
<td>-10.6</td>
<td>-8.9</td>
<td>-7.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{zz}$</td>
<td>48.8</td>
<td>53.2</td>
<td>47.0</td>
<td>40.7</td>
<td>53.6</td>
<td>43.4</td>
<td>33.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX

DIPOLAR INTEGRALS

In this appendix analytical expressions for one and two-center dipolar integrals have been listed. The symbols which appear in the expressions are as follows:

\[ Z^* = \text{the effective nuclear charge at the orbital center} \]

\[ a_o = \text{the Bohr radius, } R = \text{internuclear distance.} \]

\[ n = \text{the principal quantum number of the orbital} \]

\[ \alpha = \frac{Z^*}{a_o}; \beta = \frac{Z^*}{2a_o}; \gamma = \frac{Z^*}{a_o}; \xi = \frac{Z^*}{na_o} \]

\[ r_{\pm j} = (3r_i r_j - r^2 \delta_{ij}) r^{-5} (r_i, r_j = x, y, z) \]

1. **One-Center Integrals**

Expectation values of the dipolar operator in Equation 52 vanish for spherically symmetric orbitals. For the one-center 2P Slater orbitals, the formulae are as follows:
\[
< 2P_z | T_{zz} | 2P_z > = < 2P_x | T_{xx} | 2P_x > \\
= < 2P_y | T_{yy} | 2P_y > = \frac{4}{15} \xi^3 \\
\] (A1) Barfield (1970)

\[
< 2P_z | T_{xx} | 2P_z > = < 2P_x | T_{yy} | 2P_x > \\
= < 2P_y | T_{xx} | 2P_y > \\
= < 2P_z | T_{yy} | 2P_z > \\
= < 2P_x | T_{zz} | 2P_x > . \\
= < 2P_y | T_{zz} | 2P_y > = -\frac{2}{15} \xi^3 \\
\] (A2) Barfield (1970)

\[
< 2P_x | T_{xy} | 2P_y > = < 2P_x | T_{xz} | 2P_z > \\
= < 2P_y | T_{yz} | 2P_z > = \frac{\xi^3}{5} \\
\] (A3) Barfield (1971)
A. Two-Center Type I Integrals: (Edlund et al. 1976 and Barfield et al. 1978)\(^1\)

\[
< 1S | T_{zz} | 1S > = 2R^{-3} \{1 - (\frac{4}{3} a^3 + 2a^2 + 2a + 1)e^{-2a}\} \quad (A4)
\]

\[
< 2S | T_{xx} | 1S > = < 1S | T_{yy} | 1S > = (-1/2) < 1S | T_{zz} | 1S > \quad (A5)
\]

\[
< 2S | T_{zz} | 2S > = 2R^{-3} \{1 - (\frac{4}{9} a^5 + 2/3a^4 + 4/3a^3 + 2a^2 + 2a + 1)e^{-2a}\} \quad (A6)
\]

\[
< 2S | T_{zz} | 2P_z > = -(1/\sqrt{3} R^3) \{\frac{15}{a} - (\frac{8}{3} a^5 + 4a^4 + 10a^3 + 20a^2 + 30a + 30 + \frac{15}{a})e^{-2a}\} \quad (A7)
\]

\[
< 2S | T_{xx} | 2S > = < 2S | T_{yy} | 2S > = -\frac{1}{2} < 2S | T_{zz} | 2S > \quad (A8)
\]

\[
< 2S | T_{xx} | 2P_x > = < 2S | T_{yy} | 2P_z > = -\frac{1}{2} < 2S | T_{zz} | 2P_z > \quad (A9)
\]

\[
< 2S | T_{zx} | 2P_x > = (15/2a\sqrt{3} R^3) \{1 - (\frac{4}{15} a^5 + \frac{2}{3} a^4 + \frac{4}{3} a^3 + 2a^2 + 2a + 1)e^{-2a}\} \quad (A10)
\]

\[
< 2S | T_{zy} | 2P_y > = < 2S | T_{zx} | 2P_x > \quad (A11)
\]

\[
< 2P_z | T_{zz} | 2P_z > = 2R^{-3} \{1 + \frac{18}{a^2} - (\frac{4}{3} a^5 + 2a^4 + 6a^3 + 14a^2 + 26a + 37 + \frac{36}{a} + \frac{18}{a^2})e^{-2a}\} \quad (A12)
\]

\(^1\)Three of the integrals listed in Edlund's paper were found to be incorrect (Barfield et al. 1978).
\[ \langle 2p_z | T_{xx} | 2p_z \rangle = \langle 2p_z | T_{yy} | 2p_z \rangle \]
\[ = -(1/2) \langle 2p_z | T_{zz} | 2p_z \rangle \]  \(\text{(A13)}\)

\[ \langle 2p_z | T_{zx} | 2p_x \rangle = -(18/a^2R^3) \left( 1 - \left( \frac{1}{9} a^6 + \frac{5}{18} a^5 + \frac{2}{3} a^4 + \frac{4}{3} a^3 + 2a^2 + 2a + 1 \right) e^{-2a} \right) \]  \(\text{(A14)}\)

\[ \langle 2p_z | T_{zy} | 2p_y \rangle = \langle 2p_z | T_{xz} | 2p_x \rangle \]  \(\text{(A15)}\)

\[ \langle 2p_x | T_{zz} | 2p_x \rangle = 2R^{-3} \left( 1 - \frac{9}{a^2} + (a^3 + 4a^2 + 10a + 17 + \frac{18}{a} + \frac{9}{a^2}) e^{-2a} \right) \]  \(\text{(A16)}\)

\[ \langle 2p_x | T_{xx} | 2p_x \rangle = -R^{-3} \left( 1 - \frac{27}{2a^2} + (2a^3 + 7a^2 + 16a + 26 + \frac{27}{a} + \frac{27}{2a^2}) e^{-2a} \right) \]  \(\text{(A17)}\)

\[ \langle 2p_x | T_{yy} | 2p_x \rangle = -R^{-3} \left( 1 - \frac{9}{2a^2} + (a^2 + 4a + 8 + \frac{9}{a} + \frac{9}{2a^2}) e^{-2a} \right) \]  \(\text{(A18)}\)

\[ \langle 2p_y | T_{zz} | 2p_y \rangle = \langle 2p_x | T_{zz} | 2p_x \rangle \]  \(\text{(A19)}\)

\[ \langle 2p_y | T_{zz} | 2p_y \rangle = \langle 2p_x | T_{yy} | 2p_x \rangle \]  \(\text{(A20)}\)
\[ < 2P_y | \tau_{yy} | 2P_y > = (2P_x | \tau_{xx} | 2P_x > \quad (A21) \]

\[ < 2P_x | \tau_{xy} | 2P_y > = \left( \frac{9}{2a^2 R^3} \right) \{ 1 - \left( \frac{2}{9} a^5 + \frac{2}{3} a^4 + \frac{4}{3} a^3 + 2a^2 + 2a + 1 \right) e^{-2a} \} \quad (A22) \]

B. Two-Center Type II Integrals (Barfield et al. 1978)

\[ < 1S_A | \tau_{zz}^A | 1S_B > = \frac{8e^3}{5} \left[ \frac{5}{6} (1 + \frac{9}{a} + \frac{18}{a^2}) e^{-a} \right. \]

\[ \left. -(5/2a) \{(1 + \frac{3}{a} + \frac{3}{a^2})(\gamma + ln2a)e^{-a} \right. \]

\[ \left. + (1 - \frac{3}{a} + \frac{3}{a^2}) E_1(2a)e^{-a} \} \} \quad (A23) \]

\[ < 1S_A | \tau_{xx}^A | 1S_B > = < 1S_A | \tau_{yy}^A | 1S_B > = \frac{1}{2} < 1S_A | \tau_{zz}^A | 1S_B > \quad (A24) \]

where \( \gamma \) is Euler's Constant, and \( E_1(z) \) is the exponential integral (Gautschi and Cahill 1966) and \( a = \beta R \).

For the integral \( < 1S_A | \tau_{zz}^A | 2S_B > \), \( \beta a_o \) is the effective nuclear charge of the 1S atomic orbital, \( \alpha = Z^*/2a_o \) is the coefficient in the exponent of the 2S atomic orbital, and \( a = \alpha R \):

\[ < 1S_A | \tau_{zz}^A | 2S_B > = (8/\sqrt{3})(\alpha \beta)^{3/2}(V_1 + V_2 + V_3 + V_4) \quad (A25) \]

where

\[ V_1 = -(a/3)e^{-a}(1 + 3/a + 6/a^2 + 9/a^3 + 9/a^4) \]

\[ -3/2 n^2(1 + \frac{9}{a} + \frac{39}{a^2} + \frac{90}{a^3} + \frac{90}{a^4}) + 3(1 - n^2)^{-1} \]
\[ x \left( \frac{1}{a^2} + \frac{3}{a^3} + \frac{3}{a^4} \right) \]

\[ V_2 = -e^{-\eta a} \left( \frac{1}{a} - \frac{3}{a^3} + \eta \left( 1 + \frac{30}{a^2} \right) \right) \]
\[ + \left( 9\eta^2/2 \right) \left( \frac{1}{a} + \frac{10}{a^3} \right) - (1 - \eta^2)^{-1} \left\{ \left( \frac{1}{a} + \frac{3}{a^3} \right) + 3n a^2 \right\} \]

\[ V_3 = (\eta e^{-a/4}) \left[ 1 + \frac{5}{a} + \frac{17}{a^2} + \frac{36}{a^3} + \frac{36}{a^4} - \eta^2 \left( 1 + \frac{9}{a} + \frac{39}{a^2} + \frac{90}{a^3} + \frac{90}{a^4} \right) \right] x \]
\[ \left[ \mu_{\eta} \left| \frac{1+\eta}{1-\eta} \right| + E_i(a-\eta) \right] \]

\[ V_4 = (\eta e^{a/4}) \left\{ 1 - \frac{5}{a} + \frac{17}{a^2} - \frac{36}{a^3} + \frac{36}{a^4} - \eta^2 \left( 1 - \frac{9}{a} + \frac{39}{a^2} \right) \right. \]
\[ - \left. \frac{90}{a^3} + \frac{90}{a^4} \right\} E_1(a(1 + \eta)) \]

\[ <1S_A| T_A^{zz} | 2P_{zB}> = \left( \frac{8}{5} \right) (a^2)^{3/2} (W_1 + W_2 + W_3 + W_4) \] (A26)

where

\[ W_1 = e^{-a}\left\{ (5a/6)(2 - 3\eta^2) + 5(1 - \frac{9\eta^2}{2}) + (5/a) \right\} \]
\[ \left( 3 - \frac{45\eta^2}{2} + \frac{1}{1 - \eta^2} \right) + (5/a^2)(8 - 75\eta^2 + \]
\[ \frac{4}{1 - \eta^2} + 75(1 - \frac{21\eta^2}{2} + \frac{3}{5} \frac{1}{1 - \eta^2})(a^{-3} + a^{-4}) \} \]

\[ W_2 = e^{-na}\left\{ (5/2)\eta^2 + (5n/a)(4 - \frac{1}{1 - \eta^2}) + (5/2a^2) \right\} \]
\[ \left( 8 + 45\eta^2 - \frac{8}{1 - \eta^2} \right) + (15n/2a^3)(35 - \frac{6}{1 - \eta^2}) \]
- (75/a^4)(1 - \frac{21n^2}{2} + \frac{3}{5} \frac{1}{1 - n^2})

W_3 = (5\pi/4)e^{-\alpha}(a(n^2 - 1) + (9n^2 - 5) + (3/a)

(15n^2 - 7) + (6/a^2)(25n^2 - 11) - 45(3 + 7n^2)

(a^{-3} + a^{-4})\{1n|\frac{1 + n}{1 - n}| + E_i{(1 - n)a}

W_4 = (5\pi/4)e^{\alpha}(1 - n^2)a + (9n^2 - 5) + (3/a)(7 - 15n^2)

+ (6/a^2)(25n^2 - 11) + 45(3 - 7n^2)(a^{-3} - a^{-4})} \times

E_i{(1 + n)a}

Also,

< 1S_A | T_{xx}^A | 2P_z^B > = < 1S_A | T_{yy}^A | 2P_{zB} > =

-(1/2) \quad < 1S_A | T_{zz}^A | 2P_{zB} > (A27)

and it follows by symmetry that

< 1S_A | T_{zz}^A | 2P_x^B > = < 1S_A | T_{zz}^A | 2P_{yB} > = 0 (A28)

< 1S_A | T_{xx}^A | 2S_B > = < 1S_A | T_{yy}^A | 2S_B > =

-(1/2) \quad < 1S_A | T_{zz}^A | 2S_B > (A29)
REFERENCES


