AB INITIO CALCULATIONS

OF

NMR AND ESR COUPLING CONSTANTS

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STATEMENT

The work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester between October 1971 and September 1975.

The work has not been presented and is not being concurrently presented for any other degree.

Signed:

Richard E. Overell

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PART ONE

The Calculation of
Nuclear Spin-Spin Coupling Constants
by the Self-Consistent Field
Perturbation Method
1. **Nuclear Spin-Spin Coupling Constants and their Importance.**

Ever since the field-independent, hyperfine splittings in the nuclear magnetic resonance (NMR) spectra of molecules were first observed around 1950 [1-5], they have presented a formidable challenge to theoretical chemists and physicists. Ramsey & Purcell [6] suggested that the splittings were due to the indirect coupling of nuclear spin magnetic moments via interaction with electron spins, which are in turn exchange-coupled together. They showed that such a mechanism would give rise to an interaction of the observed form

\[ E_{AB} = \hbar J_{AB} I_A I_B \]  

(1.1)

and that the interaction should be of the correct order of magnitude. In (1.1), \( E_{AB} \) is the interaction energy between the nuclei A and B with spins \( I_A \) and \( I_B \), \( \hbar \) is Planck's constant and \( J_{AB} \) is the observed nuclear spin-spin coupling constant between A and B. Ramsey [7] went on to show that there are three mechanisms by which a nuclear magnetic moment can interact with the surrounding electrons to produce magnetic fields at the sites of the other nuclei in the molecule. Two of these mechanisms involve the electron spin angular momentum and result in electron-spin polarisation, while the third considers the orbital electronic currents induced by a nuclear moment.

The Hamiltonian operator for the Fermi contact interaction [8] which describes the magnetic coupling between the nuclear moments and the electron spins in contact with each nucleus, was formulated by Abragam & Pryce [9] as

\[ \mathcal{H}^{(3)} = \left(8\pi/3\right) g_e \beta_e \sum_A \sum_k \delta(r_{kA}) \mu_A \cdot S_k \]  

(1.2)
where $g_e$ is the electronic g-value,  
$\beta_e$ is the Bohr magneton,  
$\mu_A$ is the magnetic moment of nucleus A,  
$S_k$ is the spin angular momentum operator for electron k  
and $\delta(r_{kA})$ is the three-dimensional Dirac delta function for electron k at nucleus A, which has the property that

$$\int f(r_k) \delta(r_{kA}) \, dr_k = f(r_A)$$

where $f(r_k)$ is an arbitrary function of the coordinates of electron k and $r_{kA} = r_k - r_A$.

The operator for the spin-dipolar interaction, which describes the dipole interaction between the nuclear magnetic moments and the electron spins, is given by

$$H = g_e \beta_e \sum_k \sum_A [3(\mu_A \cdot r_{kA})(S_k \cdot r_{kA}) r_{kA}^5 - (\mu_A \cdot S_k) r_{kA}^3]$$

(1.3)

The dipole field produced by a nuclear magnetic moment also induces electronic orbital motion to produce secondary magnetic fields at the positions of the other nuclear moments, giving rise to indirect spin-spin coupling. The Hamiltonian for this interaction consists of two parts, one linear in $\mu_A$ and the other bilinear in $\mu_A$ and $\mu_B$.

$$H^{(1a)} = (e^2 / 2mc^2) \sum_{A \neq B} \sum_k [(\mu_A \times r_{kA}) r_{kA}^3].[(\mu_B \times r_{kB}) r_{kB}^3]$$

(1.4)

$$H^{(1b)} = 2\beta_e \sum_A \sum_k (\mu_A \cdot L_{kA}) r_{kA}^3$$

(1.5)

where $L_{kA}$ is the orbital angular momentum operator for electron k about nucleus A [Equation (4.3)].

A reduced coupling constant $K_{AB}$ [10], defined as the proportionality
constant between the interaction energy and the product of the nuclear moments, is sometimes used and (1.1) becomes

\[ E_{AB} = K_{AB} \mu_A \cdot \mu_B \] (1.6)

where the magnetogyratic ratio relates \( \mu_A \) to \( I_A \) by

\[ \gamma_A = \mu_A / (I_A \ h) \]

Equation (1.1) can be rewritten as

\[ J_{AB} = E_{AB}^{(2)} \gamma_A \gamma_B \hbar / (2\pi) \] (1.7)

where \( E_{AB}^{(2)} \) is the second order energy of interaction of the nuclear magnetic moments \( \mu_A \) and \( \mu_B \),

\[ E_{AB}^{(2)} = (\partial^2 E_{AB} / \partial \mu_A \partial \mu_B) |_{\mu_A = \mu_B = 0} \]

Thus indirect nuclear spin-spin coupling is a second order molecular property, and involves the distortion or polarisation of the electron distribution by the nuclear moments. Ramsey [7] applied conventional perturbation theory [Section 2.1] to the interactions and obtained expressions for the contributions to the total coupling constant. He showed that for a molecule undergoing sufficiently frequent collisions to effectively average over all molecular orientations, the direct dipole-dipole magnetic interaction of the nuclei and the spin dipolar-Fermi contact cross-term both average to zero. In addition, if there is no strong electron spin-orbital coupling in the molecule, then the spin dipolar-orbital and Fermi contact-orbital cross-terms will be negligible. For this reason, most of the calculations for NMR coupling constants which have been performed in the last twenty-five years have included only the 'diagonal' terms, and the great majority have been restricted to the Fermi contact term only.
Since the pioneering work of Ramsey [7], a large number of semi-empirical and \textit{ab initio} calculations of nuclear spin-coupling constants have been made. This activity reflects the increasing importance of this molecular property, for both the experimental chemist and the theoretician. Experimentally, NMR coupling constants provide the preparative chemist with invaluable information for the identification and structural elucidation of complex molecules, while the physical chemist may study intra-molecular motions and the effects of solvation and molecular environment using the technique. Because the indirect spin-coupling represents such a small effect energetically (1\text{Hz} \sim 10^{-16} \text{ Hartrees}) it has become a highly sensitive technique for investigating very subtle changes in the electronic distribution of a molecule. This is also the principal reason for the considerable theoretical interest in the subject, for not only is it desirable to be able to assist the experimentalist with reliable theoretical predictions and confirmations of chemically interesting NMR coupling constants, but it is equally important to gain a deeper theoretical insight into how the physical processes which give rise to spin-coupling are best treated and interpreted within the framework of molecular quantum mechanics.

2. \textbf{The Self Consistent Field Perturbation Method For Nuclear Spin-Spin Coupling Constants}

2.1 \textbf{Introduction}

Rayleigh-Schrödinger Perturbation Theory [11] may be applied to the ground state of a closed shell molecule in an attempt to solve the eigenvalue problem.
\[ H(\lambda) \psi(\lambda) = E(\lambda) \psi(\lambda) \]  

(2.1)

where

\[ H(\lambda) = H^0 + \sum_r \lambda_r H_r' \]  

(2.2)

is the molecular Hamiltonian consisting of the zero order (unperturbed) part and the additional perturbations. The \( \lambda_r \), which form the set \( \lambda \), are the perturbation parameters, and correspond to particular components of the (internal or external) perturbations being considered in a molecular property calculation. The molecular properties are usually defined by expanding the energy as a Taylor series in powers of the perturbation parameters, representing the magnitudes of the various perturbations:

\[
E(\lambda) = E^{(0)} + \sum_r \lambda_r \left( \frac{\partial E(\lambda)}{\partial \lambda_r} \right)_0 + \frac{1}{2} \sum_r \sum_s \lambda_r \lambda_s \left( \frac{\partial^2 E(\lambda)}{\partial \lambda_r \partial \lambda_s} \right)_0 + \ldots.
\]

(2.3)

where \( E^{(0)} \) is the energy of the unperturbed molecule and \( E^{(1)}_r \), \( E^{(2)}_s \) are respectively first and second order properties of the molecule, associated with the perturbing effects of \( \lambda_r \), \( \lambda_s \). For first order properties, the Hellman-Feynman Theorem [12,13] reduces the derivative to simply the expectation value of \( H_r' \) with the unperturbed wavefunction

\[
E^{(1)}_r = \langle \psi^{(0)} | H_r' | \psi^{(0)} \rangle
\]

(2.4)

For second and higher order properties it is necessary to use perturbation theory, in which the molecular wavefunction is also expanded as a Taylor series powers of the \( \lambda_r \):

\[
\psi(\lambda) = \psi^{(0)} + \sum_r \lambda_r \left( \frac{\partial \psi(\lambda)}{\partial \lambda_r} \right)_0 + \frac{1}{2} \sum_r \sum_s \lambda_r \lambda_s \left( \frac{\partial^2 \psi(\lambda)}{\partial \lambda_r \partial \lambda_s} \right)_0 + \ldots
\]
\[ \psi^{(0)} + \sum_{\mathbf{r}} \lambda_{\mathbf{r}} \psi^{(1)}_{\mathbf{r}} + \sum_{\mathbf{r}, \mathbf{s}} \lambda_{\mathbf{r}} \lambda_{\mathbf{s}} \psi^{(2)}_{\mathbf{r}, \mathbf{s}} + \ldots \quad (2.5) \]

where \( \psi^{(0)} \) is the unperturbed wavefunction and \( \psi^{(1)}_{\mathbf{r}}, \psi^{(2)}_{\mathbf{r}, \mathbf{s}} \) are respectively first and second order changes in \( \psi^{(0)} \) due to the additional perturbations in the Hamiltonian (2.2). Substituting the expansions (2.2), (2.3) and (2.5) into (2.1), and separating the orders as powers of \( \lambda_{\mathbf{r}} \) yields the zero, first and second order equations:

\[
\begin{align*}
(H^0 - E^{(0)}) \psi^{(0)} &= 0 \\
(H^0 - E^{(0)}) \psi^{(1)}_{\mathbf{r}} &= (E^{(1)}_{\mathbf{r}} - H^0) \psi^{(0)} \\
(H^0 - E^{(0)}) \psi^{(2)}_{\mathbf{r}, \mathbf{s}} &= 2(E^{(1)}_{\mathbf{r}} - H^0) \psi^{(1)}_{\mathbf{s}} + E^{(2)}_{\mathbf{r}, \mathbf{s}} \psi^{(0)}
\end{align*}
\]

(2.6)

(2.7)

(2.8)

The ground state, zero order problem (2.6) is assumed to have been solved for \( \psi^{(0)} \) and \( E^{(0)} \). It is however not necessary to solve (2.8) to obtain \( E^{(2)}_{\mathbf{r}, \mathbf{s}} \), since if the expansion (2.5) is truncated at first order to give

\[
\psi(\lambda) = \psi^{(0)} + \sum_{\mathbf{r}} \lambda_{\mathbf{r}} \psi^{(1)}_{\mathbf{r}} + \ldots \quad (2.9)
\]

then the resulting second order equation is

\[
(E^{(1)}_{\mathbf{r}} - H^0_{\mathbf{r}}) \psi^{(1)}_{\mathbf{r}} + \frac{1}{2} E^{(2)}_{\mathbf{r}, \mathbf{s}} = 0 \quad (2.10)
\]

whence, pre-multiplying by \( \psi^{(0)} \) and integrating over all space,

\[
\frac{1}{2} E^{(2)}_{\mathbf{r}, \mathbf{s}} = \frac{\langle \psi^{(0)} | H^0_{\mathbf{r}} | \psi^{(1)}_{\mathbf{s}} \rangle}{E^{(0)}_{\mathbf{r}} - E^{(0)}_{\mathbf{s}}} \quad (2.11)
\]

since the normalisation of \( \psi(\lambda) \) and \( \psi^{(0)} \) requires that \( \langle \psi^{(0)} | \psi^{(1)}_{\mathbf{s}} \rangle = 0 \).

In non-degenerate infinitesimal perturbation theory, (2.11) is usually solved by expanding \( \psi^{(1)}_{\mathbf{s}} \) in the complete set of excited eigenfunctions of \( H^0 \), giving the well-known equations

\[
\psi^{(1)}_{\mathbf{s}} = \sum_{h=1}^{\infty} \frac{\langle \psi^{(0)}_n | H^0_{\mathbf{s}} | \psi^{(0)}_{\mathbf{n}} \rangle}{E^{(0)}_{\mathbf{n}} - E^{(0)}_{\mathbf{s}}} \psi^{(0)}_n \quad (2.12)
\]
\[
E_r^{(2)} = \sum_{n=1}^{\infty} \frac{\langle \psi_n^{(0)} | H_\alpha' | \psi_n^{(0)} \rangle < \psi_n^{(0)} | H_\gamma' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_r^{(0)}}
\]

(2.13)

where \(\psi_n^{(0)}\), \(E_n^{(0)}\) are respectively the eigenfunctions and eigenvalues associated with \(H^0\), corresponding to the \(n^{th}\) excited state of the unperturbed molecule. Clearly the evaluation of a second order property by (2.13) is extremely difficult without resorting to approximations, since an accurate knowledge of the complete set of eigenstates of \(H^0\) (including the continuum) is involved. However, the use of approximations such as severe truncation of the expansion or a poor representation of the excited states may jeopardise the convergence of (2.13) [14].

An alternative approach to the solution of (2.11) involves choosing a suitable trial function for \(\psi_s^{(1)}\) and then solving the equation variationally for \(E_r^{(2)}\) with respect to the trial function. However, quite apart from the difficulties of choosing the form of \(\psi_s^{(1)}\) and of evaluating (2.11), the stationary point obtained cannot be shown to be a minimum [15] and \(E_r^{(2)}\) is not bounded [24] when only part of the total second order energy \(E^{(2)}\) is calculated. In particular, the calculation of nuclear spin-coupling constants poses serious problems because the self-coupling terms \(E_r^{(2)}\) diverge to infinity when the Fermi contact operator is represented by the Dirac delta function [16]. Attempts to overcome this difficulty by using the Blinder operator [17,18] or its exponential approximation [19] have been made [20-24], but although they yield finite self-energies these operators have been criticised as unphysical [45,46]. Finite nucleus models [47] and trial functions which cancel the delta function singularities [25] have also been studied in this context.

Within the Hartree-Fock approximation formulated in terms of molecular orbitals a similar bifurcation can be distinguished, with the restriction
that the perturbed and unperturbed wavefunctions, \( \psi \) and \( \psi^{(0)} \) are constrained to be single determinants of the molecular orbitals \( \psi_i \). In the conventional Molecular Orbital Sum-Over-States (MO SOS) method, the excited states are generated by excitations from the occupied MOs into a set of Virtual MOs (VMO) [10], sometimes followed by Configuration Interaction (CI) among the excited states [30]. Due to the limited number of VMOs usually available and their unsuitability for describing excited states, the convergence of the simple MO SOS expansion

\[
E_{r}^{(2)} = k \sum_{\text{occ}} \sum_{\text{virt}} \frac{\langle \psi_1 | H_{r} \psi_1 \rangle - \langle \psi_1 | H_{s} \psi_1 \rangle}{E_{r+1} - E_0} \quad \text{(2.14)}
\]

is often highly erratic, and is not always improved after CI [30,48].

A Variational Perturbation approach can be formulated within the Hartree-Fock approximation [49,50] using a polynomial to represent the perturbation to each MO, and then varying the polynomial coefficients to make the second order variational functional stationary. A similar effect can also be achieved by expanding the perturbation to the wavefunction in terms of a set of singly excited states obtained by promotions into the virtual MOs, and making the variational functional stationary with respect to the expansion coefficients. This method is equivalent to the MO SOS method after CI amongst the excited states [44]. A closely related group of methods attempt to solve the perturbed Hartree-Fock equations directly to first order, in the presence of a finite or infinitesimal one-electron perturbation. These Self-Consistent Perturbation methods use a variety of techniques to obtain the first order change in the wavefunction due to the effect of the perturbation. The Self-Consistent Field Perturbation method (SCFPM) developed by Amos & Hall [51] uses one such technique, involving the expansion of the first order MOs in terms of the unperturbed MOs followed by
the iterative solution of the resulting non-linear first order equations
[52].

McWeeny & Diercksen [53,54] formulated the same procedure directly
in terms of the perturbed density matrix, and McWeeny [52] has clarified
the relationship between the two approaches. In the Coupled Hartree-Fock
Perturbation Method (CHFPM) [55,56,57], which is theoretically equivalent
to the SCFPM, the first order orbitals arising from an infinitesimally
applied perturbation are found by solving a large system of linear
inhomogeneous equations in the basis of the unperturbed molecular orbitals.
In the Finite Perturbation Method (FPM) of Pople et al. [58,59], a pertur­
bation of finite and artificially large magnitude is introduced directly
into the SCF calculation, and the first order density matrix is evaluated
numerically by application of the truncated Newton-Stirling finite difference technique. The FPM becomes equivalent to the SCFPM and CHFPM
in the limit as the magnitude of the perturbation tends to zero. A com­
parative analysis of the FPM and the MO SOS method in the calculation of
electric polarisabilities and nuclear spin-spin coupling constants has been made by Murrell and co-workers [41], and it was demonstrated that the FPM
cannot induce singly excited states into the perturbed wavefunction without
at the same time introducing doubly excited states in a restricted way.
The Coupled Hartree-Fock Method (CHFM) developed by Roothaan & Cohen [60]
for calculating atomic polarisabilities is similar to the FPM except that
several calculations are necessary at different values of the applied field
in order to compute the second order energy as a function of the field. This
approach has been criticised as both expensive and seldom of sufficient
accuracy [67].

A brief summary of the Restricted Hartree-Fock method, which is applied
to the unperturbed molecule, will now be given in order to set out the
equations and to define the basic quantities and the symbols required in
the following sections.

2.2 The Restricted Hartree-Fock method for the unperturbed molecule

The closed shell RHF method was formulated in terms of the Linear
Combinations of Atomic Orbitals-Molecular Orbitals (LCAO-MO) to give the
Self-Consistent Field equations by Hall [61] and Roothaan [62]. The wave­
function of a closed-shell molecule with \(2n\) electrons is expressed as a
single normalised Slater determinant of molecular orbitals

\[
\psi_{\text{RHF}}^{(0)} = (2n!)^{-\frac{1}{2}} \det \left| \psi^{(0)}_1(1)\alpha(1)\psi^{(0)}_1(2)\beta(2) \ldots \psi^{(0)}_n(2n-1)\alpha(2n-1) \right|
\]

(2.15)

where each unperturbed MO \(\psi^{(0)}_i\) contains one \(\alpha\)-spin and one \(\beta\)-spin electron. Without loss of generality the \(\psi^{(0)}_i\) may be assumed orthonormal

\[
\int \psi^{(0)*}_i \psi^{(0)}_j \, d\tau = \delta_{ij}
\]

(2.16)

In order to determine the optimal MOs, the \{\(\psi^{(0)}_i\}\} are expanded as a LCAO using a set of \(m\) (\(>n\)) basis functions \{\(\omega_i\}\) centred at the various nuclei (AOs)

\[
\psi^{(0)}_j = \sum_{i=1}^{m} C^{(0)}_{ij} \omega_i
\]

(2.17)

The \(\{\omega_i\}\) are themselves constructed from a set of primitive functions \{\(X_j\}\} which are usually either Slater-type functions (STF) or Gaussian-type functions (GTF)

\[
\omega_i = \sum_j d_j \, X_j
\]

(2.18)
Using the RHF wavefunction, the electronic Schrödinger equation for the molecule is

\[ H^0 \psi^{(0)}_{\text{RHF}} = E_{\text{RHF}}^{(0)} \psi^{(0)}_{\text{RHF}} \]  

(2.19)

where the non-relativistic Hamiltonian operator for the electronic energy is

\[ H^0 = \sum_{i=1}^{2n} h(i) + \sum_{i=1}^{2n} \sum_{j>i} g(i,j) \]  

(2.20)

Here,

\[ h(i) = -\frac{1}{2} \nabla_i^2 - \sum_{\nu=1}^{N} \frac{Z_\nu}{r_{i\nu}} \]  

(2.21)

is the one-electron part of \( H^0 \), describing both the kinetic energy and the electrostatic attraction by the \( N \) nuclei of charge \( Z_\nu \), of each electron and

\[ g(i,j) = \frac{1}{r_{ij}} \]  

(2.22)

is the two-electron part, describing the interelectronic repulsion. In the Born-Oppenheimer approximation the nuclei are treated as classical stationary point-charges and the internuclear repulsion term

\[ V = \sum_{\mu=1}^{N} \sum_{\nu>\mu} Z_\mu Z_\nu / R_{\mu\nu} \]  

(2.23)

is evaluated classically.

Defining the overlap matrix of the basis functions

\[ S_{ij} = \int \omega_i^* \omega_j \, dt \]  

(2.24)

and the charge and bond order matrix
\[ 2P_{ij}^{(0)} = 2 \sum_{k=1}^{n} C_{ik}^{(0)} C_{jk}^{(0)*} \]  
\[ (2.25) \]

or
\[ P^{(0)} = C^{(0)} C^{(0)*} \]  
\[ (2.26) \]

then \( P^{(0)*} \) is idempotent and
\[ \text{Tr}(P^{(0)*}) = n \]  
\[ (2.27) \]

due to the orthonormality of the molecular orbitals
\[ C^{(0)*} S C^{(0)} = I, \]  
\[ (2.28) \]

The RHF energy for the normalised determinant

\[ E_{\text{RHF}}^{(0)} = \int \psi_{\text{RHF}}^{(0)*} H^{0} \psi_{\text{RHF}}^{(0)} \, d\tau \]  
\[ (2.29) \]

\[ = 2\text{Tr}(P^{(0)}H) + \text{Tr}(P^{(0)}G^{(0)}) \]  
\[ (2.30) \]

where
\[ H_{ij} = \int \omega_i^{*} \omega_j \, d\tau \]  
\[ (2.31) \]

and
\[ G_{ij}^{(0)} = \sum_{k, l} \left| P_{kl}^{(0)} \right| \left[ 2 \langle i|k \rangle \langle j|l \rangle - \langle i|k \rangle \langle l|j \rangle \right] = 2J_{ij}^{(0)} - K_{ij}^{(0)} \]  
\[ (2.32) \]

where
\[ \langle i|k \rangle = \int \omega_i^{*}(1) \omega_j^{*}(2) \left[ \tau_{12}^{-1} \right] \omega_k(1) \omega_l(2) \, d\tau_1 \, d\tau_2 \]  
\[ (2.33) \]

In addition,
\[ P^{(0)} = H + G^{(0)} \]  
\[ (2.34) \]

is the matrix of the Hartree-Fock Hamiltonian over the basis functions \( \{\omega_i\} \).

The Coulomb matrix elements \( J_{ij}^{(0)} \) represent the electrostatic repulsions between all pairs of electrons, while the exchange matrix elements \( K_{ij}^{(0)}(ij) \) describe the non-classical exchange interactions of pairs of electrons with like spins in different orbitals (Fermi correlation).
Optimisation of \( E_{RHF}^{(0)} \) with respect to \( \psi_{RHF}^{(0)} \) is effected by variation of the MO coefficients in \( C^{(0)} \). Application of the variational condition for a stationary energy

\[
\frac{\partial E_{RHF}^{(0)}}{\partial C_{ik}^{(0)}} = 0 \quad \text{(all } i,k) \tag{2.35}
\]

subject to the constraint that the MOs remain orthonormal, leads to the set of one-electron pseudo-eigenvalue equations for \( C^{(0)} \)

\[
F^{(0)} \bar{C}^{(0)} = S \bar{C}^{(0)} \varepsilon^{(0)} \quad (\varepsilon^{(0)} \text{ diagonal}) \tag{2.36}
\]

known as the matrix Hartree-Fock equations. Standard eigenvalue form may be attained by Löwdin orthogonalisation [63] which effectively absorbs the S in (2.36), giving

\[
\bar{F}^{(0)} \bar{C}^{(0)} = \bar{C}^{(0)} \varepsilon^{(0)} \quad (\varepsilon^{(0)} \text{ diagonal}) \tag{2.37}
\]

The eigenvalue problem (2.37) may then be solved by diagonalisation of the matrix \( \bar{F}^{(0)} \) to yield the eigenvectors \( \bar{C}^{(0)} \) and eigenvalues \( \varepsilon^{(0)} \), and hence \( C^{(0)} \) and \( \varepsilon^{(0)} \). However since \( F^{(0)} \) is a function of \( C^{(0)} \), the equations (2.36) must be solved iteratively until the MO coefficients become self-consistent, when \( \psi_{RHF}^{(0)} \) is the SCF MO wavefunction, and \( \varepsilon^{(0)} \) is the diagonal matrix of SCF orbital energies. The stationary value of \( E_{RHF}^{(0)} \) will be a minimum if the \( n \) lowest energy molecular orbitals are selected for the \( 2n \) electrons at each iteration. The remaining \( (m-n) \) virtual MOs play no part in describing the unperturbed closed-shell molecule, although they are often used either in their canonical or a modified form in perturbation and CI calculations.
2.3 The SCF Perturbation Method

The Self-Consistent Field Perturbation Method was formulated for nuclear spin-spin coupling by Blizzard & Santry [64] in the INDO approximation, and independently by Ditchfield and Snyder [65] at the \textit{ab initio} level. Their intention was to formulate a conceptually straightforward model for each of the nuclear spin-coupling mechanisms, within the framework of Hartree-Fock Perturbation Theory, with a view to applying it to molecules of chemical interest. In essence, the Hartree-Fock equations for the molecule are solved for the first order change in the wavefunction due to the presence of an infinitesimal one-electron perturbation by a nuclear moment, corresponding to the particular electron-nuclear coupling mechanism under consideration. The method has the advantages of avoiding the calculation of the problematical sum over excited states (Section 2.1), and of including interelectronic interaction in the perturbed wavefunction to the same extent as in the unperturbed wavefunction [64]. So far the only \textit{ab initio} calculation of nuclear spin-spin coupling by this method has been performed on the CH$_3$F molecule [65] using the slightly extended 4-31 G basis set, and has yielded promising results. Furthermore, since its inception, the SCFPM has been applied with considerable success to the calculation of several other molecular properties including \pi-electron polarisabilities [66], electric polarisabilities and dipole hyperpolarisabilities [67-69], magnetic susceptibilities [69,70] and nuclear magnetic shielding constants [71,72].

The indirect coupling constant $J_{AB}$ between the nuclei A and B is related to the second order energy of interaction $E_{AB}^{(2)}$ between the nuclear magnetic moments $\mu_A$ and $\mu_B$ by

$$J_{AB} = E_{AB}^{(2)} \gamma_A \gamma_B \hbar/(2\pi)$$  \hspace{1cm} (2.38)
\[ E_{AB}^{(2)} = \left( \frac{\partial^2 E_{AB}}{\partial \mu_A \partial \mu_B} \right)_{\mu_A=\mu_B=0} \quad (2.39) \]

and

\[ \gamma_A = \frac{\mu_A}{(I_A \hbar)} \]

is the magnetogyric ratio of nucleus A with spin \( I_A \), and similarly for nucleus B.

The Schrödinger equation for the perturbed molecule

\[ H(\mu_A,\mu_B) \psi(\mu_A,\mu_B) = E(\mu_A,\mu_B) \psi(\mu_A,\mu_B) \quad (2.40) \]

is to be solved, where \( \psi(\mu_A,\mu_B) \) is a normalised single determinant of SCF molecular orbitals, \( E(\mu_A,\mu_B) \) is the total electronic energy of the molecule in the presence of the nuclear moments, and \( H(\mu_A,\mu_B) \) is the molecular Hamiltonian including the magnetic moment perturbations, which correspond to the particular electron-nuclear coupling mechanism under consideration.

\[ H(\mu_A,\mu_B) = H^0 + \mu_A H'_A + \mu_B H'_B \quad (2.41) \]

Therefore

\[ E(\mu_A,\mu_B) = \langle \psi(\mu_A,\mu_B) | H(\mu_A,\mu_B) | \psi(\mu_A,\mu_B) \rangle \quad (2.42) \]

Now the Hellmann-Feynman Theorem \([12,13]\), which has been shown to apply to Hartree-Fock wavefunctions \([73]\) and to SCF LCAO-MO wavefunctions (provided the perturbation in question does not depend on the nuclear configuration) \([74,58]\) may be used to differentiate, giving,

\[ \frac{\partial E(\mu_A,\mu_B)}{\partial \mu_B} = \left( \frac{\partial E_{AB}}{\partial \mu_B} \right)_{\mu_B=0} = \langle \psi(\mu_A,0) | \frac{\partial H(\mu_A,\mu_B)}{\partial \mu_B} | \psi(\mu_A,0) \rangle \quad (2.43) \]

Differentiating again,
thus it is necessary to use a perturbing Hamiltonian involving only \( \mu_A \),

\[
H(\mu_A, 0) = H_0 + \mu_A H_A
\]  \hspace{1cm} (2.45)

and once \( \Psi(\mu_A, 0) \) is obtained, it is possible to evaluate \( J_{AB} \) for every other atom B in the molecule. Therefore, at the worst \((N-1)\) perturbed wavefunctions will have to be calculated for each component of \( H_A' \) in order to obtain all the couplings, whereas if the energy \( E_{AB}^{(2)} \) were evaluated directly, as in Equation (2.13), a total of \( N(N-1)/2 \) calculations would be necessary. Molecular symmetry can often decrease these numbers substantially, however.

The technique used to obtain the perturbation corrections to the wavefunction through first order is formulated in terms of the perturbed Hartree-Fock equations:

\[
F C_j = S C_j \varepsilon_j
\]  \hspace{1cm} (2.46)

where \( F = F^{(0)} + \lambda F^{(1)} \) is the perturbed Fock matrix in the AO basis \( \{ \omega_i \} \),

\[
\varepsilon_j = \varepsilon_j^{(0)} + \lambda \varepsilon_j^{(1)}
\]

is the energy of the perturbed \( j^{th} \) MO,

\[
C_j = C_j^{(0)} + \lambda C_j^{(1)}
\]

is the coefficient vector for the perturbed \( j^{th} \) MO, assuming that the first order orbitals may be expanded in the same basis set as the unperturbed orbitals [55],
\[ \psi_j = \sum_{i=1}^{m} (C_{ij}^{(0)} + \lambda C_{ij}^{(1)}) \omega_i \quad , \quad (2.47) \]

and \( \lambda \) is a perturbation parameter which will be set to unity.

Expanding (2.46) to first order,

\[ (F^{(0)} + \lambda F^{(1)})(C_j^{(0)} + \lambda C_j^{(1)}) = S(C_j^{(0)} + \lambda C_j^{(1)}) (\varepsilon_j^{(0)} + \lambda \varepsilon_j^{(1)}) \quad (2.48) \]

Collecting terms in zero order,

\[ F^{(0)} C_j^{(0)} = S C_j^{(0)} \varepsilon_j^{(0)} \quad (j \text{ occupying and virtual}) \]

are the Hartree-Fock equations for the unperturbed molecule, which by assumption are solved.

In first order, considering only the occupied orbitals,

\[ F^{(1)} C_j^{(0)} + F^{(0)} C_j^{(1)} = S C_j^{(0)} \varepsilon_j^{(1)} + S C_j^{(1)} \varepsilon_j^{(0)} \quad (j \text{ occupied}) \quad (2.49) \]

Pre-multiplying by \( C_1^{(0)*} \) (1 virtual)

\[ C_1^{(0)*} F^{(1)} C_j^{(0)} + C_1^{(0)*} F^{(0)} C_j^{(1)} = \varepsilon_j^{(1)} C_1^{(0)*} C_j^{(0)} + \varepsilon_j^{(0)} C_1^{(0)*} C_j^{(1)} \quad (2.50) \]

And writing \( C_j^{(1)} = \sum_{k=1}^{m} a_k C_k^{(0)} \quad (2.51) \)

Equation (2.50) becomes

\[ C_1^{(0)*} F^{(1)} C_j^{(0)} + \sum_{k=1}^{m} a_k C_1^{(0)*} F^{(0)} C_k^{(0)} = \varepsilon_j^{(1)} C_1^{(0)*} C_j^{(0)} + \varepsilon_j^{(0)} \sum_{k=1}^{m} a_k C_1^{(0)*} C_k^{(0)} \quad (2.52) \]

From the orthonormality property of the molecular orbitals

\[ C_1^{(0)*} S C_j^{(0)} = \delta_{ij} \quad (2.53) \]
and since the canonical molecular orbitals diagonalise the Hartree-Fock matrix

$$C_i^{(0)*} F^{(0)} C_j^{(0)} = \delta_{ij} \epsilon_i^{(0)}$$ (2.54)

then Equation (2.52) reduces to

$$C_i^{(0)*} F^{(1)} C_j^{(0)} + a_1 \epsilon_i^{(0)} = a_1 \epsilon_j^{(0)}$$ (2.55)

Therefore

$$a_1 = \frac{C_j^{(0)*} F^{(1)} C_j^{(0)}}{\epsilon_j^{(0)} - \epsilon_i^{(0)}}$$ (1 virtual) (2.56)

And so

$$C_j^{(1)} = \sum_k^{\text{virtual}} \frac{C_k^{(0)*} F^{(1)} C_j^{(0)}}{\epsilon_j^{(0)} - \epsilon_i^{(0)}} C_k^{(0)}$$ (2.57)

where only the virtual manifold contributes to the summation over $k$. Terms arising from the occupied manifold correspond to mixing of the occupied orbitals amongst themselves, a process to which the wavefunction is invariant [55]. It should be noted that the derivation of (2.57) assumes that the canonical Hartree-Fock eigenvectors and eigenvalues are used.

Furthermore, since the perturbed molecular orbitals $\psi_1$ must remain orthonormal

$$C_i^\dagger S C_j = \delta_{ij} \quad (i,j \text{ occupied})$$ (2.58)

That is,

$$(C_i^{(0)} + \lambda C_i^{(1)*})^\dagger S (C_j^{(0)} + \lambda C_j^{(1)*}) = \delta_{ij}$$ (2.59)

Therefore, using Equation (2.53)

$$C_i^{(1)*} S C_j^{(0)} + C_i^{(0)*} S C_j^{(1)} = 0$$ (2.60)

to first order. That is to say, the change $C_j^{(1)}$ must be orthogonal to all the $C_j^{(0)}$, so that the perturbation to every occupied MO is confined to the
virtual orbital subspace, which is orthogonal to that spanned by the occupied MOs [52].

In Equation (2.57), \( F^{(1)} \) is composed of two separate contributions,

\[
F_{ij}^{(1)} = G_{ij}^{(1)} + H_{Aij}^{'}
\]

(2.61)

where \( H_{A}^{'} \) is the one-electron perturbation operator under consideration at nucleus A and \( G_{ij}^{(1)} \) is the matrix for the corresponding first order response of the Hartree-Fock field determined by the perturbed electron distribution [52]. Thus \( F^{(1)} \) depends upon the \( G_{ij}^{(1)} \) and therefore (2.57) must be solved iteratively until the first order wavefunction becomes self-consistent. The iterative procedure is conveniently initiated by setting \( G_{ij}^{(1)} = 0 \) [69].

The one-electron perturbation operators \( H_{A}^{'} \) are conveniently classed either as spin-independent (the electron-orbital operator) or as spin-linear (the Fermi contact and spin-dipolar operators). In self-consistent perturbation theory, when the operator is of the former type the perturbed wavefunction is written in a restricted Hartree-Fock (RHF) form, since it can be expressed to first order as a sum of the unperturbed RHF wavefunction and all singly excited singlets [75]. However, when the perturbation operator is of the latter type, the unperturbed ground state singlet wavefunction is mixed with singly excited triplets, which can be accomplished by writing the perturbed wavefunction in an unrestricted Hartree-Fock (UHF) form [140].

The particular formulations employed to evaluate \( E_{AB}^{(2)} \) for the Fermi contact, electron orbital and spin-dipolar coupling mechanisms will be described separately. For molecules in solution, the Fermi contact-spin dipolar cross-term averages to zero through isotropic molecular tumbling, and the Fermi contact-orbital cross-term can be neglected if spin-orbit coupling is small [65]. The contribution from the orbital perturbation
which is bilinear in \( \mu_A \) and \( \mu_B \) \((H_A^{(1a)})\) has also been omitted because the corresponding value of \( E_{AB}^{(2)} \) has been shown to depend only on the unperturbed wavefunction, and is expected to always be very small [65].

A. The Fermi contact term

In the representation of Abragam & Pryce [9] the perturbation operator for the Fermi contact interaction of all the electrons \( k \) in contact with nucleus \( A \) is

\[
\mu_A H_A' = \frac{8}{3} \pi g_e \beta_e \sum_k \delta(r_{KA}) S_{kz} \mu_A
\]  

(2.62)

where \( g_e \) is the electronic \( g \)-value, \( \beta_e \) is the Bohr magneton, \( (r_{KA}) \) is the three-dimensional Dirac delta function and \( S_{kz} \) is the \( z \) component of the spin angular momentum operator for electron \( k \). This operator causes electron spin polarisation in the wavefunction due to the property

\[
S_z \left( \frac{\alpha}{\beta} \right) = \frac{1}{2} \left( \begin{array}{c} \alpha \\ -\beta \end{array} \right)
\]

(2.63)

and therefore the perturbed wavefunction is cast in the unrestricted Hartree-Fock (UHF) form [76]

\[
\Psi(\mu_A, 0) = (2n!)^{-\frac{1}{2}} \det | \psi_1(1) \alpha(1) \ldots \psi_n(n) \alpha(n) \phi_1(n+1) \beta(n+1) \ldots \phi_n(2n) \beta(2n)|
\]

(2.64)

where the spatial parts of the \( \alpha \)- and \( \beta \)-spin molecular orbitals, \( \psi_i \) and \( \phi_i \) respectively, may differ from each other.

Then using Slater's rules for the matrix elements of a one-electron operator, the expression for \( E_{AB}^{(2)} \) (2.44) becomes

\[
E_{AB}^{(2)} = \left( \frac{\partial}{\partial \mu_A} \right) \left[ \sum_{i=1}^n \langle \psi_i | H_B | \psi_i \rangle - \langle \phi_i | H_B | \phi_i \rangle \right] \quad \mu_A = 0
\]

(2.65)
where $H_B^\prime$ is the one-electron version of $\mu_B H_B^\prime$ after differentiation with respect to $\mu_B$ and with the electron spin operation (2.63) complete

$$H_B^\prime = (4/3) \pi g_e \beta_e \delta(r_B)$$  \hfill (2.66)

In the LCAO-MO approximation

$$\psi_j = \Sigma C_{ij}^a \omega_j \quad \text{and} \quad \phi_j = \Sigma C_{ij}^\beta \omega_j$$  \hfill (2.67)

Defining the $\alpha$- and $\beta$- electron density matrices as

$$p_{1ij}^\alpha = \sum_{k=1}^n C_{ik}^a C_{jk}^a \quad \text{and} \quad p_{1ij}^\beta = \sum_{i=1}^n C_{ik}^\beta C_{jk}^\beta$$  \hfill (2.68)

(2.65) becomes

$$E_{AB}^{(2)} = \left( \frac{\partial}{\partial \mu_A} \right) \left[ \sum_i \sum_j (p_{1ij}^\alpha - p_{1ij}^\beta) H_{B1j}^\prime \right] \mu_A = 0$$  \hfill (2.69)

where

$$H_{B1j}^\prime = <\omega_i | H_B^\prime | \omega_j>$$  \hfill (2.70)

is independent of $\mu_A$.

The spin density matrix $p = p^\alpha - p^\beta$ enables (2.69) to be rewritten

$$E_{AB}^{(2)} = \sum_i \sum_j \left[ \left( \frac{\partial p_{1ij}}{\partial \mu_A} \right) \mu_A = 0 \right] H_{B1j}^\prime$$  \hfill (2.72)

Expanding $p^\alpha$ to first order (2.68)

$$p_{1ij}^\alpha = \sum_{k=1}^n \left( C_{ik}^{\alpha(0)} + C_{ik}^{\alpha(1)} \right) \left( C_{jk}^{\alpha(0)} + C_{jk}^{\alpha(1)} \right)$$

whence

$$p_{1ij}^{(1)\alpha} = \sum_{k=1}^n \left( C_{ik}^{\alpha(0)} C_{jk}^{\alpha(1)} + C_{ik}^{\alpha(1)} C_{jk}^{\alpha(0)} \right)$$  \hfill (2.73)

and similarly for $p^\beta$. 

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Since \[ p_{ij}^\alpha(1) = \left( \frac{\partial p_{ij}}{\partial \mu_A} \right)_{\mu_A=0}, \] (2.74)

However, since \( \mathcal{H}_A \) contains \( S_z \) which acts anti-symmetrically on \( \alpha \)- and \( \beta \)-spin electrons (2.63), it is clear that

\[ p_{ij}^\alpha(1) = -p_{ij}^\beta(1) \] (2.75)

and therefore

\[ \left( \frac{\partial p_{ij}}{\partial \mu_A} \right)_{\mu_A=0} = 2p_{ij}^\alpha(1) \] (2.76)

Finally, (2.72) becomes

\[ E_{AB}^{(2)} = 2 \sum_i \sum_j p_{ij}^\alpha(1) H_{bij} \] (2.77)

so that it is necessary only to perform the iterative solution of (2.57) for the \( \alpha \)-spin electrons. The electron-repulsion correction to the \( F_{ij}^{(1)\alpha} \) matrix is

\[ G_{ij}^{\alpha(1)} = \sum_k^m \sum_l^m \left\{ (p_{kl}^{\alpha(1)} + p_{kl}^{\beta(1)}) <ik|j1> - p_{kl}^{\alpha(1)} <ik|lj> \right\} \]
\[ = -\sum_k^m p_{kl}^{\alpha(1)} <ik|lj> \] (2.78)

Therefore Equations (2.57), (2.73), (2.77), (2.78) and (2.61) form the basis of the iterative cycle to calculate \( E_{AB}^{(2)} \).
B The Orbital Term

The Hamiltonian operator for the interaction of a nuclear moment at A in the z direction and the orbital motion of the electrons k is

\[ \mu_A \mathcal{H}_A' = \frac{(2\beta e/h)}{\sum_k \left( L_{kZ}/r_{kA} \right)^3} \mu_A \]  \hspace{1cm} (2.79)

where \( L_{kZ} \) is the operator for the z component of the orbital angular momentum of electron k about nucleus A, which is imaginary (4.3), and thus causes the wavefunction to become complex. Since the operator is not spin-dependent the perturbed wavefunction is written in the restricted form

\[ \psi(\mu_A, 0) = (2\pi!)^{-\frac{1}{4}} \det |\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots\psi_n(2n-1)\alpha(2n-1)\psi_n(2n)\beta(2n)| \]  \hspace{1cm} (2.80)

Using Slater's rules, making the LCAO-MO approximation and defining

\[ P_{ij} = 2 \sum_{k=1}^{n} C_{ik}^* C_{jk} \]  \hspace{1cm} (2.81)

\[ = 2 \sum_{k=1}^{n} \left( C_{ik}^{(0)} - i C_{ik}^{(1)} \right) \left( C_{jk}^{(0)} + i C_{jk}^{(1)} \right) \]

whence

\[ \left( \frac{\partial^2 P_{ij}}{\partial \mu_A^2} \right) = P_{ij}^{(1)} = 2 i \sum_{k=1}^{n} \left( C_{ik}^{(0)} C_{jk}^{(1)} - C_{ik}^{(1)} C_{jk}^{(0)} \right), \]  \hspace{1cm} (2.82)

\[ \mu_A = 0 \]

Then

\[ E_{AB}^{(2)} = \sum_i \sum_j P_{ij}^{(1)} H_{Bij} \]  \hspace{1cm} (2.83)

where

\[ H_{Bij} = < \omega_i | H_B | \omega_j > \]  \hspace{1cm} (2.84)
and \[ H_B = (2\beta_e/\hbar) L_B r_B^3 \] (2.85)

The first order change in the electron interaction matrix is

\[ G^{(1)}_{ij} = \sum_k \sum_l \gamma_{k1}^{(1)} [\langle ik|jl\rangle - i \langle ik|lj\rangle] \]

\[ = -i \sum_k \gamma_{k1}^{(1)} \langle ik|lj\rangle \] (2.86)

since \( \gamma_{k1}^{(1)} = -\gamma_{1k}^{(1)} \) from (2.82) (2.87)

and \( \langle ik|jl\rangle = \langle ii|jk\rangle \) from (2.33)

The iterative solution is then based on (2.57), (2.82), (2.83), (2.86) and (2.61). The calculation must be repeated with the nuclear moment in the x and y directions, and the results of all three calculations are averaged.

C The Spin-Dipolar Term

The Hamiltonian operator for the spin-dipolar interaction of the nuclear moment of atom A lying in the z direction with the electrons k is

\[ \mu_A H_A' = g_\beta e [3x_{kA} z_{kA} S_{kx} + 3y_{kA} z_{kA} S_{ky} + (z_{kA}^2 - r_{kA}^2)S_{kz} - r_{kA}^5 \mu_A] \] (2.88)

As a result of the properties of the spin operators

\[ S_x^{(\alpha/\beta)} = i \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \] (2.89)

\[ S_y^{(\alpha/\beta)} = i \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \] (2.90)

\[ S_z^{(\alpha/\beta)} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \] (2.63)
the spin-dipolar operator causes spin-polarisation, and real and imaginary mixing of \( \alpha \)- and \( \beta \)-spin into a single molecular orbital. This behaviour invalidates the use of molecular spin orbitals, and it is convenient to use an unrestricted Hartree-Fock formulation extended in such a way that the molecular orbitals are expanded as linear combinations of \( 2m \) spin atomic orbitals \( \{ \omega_1^\alpha ; \omega_1^\beta \} \), which in effect doubles the basis set size. Fortunately the problem is separable into several separate calculations with the original basis size \( m \).

The perturbed UHF equations now become [64]

\[
\begin{bmatrix}
F^\alpha \alpha & F^\alpha \beta \\
F^\beta \alpha & F^\beta \beta
\end{bmatrix}
\begin{bmatrix}
C^\alpha_j \\
C^\beta_j
\end{bmatrix}
= S \varepsilon_j
\begin{bmatrix}
C^\alpha_j \\
C^\beta_j
\end{bmatrix}
\]  

(2.91)

where \( C^\alpha_j \) is the vector of coefficients of \( \{ \omega_1^\alpha \} \) for the \( j \)th MO, and similarly for \( C^\beta_j \).

Rewriting Equations (2.91) in the matrix form

\[
\begin{bmatrix}
F^\alpha \alpha & F^\alpha \beta \\
F^\beta \alpha & F^\beta \beta
\end{bmatrix}
\begin{bmatrix}
C^\alpha_j \\
C^\beta_j
\end{bmatrix}
= S
\begin{bmatrix}
C^\alpha \alpha & C^\alpha \beta \\
C^\beta \alpha & C^\beta \beta
\end{bmatrix}
\begin{bmatrix}
\varepsilon^\alpha & 0 \\
0 & \varepsilon^\beta
\end{bmatrix}
\]  

(2.92)

where \( C^\beta_j \) is the coefficient vector of \( \beta \)-spin contributions induced into the \( j \)th \( \alpha \)-spin MO by the perturbation (2.88), permits a factoring of the perturbation equations into four equations involving only the \( (m \times m) \) submatrices. Therefore multiplying (2.92) out for \( C^\alpha \) and \( C^\beta \)

\[
F^\alpha \alpha C^\alpha_j + F^\alpha \beta C^\beta_j = S C^\alpha_j \varepsilon^\alpha
\]  

(2.93)

and

\[
F^\beta \alpha C^\alpha_j + F^\beta \beta C^\beta_j = S C^\beta_j \varepsilon^\alpha
\]  

(2.94)
Expanding each quantity to first order, collecting the orders and remembering that

\[ C^\alpha(0) = C^\beta(0) = 0 \]  \hspace{1cm} (2.95)

\[ F^\alpha(0) = F^\beta(0) = 0 \]  \hspace{1cm} (2.96)

leads to the equations

\[ F^\alpha(0) C^\alpha(1) + F^\alpha(1) C^\alpha(0) = S C^\alpha(0) \varepsilon^\alpha(1) + S C^\alpha(1) \varepsilon^\alpha(0) \]  \hspace{1cm} (2.97)

and

\[ F^\beta(0) C^\alpha(0) + F^\beta(0) C^\alpha(1) = S C^\beta(1) \varepsilon^\alpha(0) \]  \hspace{1cm} (2.98)

But \( F^\alpha(0) \) and \( F^\beta(0) \), \( C^\alpha(0) \) and \( \varepsilon^\alpha(0) \) are respectively just the \( F^0 \), \( C^0 \) and \( \varepsilon^0 \) matrices for the unperturbed molecule.

Therefore, in vector notation, (2.97) and (2.98) become

\[ F^0 C^\alpha(1) + F^\alpha(1) C^0 = S C^0 \varepsilon^\alpha(1) + S C^\alpha(1) \varepsilon^0 \]  \hspace{1cm} (2.99)

and

\[ F^\beta(0) C^0 + F^\beta(0) C^\alpha(1) = S C^\alpha(1) \varepsilon^0 \]  \hspace{1cm} (2.100)

Equations (2.99) and (2.100) are to be solved self-consistently for \( C^\alpha(1) \) and \( C^\beta(1) \) respectively using (2.57).

1. The Spin Polarisation contribution

\[ F^\alpha(1)_{ij} = H^\alpha_{Aij} + C^\alpha(1)_{ij} \]  \hspace{1cm} (2.101)

where \( H^\alpha_{Aij} = \langle \omega_1 | g_e \bar{e}_e (3z^2 - r_A^2) r_A^{-5} S_z | \omega_j \rangle \)  \hspace{1cm} (2.102)
Because of the spin anti-symmetry of \( S_z \) (2.63),

\[
P_{ij}^{\alpha\alpha'} = \sum_{k=1}^{n} (C_{ik}^{(0)} C_{jk}^{\alpha\alpha'} + C_{ik}^{\alpha\alpha'} C_{jk}^{(0)})
\]

\[
= -p_{ij}^{\beta\beta'}
\]

and so it is only necessary to solve for the \( \alpha \)-spin electrons.

Then

\[
E_{AB}^{(2)} = \left( \frac{2}{\beta \mu_A} \right) \left[ \sum_{i} \sum_{j} (p_{ij}^{\alpha\alpha'} - p_{ij}^{\beta\beta'}) h_{B1j}^{\alpha\alpha'} \right] \mu_A = 0
\]

\[
= 2 \sum_{i} \sum_{j} p_{ij}^{\alpha\alpha'} h_{B1j}^{\alpha\alpha'}
\]

and

\[
G_{ij}^{\alpha\alpha'} = -\sum_{k, l} p_{kl}^{\alpha\alpha'} \langle ik | lj \rangle ,
\]

\[
h_{B1j}^{\alpha\alpha'} = \langle i | g_{e\beta e} (3z_B^2 - r_B^2) r_B^5 | j \rangle .
\]

Equations (2.57), (2.103), (2.104), (2.105) and (2.101) then form the basis for the iterative solution.

2. The Spin Mixing contributions

The matrix \( F_{ij}^{\beta\alpha} \) is clearly complex due to the effect of the \( S_x \) and \( S_y \) operators which cause the spin mixing. It is convenient to consider the real and imaginary contributions separately.

(a) The real part

\[
F_{ij}^{\beta\alpha} = h_{A1j}^{\beta\alpha'} + G_{ij}^{\beta\alpha}
\]

where

\[
h_{A1j}^{\beta\alpha'} = \langle i | g_{e\beta e} 3x_A z_A r_A^5 S_x | j \rangle
\]
From the spin symmetry of the $S_x$ operator (2.89),

$$p_{ij}^{a(1)} = \sum_{k=1}^{n} \left( c_{ik}^{(0)} c_{jk}^{a(1)} + c_{ik}^{a(1)} c_{jk}^{(0)} \right)$$

$$= p_{ij}^{\beta \alpha (1)}$$

(2.108)

since $c_{j}^{a(1)} = c_{j}^{\beta \alpha (1)}$,

and so it is only necessary to solve the equations for $c_{j}^{\beta \alpha (1)}$.

Then

$$E_{AB}^{(2)} = \left( \frac{\partial}{\partial \mu_{A}} \right) \left[ \sum_{i} \sum_{j} \left( p_{ij}^{a(1)} + p_{ij}^{\beta \alpha} \right) H_{Bij}^{a(1)} \right]_{\mu_{A}=0}$$

$$= 2 \sum_{i} \sum_{j} p_{ij}^{a(1)} H_{Bij}^{a(1)}$$

(2.109)

and

$$G_{ij}^{\alpha (1)} = - \sum_{k,l} p_{kl}^{a(1)} < ik|lj > ,$$

(2.110)

$$H_{Bij}^{a(1)} = \frac{1}{2} < \omega_{i} | g_{e} e_{3x} e_{B} z_{B} r_{B}^{-5} | \omega_{j} > .$$

(b) **The imaginary part**

$$p_{ij}^{\beta \alpha (1)} = H_{Aij}^{\beta \alpha} + G_{ij}^{\beta \alpha (1)}$$

where

$$H_{Aij}^{\beta \alpha} = < \omega_{i} | g_{e} e_{3y} e_{A} z_{A} r_{A}^{-5} S_{y} | \omega_{j} > .$$

(2.111)

From the spin anti-symmetry of the $S_y$ operator (2.90),

$$p_{ij}^{a(1)} = i \sum_{k=1}^{n} \left( c_{ik}^{(0)} c_{jk}^{a(1)} + c_{ik}^{a(1)} c_{jk}^{(0)} \right)$$

(2.112)
since $C_{ij}^{\alpha\beta(1)} = -C_{ij}^{\beta\alpha(1)}$

and so again it is only necessary to solve the equations for $C_{ij}^{\beta\alpha(1)}$.

Then $E_{AB}^{(2)} = \left( \frac{\partial}{\partial \mu_A} \right) \left[ \sum_i \sum_j (P_{ij}^{\alpha\beta} - P_{ij}^{\beta\alpha}) H_{Bij}^{\beta\alpha'} \right]_{\mu_A=0}$

$$= -2 \sum_i \sum_j P_{ij}^{\alpha\beta(1)} H_{Bij}^{\beta\alpha'}$$

(2.113)

and $G_{ij}^{\alpha\beta(1)} = - \sum_{k,l} P_{kl}^{\alpha\beta(1)} < ik|lj >$  

(2.114)

$H_{Bij}^{\beta\alpha'} = i \omega \langle \gamma_e \gamma_e \gamma_B \gamma_B \rangle$  

The total spin dipolar contribution for the nuclear moment lying in the $z$ direction is obtained by summing the three contributions to $E_{AB}^{(2)}$. Finally, the calculation must be repeated with the nuclear moment in each of the $x$ and $y$ directions, and the total spin-dipolar coupling is obtained by averaging the result over the three directions.

3. The Computer Programs

The Hartree-Fock SCF Perturbation Method of Blizzard & Santry [64] and Ditchfield & Snyder [65] has been implemented at the ab initio level on the ELLIOTT 4100 computer system at the University of Leicester. The programs were written in ALGOL 60 and were designed to be compatible with the existing Gaussian integral and SCF programs.

The integrals required for the Fermi contact term (which are trivial)
and for the spin-dipolar term, were obtained from existing integral programs for the calculation of E.S.R. isotropic and anisotropic hyperfine coupling constants respectively (vide Part II). The general and special formulae for the dipolar integrals over Gaussian functions have already been obtained [77,78]. The corresponding formulae for the orbital integrals have been derived in a similar manner, and are presented fully in Section 4. A program was written to compute the required orbital integrals using the special formulae (Eqs. (4.12)). This program was checked by writing a second program to evaluate the same integrals from the general formulae (Eqs. (4.9)). The second program (albeit not completely optimized) was about an order of magnitude slower than the first program, demonstrating the usefulness of the special formulae for efficient computation. It was later possible to make a second independent check on the orbital integrals, against those generated by the ATOML 2 molecular properties integral program [79], where the orbital integrals are obtained by linearly combining electric field integrals as in Eqs. (4.4)-(4.6) [80]. The integrals in this work are believed to be accurate to 10 significant figures.

The perturbation program was written to follow the standard RHF SCF closed shell program, and consists of three independent routines, one for each coupling mechanism, based on the equations given in Section 2.3. These routines were supplied with restart facilities and were designed to be sufficiently flexible to evaluate any specified combination of coupling constants. Each iterative perturbation calculation was initiated from a Hückel-type approximation, and was terminated when the magnitudes of all coupling constants changed by less than 0.1 per cent in successive iterations. Full use was made of the symmetry properties of the matrices involved in the perturbation calculations in order to develop as efficient a program as possible. In particular, it was found that the first-order perturbation
calculation should be programmed in the form given by Eq. (2.57) and not as in Eq. (5) of [64], since the latter method is effectively an \( N^k \) algorithm and over an order of magnitude slower in a double-zeta calculation on methane, than the effectively \( N^3 \) algorithm of Eq. (2.57).

The overall structure of the suite of programs is summarised in the block diagram (Fig. 1). When completely assembled, the whole program system was tested by reproducing the only published \textit{ab initio} results using this method - the coupling constants of methyl fluoride in the 4-31 G basis [65]. Following a request from the Atlas Computer Laboratory, the perturbation program was recently modified and implemented on the Rutherford Laboratory IBM 360/195 computer as part of the ATMOL 3 program system by Drs. M. F. Guest and V. R. Saunders, assisted by the author.
FIGURE 1: COMPUTER PROGRAM ORGANISATION
4. Analytical Formulae for Orbital Integrals

Analytical expressions for integrals of the form

\[ \langle g_A | \mathcal{L}_i(C) | g_B \rangle \]  \hspace{1cm} (4.1)

are required, where \( g_A \) is a Gaussian function centered at \( A \) (with co-ordinates \( A_x, A_y, A_z \)).

\[ g_A = N A_x A_y A_z A_x A_y A_z \exp(-\alpha A r_A^2) = (A_x, A_y, A_z, \alpha A, \lambda A, \mu A, \nu A) \]

\( x_A = x - A_x \)
\( r_A^2 = x_A^2 + y_A^2 + z_A^2 \)
\( N_A \) is the normalization constant; \( \lambda A, \mu A, \nu A \) are non-negative integers.

Similarly, \( g_B = (B_x, B_y, B_z) \) for a Gaussian function centered at \( B \) (with co-ordinates \( B_x, B_y, B_z \)).

\[ \mathcal{L}_i(C) = L_i(C)/r_c^3 \]  \hspace{1cm} (4.2)

where \( L_i(C) \) is the \( i \)-component (\( i = x, y, z \)) of the orbital angular momentum operator about center \( C \) (with co-ordinates \( C_x, C_y, C_z \)).

\[ L(C) = -i \hbar \begin{vmatrix} i & j & k \\ x_C & y_C & z_C \\ \frac{\partial}{\partial x_C} & \frac{\partial}{\partial y_C} & \frac{\partial}{\partial z_C} \end{vmatrix} \]  \hspace{1cm} (4.3)

Then, for example, \( \mathcal{L}_z(C) = -i \hbar \begin{vmatrix} x_C & y_C & z_C \\ x_C & \frac{\partial}{\partial y_C} & \frac{\partial}{\partial z_C} \\ \frac{\partial}{\partial x_C} & \frac{\partial}{\partial y_C} & \frac{\partial}{\partial z_C} \end{vmatrix} \)

Since \( x_B = x_C - \overline{BC}_x \),

\[ g_B = N_B(x_C - \overline{BC}_x) y_B (y_C - \overline{BC}_y) z_B (z_C - \overline{BC}_z) \exp(-\alpha_B(x_C - \overline{BC}_x)^2) \exp(-\alpha_B(y_C - \overline{BC}_y)^2) \exp(-\alpha_B(z_C - \overline{BC}_z)^2) \]

so that \( \frac{\partial}{\partial y_B} (g_B) = m_B(B, \alpha_B, 1_B, (m_B-1), n_B) - 2\alpha_B(B, \alpha_B, 1_B, (m_B+1), n_B) \)

and similarly for \( \frac{\partial}{\partial x_B} (g_B) \).
Then \( \langle g_A \mid \mathcal{L}(C) \mid g_B \rangle = -i \hbar \left\{ n_B \langle (A, \alpha_A, l_A, m_A, n_A) \left| \frac{X_c}{r_c} \right| (B, \alpha_B, l_B, (m_B-1), n_B) \rangle - 2 \alpha_B \langle (A, \alpha_A, l_A, m_A, n_A) \left| \frac{X_c}{r_c} \right| (B, \alpha_B, l_B, (m_B+1), n_B) \rangle - l_B \langle (A, \alpha_A, l_A, m_A, n_A) \left| \frac{Y_c}{r_c} \right| (B, \alpha_B, (l_B-1), m_B, n_B) \rangle + 2 \alpha_B \langle (A, \alpha_A, l_A, m_A, n_A) \left| \frac{Y_c}{r_c} \right| (B, \alpha_B, (l_B+1), m_B, n_B) \rangle \right\} \)

(4.4)

Similarly \( \langle g_A \mid \mathcal{X}(C) \mid g_B \rangle \)

\[
= -i \hbar \left\{ n_B \mathcal{W}_x \langle (1B-1), m_B, n_B-2 \alpha_B \mathcal{W}_x (1B+1), m_B, n_B-1 \mathcal{W}_X (1B-1), m_B, n_B+2 \alpha_B \mathcal{W}_x (1B+1), m_B, n_B \rangle \right\}
\]

(4.5)

and \( \langle g_A \mid \mathcal{X}(C) \mid g_B \rangle \)

\[
= -i \hbar \left\{ n_B \mathcal{W}_y \langle 1B, m_B, (n_B-1) - 2 \alpha_B \mathcal{W}_y (1B+1), m_B, (n_B-1) - 2 \alpha_B \mathcal{W}_y (1B+1), m_B, (n_B+1) \rangle \right\}
\]

(4.6)

Thus all the integrals required in (4.1) are expressible in terms of integrals of the form

\[
\mathcal{W}_q \langle 1B, m_B, n_B \rangle = \langle (A, \alpha_A, l_A, m_A, n_A) \left| \frac{q_c}{r_c} \right| (B, \alpha_B, l_B, m_B, n_B) \rangle, \quad q = x, y, z \quad (4.7)
\]

The method used to obtain analytical expressions for these integrals [77,78] follows closely the procedure employed by Claxton and Smith for anisotropic integrals, and relies upon the general Laplace Transform [81,82]

\[
r^{-\lambda} = \left\{ \Gamma(\lambda/2) \right\}^{-1} \int_0^\infty \lambda^{1/2-1} \exp(-sr^2)ds, \quad \lambda > 0 \text{ and integral.}
\]

Thus \( \frac{1}{r^3} = \left\{ \Gamma(3/2) \right\}^{-1} \int_0^\infty s^{1/2} \exp(-sr^2)ds \)

\[
= 4(\pi)^{-1/2} \int_0^\infty u^2 \exp(-r^2u^2)du \\
= 4(\pi)^{-1/2} \int_{1-v^2}^1 \frac{v^2}{1-v^2} \exp\left(\frac{r^2y^2}{1-v^2}\right)(1-v^2)^{-3/2}dv 
\]

(4.8)
Then, after straightforward although tedious manipulation, the integrals in (4.7) may be written as

\[
W_x^{1_B, m_B, n_B} = \Delta \left[ ZV_1^{i_1} - CP_x V_1^{i_1} \right]
\]

\[
W_y^{1_B, m_B, n_B} = \Delta \left[ ZV_1^{i_1} - CP_y V_1^{i_1} \right]
\]

\[
W_z^{1_B, m_B, n_B} = \Delta \left[ ZV_1^{i_1} - CP_z V_1^{i_1} \right]
\]  

(4.9)

where \( \Delta = N_B N_B 4\pi \exp \left( -\frac{\alpha_{AB}}{\alpha_A + \alpha_B} \overline{AB}^2 \right) \)

and \( \overline{AB}^2 = (A_x - B_x)^2 + (A_y - B_y)^2 + (A_z - B_z)^2 \)

Also \( CP_x = -PC_x = Cx - Px \) where \( Px = \frac{\alpha_A Ax + \alpha_B Bx}{\alpha_A + \alpha_B} \)

In Eqs. (4.9)

\[
V_{t_1 t_2 t_3}^{s_1 s_3} = \sum_{i_1 = s_1}^{(1_A + 1_B)} \sum_{i_2 = s_2}^{(i_1 - s_1)/2} \sum_{i_3 = s_3}^{(i_2 - s_2)/2} R_{i_1 i_2 i_3}^{s_1 s_2 s_3} (1_A, 1_B, Ax, Bx, Cx, \gamma)
\]

\[
X \sum_{i_1 = s_1}^{(1_A + 1_B)} \sum_{i_2 = s_2}^{(i_1 - s_1)/2} \sum_{i_3 = s_3}^{(i_2 - s_2)/2} R_{i_1 i_2 i_3}^{s_1 s_2 s_3} (m_A, m_B, A_y, B_y, C_y, \gamma)
\]

\[
X \sum_{i_1 = s_1}^{(1_A + 1_B)} \sum_{i_2 = s_2}^{(i_1 - s_1)/2} \sum_{i_3 = s_3}^{(i_2 - s_2)/2} R_{i_1 i_2 i_3}^{s_1 s_2 s_3} \left( n_A, n_B, Az, Bz, Cz, \gamma \right)
\]

\[
X \sum_{u=0}^{r-t+s} \left( \frac{r-t+s}{u} \right) (-1)^u Fv(\overline{CP}^2)
\]

where

\[
r = r_1 + r_2 + r_3, \quad i = i_1 + i_2 + i_3, \quad s = s_1 + s_2 + s_3
\]

\[
t = t_1 + t_2 + t_3, \quad v = i - 2r + u + 1 - s
\]

and

\[
Fv(g) = \int_0^1 u^{2v} \exp (-gu^2) du
\]

is a form of the Incomplete Gamma Function.
The general expression for the $R$'s in Eq. (4.10) is

$$
R_{i r}^S = f_i(k_A, k_B, A_q, B_q, C_q, \gamma) = f_i(k_A, k_B, \bar{A}_q, \bar{B}_q) \times \frac{i!CP_q i-2r-s r+t (2r+1)t-s}{r! (i-2r-s)!}
$$

where $\gamma = \alpha_A + \alpha_B$

$$\varepsilon = 1/(4\gamma)$$

and

$$f_j(l, m, a, b) = \sum_{i=\max(0, j-m)}^{i=\min(j, l)} \binom{1}{i} \binom{m}{j-i} a^{l-i} b^{m-i-j}$$

is an auxiliary function.

The formulae are general for any Gaussian type orbitals $g_A$ and $g_B$. However, in the application of the integrals to molecular calculations, it is computationally convenient to have special formulae for the $s$- and $p$-type Gaussian functions. Using the terminology of Clementi and Davis [83]
\[ \langle \pi_A | \mathcal{L}_y(C) | \pi_B \rangle = \mathcal{T} \left[ S_{0y}L_{yj} - S_{0z}L_{yj} + S_{xj}L_{zi} - S_{zj}L_{xi} + S_{xi}L_{zi} - S_{zi}L_{xi} + S_{xj}L_{yi} - S_{yj}L_{xi} \right] \\
\langle \pi_A | \mathcal{L}_z(C) | \pi_B \rangle = \mathcal{T} \left[ S_{0y}L_{yj} - S_{0x}L_{yj} + S_{yj}L_{zi} - S_{xj}L_{zi} + S_{yj}L_{xi} - S_{xi}L_{zi} + S_{yj}L_{yi} - S_{xj}L_{yi} \right] \\
\]

where

\[ S^{\infty} = \frac{NAB[\pi/(\alpha A + \alpha B)]^2}{\sqrt{\alpha A + \alpha B}} \exp \left( -\frac{\alpha A \alpha B}{\alpha A + \alpha B} AB \right) \]

\[ S^{-i} = [\alpha A/(\alpha A + \alpha B)](A_i - B_i)S^{\infty} \]

\[ = (-\alpha A/\alpha B)S^{i0} \]

\[ S^{ij} = [2\epsilon_{ij} - (A_i - B_i)(A_j - B_j)\alpha A \alpha B/(\alpha A + \alpha B)^2]S^{\infty} \]

\[ = (-\alpha A/\alpha B)S^{ij} \]

\[ S^{ijk} = [2\epsilon_{iak}/S_i(\delta_{ij}A_k + \delta_{ik}A_j + \delta_{jk}A_i) - A_k A_j A_i A_k \alpha^2 \alpha B / S_i^3]S^{\infty} \]

\[ \text{Lo} = \text{Li}^0 = \overline{CP}_i F_1(t) \]

\[ \text{Li}^j = \overline{CP}_i \overline{CP}_j F_2(t) - 2\epsilon F_1(t) \delta_{ij} \]

\[ \text{L}_{ijk} = \overline{CP}_i \overline{CP}_j \overline{CP}_k F_3(t) - 2\epsilon F_3(t) \left[ \delta_{ij} \overline{CP}_k + \delta_{jk} \overline{CP}_i + \delta_{ik} \overline{CP}_j \right] \]

\[ \epsilon = \left[ 4(\alpha A + \alpha B) \right]^{-1} \]

\[ \overline{CP}_i = C_i - P_i \]

\[ \overline{AB}_i = A_i - B_i \]

\[ P_i = (\alpha A A_i + \alpha B B_i)/(\alpha A + \alpha B) \quad (i,j,k = x,y \text{ or } z) \]

\[ \mathcal{T} = -ih\beta (S_i^3/\pi)^{1/2} \]

\[ t = S_i\beta^2 \]

\[ S_i = \alpha A + \alpha B \]

Kern and Karplus [82] have used the Laplace Transform method for obtaining molecular property integrals over Gaussian-type functions, and they give a special formula for \( \langle s_A | \mathcal{L}_x(C) | s_B \rangle \) which is equivalent to the one presented here.

Matsuoka [84, 85] has recently derived general formulae for various
integrals of molecular properties and relativistic interactions over Gaussian-type functions, using the Fourier Transform method [86]. The general expression obtained for the field integral [84] is equivalent to the one given here, and a corresponding formula for the $\langle g_A | \mathcal{L}_x(C) | g_B \rangle$ integral has subsequently been derived [85], for use in calculations of the electron spin-same orbit interaction.
5. Results of the N.M.R. Calculations

5.1 Introduction

The theoretical equivalence of the Self-Consistent Field Perturbation Method (SCFPM) and the Coupled Hartree-Fock Perturbation Method (CHFPM) has already been mentioned in Section 2. However, in order to reduce the computational labour involved in the calculation of atomic and molecular properties, the CHFPM has been approximated by various uncoupled Hartree-Fock perturbation methods (UCHFPM) [87-89,49,50]. The first and conceptually the most straightforward uncoupling scheme was that proposed by Dalgarno [87], in which all the electron repulsion integrals in the perturbation calculation are neglected. While the Dalgarno uncoupled Hartree-Fock Perturbation Method (DUCHFPM) is by no means the best uncoupling scheme available, being a "Hückel type" perturbation calculation [50], it is of considerable interest to be able to compare the results of the coupled (SCFPM) and Dalgarno uncoupled calculations for nuclear spin-coupling. Therefore the DUCHFPM results, which are conveniently obtained by interrupting the SCF perturbation calculation after the first iteration, have also been included in the Tables.

Initially, calculations were performed on the hydrogen molecule. Subsequently the calculations were extended to a series of small polyatomic molecules, using two forms of optimized minimal basis set. As a result of these calculations, the basis sets for methane, ammonia and water were extended to optimized double-zeta quality and the calculations were repeated at this level. Finally, extended basis set calculations were performed on CH₄, NH₃, H₂O and HF.
5.2 The Hydrogen Molecule

The hydrogen molecule was taken as the starting point for this study of nuclear spin-spin coupling constants using the SCF Perturbation Method [64,65]. It has been shown that the orbital and dipolar interactions together contribute significantly less than 10 per cent to the total coupling in $H_2$ [7], and therefore calculations on $H_2$ which include only the Fermi-contact interaction should not be greatly in error on this account. However, it has been a feature of many of the \textit{ab initio} calculations of the coupling constant in $H_2$ (or HD) [21-44], that the results have not always been in good agreement with the experimental value [90]. In this connection, the importance of a correlated zero order wavefunction and the near-completeness of both the atomic basis set and the basis of excited configurations describing the first order wavefunction has recently been stressed [30,31].

It seems clear therefore that any agreement with experiment from calculations on $H_2$ which employ some form of Hartree-Fock perturbation theory in conjunction with fairly small basis sets, is likely to be fortuitous. This conclusion is borne out by the results for $H_2$, in a variety of minimal and extended basis sets, using the Finite Perturbation Method [41-43], the Coupled Hartree-Fock Perturbation Method [44], the MD Sum over States method [30,41,44] and a Hartree-Fock Variation Perturbation scheme [44]. In general it is found that the negative contribution from each $^3\Sigma_u^+$ state almost cancels the positive contribution from the corresponding $^3\Sigma_g^+$ state, due to the molecular symmetry [30,44]. There is no sign of convergence in the perturbation expansion [30]. Nor do the results converge as the atomic basis set is extended [31,44].

Bearing in mind the similarity of the SCF Perturbation Method to the FPM and the CHFPM, the results for the coupling in $H_2$ obtained in this study with the SCFPM are expected to be comparable with those from the other
Hartree-Fock perturbation methods. The results of the calculations performed on the hydrogen molecule are presented in Table I, together with details of the bond lengths and basis sets used and the total energies obtained. The calculations were restricted to evaluate only the Fermi contact interaction. The SCFPM minimal basis set results resemble closely the corresponding values from the other Hartree-Fock methods [41,42,44], which are too large. In this basis, there is only one virtual MO in which to expand the first order correction to the wavefunction. As the basis set is extended, the coupling constant falls (Table I), and with still larger basis sets it drops well below the experimental value [31].

The DUCHFPM results in Table I are actually rather close to the experimental value, but the fact that they are about one third of the magnitude of the SCFPM results highlights the effect of neglecting the self-consistency condition for the perturbed Hartree-Fock operator. The waywardness of the results for H₂ precludes a reliable assessment of the importance of vibrational corrections to the coupling constant from Table I. However, other studies [31,32,38] have indicated that this effect is not very significant in H₂.

5.3 Some Polyatomic Molecules

As a step towards assessing the usefulness of the SCF Perturbation Method [64,65], it was of considerable interest to discover whether this method could reliably reproduce a range of experimentally known NMR coupling constants in small polyatomic molecules, using basis sets of similar quality to the minimal sets of SCF atomic orbitals which have been employed rather successfully in conjunction with the UHF method to calculate ESR coupling constants (vide Part II and references therein).
Some justification for expecting the SCFFM to be rather more reliable for calculating NMR coupling constants in polyatomic molecules generally than in the case of \( \text{H}_2 \), is provided by the double perturbation calculations of Barbier et alia [91], where optimized minimal basis sets of STO's were used with Boys-localised MO's, and electronic correlation was included to second order. For spin-dependent perturbations this method retains the same contributions to the coupling constants as are contained in the CHFFM [91], and the results obtained for the geminal H-H couplings in \( \text{CH}_4 \), \( \text{NH}_3 \), \( \text{H}_2\text{O} \), \( \text{C}_2\text{H}_6 \), \( \text{C}_6\text{H}_6 \) and \( \text{H}_2\text{CO} \) were quite satisfactory. However, the results for some polyatomic molecules in minimal STO basis sets using the FPM were rather disappointing [42], displaying in general correct signs but overestimated magnitudes for both directly bonded X-H couplings (X=C, N) and geminal H-H couplings. The major exception was the HF molecule where a large negative Fermi contact coupling was calculated [42], similar to the result found with the MO SOS method in a minimal basis set [92]. However, the experimental value is +530 Hz [93], and several extended basis set MO SOS calculations have indeed yielded large positive values [92,94,95] but the variation of the sign and magnitude of the coupling with basis set is highly erratic, due principally to the complete lack of convergence of the perturbation expansion [95].

The ten-electron series of molecules \( \text{BH}_4^- \), \( \text{CH}_4 \), \( \text{NH}_4^+ \), \( \text{NH}_3 \), \( \text{H}_2\text{O} \) and HF, together with \( \text{CH}_3\text{F} \) and \( \text{H}_2\text{CO} \) were selected for the present study, and calculations for the Fermi-contact, electron orbital and spin-dipolar contributions to each coupling constant were performed using optimized minimal basis sets of both (9s,5p/6s) SCF atomic orbitals [96] and Slater-type orbitals in the STO-6 G expansion [97]. Details of the molecular geometries and atomic orbital exponents employed in the calculations are given in Table II, together with the resulting total energies. The results
of the SCFPM calculations using each basis set are presented in Tables III and IV, while the Dalgarno-uncoupled results are collected in Tables V and VI. Throughout this study, the coupling constants refer to the nuclear isotopes $^1\text{H}$, $^{11}\text{B}$, $^{13}\text{C}$, $^{14}\text{N}$, $^{17}\text{O}$ and $^{19}\text{F}$.

Tables III and IV show that the results of the minimal basis set SCFPM calculations including the Fermi-contact, orbital and dipolar contributions, are not in significantly better agreement with experiment than the FPM results for the same molecules where only the Fermi-contact interaction was evaluated [42]. Except for the C-F, H-F and C-O couplings, the orbital and dipolar contributions are small. Like the FPM, the SCFPM generally overestimates the magnitudes of the directly bonded X-H and X-Y couplings and the geminal H-H couplings. The SCFPM results for CH$_4$ and NH$_3$ in the STO-6 G basis (Table IV) are similar to the results of the corresponding FPM calculations [43], and the large negative value for the contact contribution in HF is also comparable with the FPM value [42] after allowing for the increase in magnitude of coupling constants generally found on going from the STO-6 G to a pure STO basis [43]. A MO SOS calculation on CH$_4$ using the same minimal STO basis set as in Table IV yielded coupling constants in better agreement with experiment [98], but truncated SOS results for simple molecules have generally been rather erratic [92,94, 95,98-101,48].

A comparison of Tables III and IV shows that whilst the results for each molecule in both minimal basis sets are broadly similar, a particularly critical situation develops as fewer virtual MO's become available for expanding the first order wavefunction. In the series CH$_4$, NH$_3$, H$_2$O, HF, the difference between the SCFPAO and STO-6 G results increases dramatically as the number of VMOs decreases from four to one, due principally to the highly erratic behaviour of the contact contribution to the X-H couplings.
In the case of the $\pi$-system $H_2CO$, the two electron-spin dependent terms, which are calculated in an unrestricted Hartree-Fock (UHF) formalism, are found to diverge. This is in apparent contrast with the FPM, for which values for the contact contributions to all the coupling constants in $H_2CO$ have been reported [42]. However, a similar FPM calculation on $H_2CO$, performed at the Atlas Computer Laboratory, diverged in the same fashion as the present SCFPM calculations [80]. A possible explanation of the divergence phenomenon has been given by Pople et alia [42], who suggested that contact (and spin-dipolar) perturbations may cause a closed-shell wavefunction to slip into a highly spin-polarised unrestricted state, in which the anomalously high spin densities are essentially independent of the magnitude of the perturbation. Furthermore, Barbier et alia [91] have pointed out that in the case of $\pi$ molecules, potentially important contributions to the coupling constants, involving the low-lying $\pi\rightarrow\pi^*$ triplet state, may occur.

Tables V and VI show that the Dalgarno uncoupled results for the same group of polyatomic molecules are generally smaller in magnitude than the SCFPM values, and that the geminal H-H couplings are invariably positive, in complete contrast to the self consistent results. A similar effect was reported in the case of $CH_3F$ [75].

In addition, it was conjectured that vibrational effects might significantly modify the values obtained for the coupling constants at the equilibrium nuclear configurations. To obtain some estimate of the importance of these effects, the symmetric stretching mode of methane was studied by varying the C-H bond length about the equilibrium value, using the SCFAO minimal basis set and re-optimizing the hydrogen s-orbital exponent at each bond length. The SCFPM and DUHFPM results of these calculations, which include the Fermi contact, electron orbital and spin-dipolar inter-
actions, are set out in Tables VII and VIII respectively. The results for both types of calculation indicate that the variation of the coupling constants in methane with bond length is relatively small and is not likely to modify the values calculated at the equilibrium geometry very considerably. Although no other ab initio calculations of the geometric dependence of the coupling constants in CH$_4$ exist for comparison, the recent calculations on NH$_3$ [14,102] and on HF [94] have demonstrated that the geometric dependence of NMR coupling constants can sometimes be very strong, although the effect of this on the vibrationally averaged coupling constants may not always be very great [102].

The main conclusion to be drawn from the minimal basis set calculations is that minimal basis sets are not adequate for calculating NMR coupling constants by the SCFPM, where the first order wavefunction is expanded in the available virtual molecular orbitals. While the 'chemical' nature of the minimal basis set has been stressed in relation to NMR calculations [48], the need not only to improve the Hartree-Fock description of the unperturbed molecule, but also to increase the set of virtual molecular orbitals in which to expand the first order wavefunction, strongly suggests that the basis set should be extended. This conclusion is reinforced by the observation that the coupling constants calculated for CH$_3$F by Ditchfield & Snyder using the SCFPM with the slightly extended 4-31 G basis set [65] are substantially closer to the experimental values than those reported here with either of the minimal basis sets. Similar conclusions were reached recently by Kern et alia, concerning the calculation of NMR shielding constants and magnetic susceptibilities in small molecules using the CHFPM [103], and also by Arrighini, Maestro & Moccia [70] using the SCFPM.
5.4 Extended Basis Set Calculations

Since the computer time required for conventional LCAO MO SCF calculations is roughly proportional to \( N^4 \), where \( N \) is the number of primitive basis functions in the calculation, it is clear that an extension of the basis set for polyatomic molecules involves a large increase in the computer time required for each calculation. Bearing in mind the rather limited speed of the ELLIOTT 4100 computer, it was decided to extend the basis sets to optimized double zeta quality, and to restrict the calculations to the water, ammonia and methane molecules, where the orbital and spin-dipolar coupling mechanisms are not expected to be important [14]. In this way it was hoped to gain some indication of the usefulness of the SCFPM for calculating NMR coupling constants in simple molecules.

The optimized double zeta exponents for the heavy atoms (C, N and O) were obtained from Clementi [104] and those for the hydrogens optimized in each of the molecules from Guidotti & Salvetti [105]. The Slater-type orbitals were each represented by an STO-6 G expansion [106], and the calculations were performed at the experimental geometries. Details of the basis sets, geometries and resulting total energies for each molecule are given in Table IX.

The results of the double zeta calculations on CH₄, NH₃ and H₂O are presented in Table X. Both the Dalgarno uncoupled and self consistent results refer to the Fermi contact coupling mechanism. The SCFPM values for the directly bonded X-H couplings are now in good agreement with experiment. (In the case of the O-H coupling in water, an experimental value of ±73.5 Hz has also been reported [107], which is closer to the value calculated here.) The geminal H-H couplings are still too large in magnitude, although they are smaller than the minimal basis set values.

As before, the Dalgarno uncoupled results are found to be much smaller
in magnitude than those from the self-consistent calculations, and are
generally not very close to the experimental values. The same observation
has recently been made for magnetic shielding constants calculated by
Kern et alia [103]. Karplus & Kolker [49] rationalised this in terms of
the form of the perturbation operator, which, if it is heavily weighted
close to the nucleus, will cause excitations to the lower energy virtual
orbitals to dominate the first-order wavefunction, in which case the
neglect of the Coulomb and exchange integrals in the energy denominator of
the first order coupled Hartree-Fock equations [50] will have a substantial
effect on calculated properties.

Although the good agreement of the self consistent double-zeta
calculations for the directly bonded X-H couplings is certainly most
encouraging, a thorough study of the basis set dependence of these couplings
is necessary to properly assess the reliability of the SCFPM. Unfortunately,
such a study is quite beyond the capabilities of the ELLIOTT 4100 computer,
on which the double zeta calculation on methane required over 20 hours of
CP time, and the 4-31 G test calculation on methyl fluoride (Section 3)
consumed in excess of 40 hours.

However, it has recently become possible to use the ATMOL 3 SCFPM
program implemented on the Rutherford Laboratory IBM 360/195 computer
(Section 3) to perform a series of extended basis set calculations on some
simple molecules, in collaboration with Drs. M. F. Guest and V. R. Saunders
[108].

Initially, a study of the basis set dependence of the Fermi contact
contributions to the coupling constants in H₂O was made with a view to
finding a stable basis set which would also be suitable for calculations on
atomic orbitals, the coupling constants in H₂O were calculated with various
contracted basis sets and the effect of including sets of polarisation functions on oxygen (3d) and hydrogen (2p) was examined. A summary of the most important results is given in Table XI. The [10s6p1d/5s1p] basis gives a total energy not far from the estimated Hartree-Fock limit for water (-76.066 ± 0.002 Hartrees) [137], and since the [5s3p1d/3s1p] basis closely reproduces the total energy and the coupling constants obtained from the former basis, it was concluded that it constitutes a suitable compromise between high accuracy and computational feasibility.

Using the chosen basis set, the sensitivity of the coupling constants in H2O to optimization of the hydrogen s-orbital scaling factor and to variations in molecular geometry was examined, and the results are summarised in Table XII. The insensitivity of the computed coupling constants to the spatial extension of the hydrogen-centred s-orbitals is due to the relatively large basis set employed, and is consistent with the findings of Roos and co-workers [14] using a comparable basis set for water. The geometrical dependence of the NMR coupling constants of water has not previously been studied non-empirically, but ab initio results for other simple hydrides [14,94,102] indicate that these effects may be important. The calculations predict large variations of J(O-H) with bond length, and both J(H-H) and J(O-H) are found to depend strongly on bond angle. The agreement of the calculated couplings with the experimental values is extremely good for J(O-H), but disappointing in the case of J(H-H), which is approximately three times too large.

Calculations similar to those on water have also been performed on ammonia (Table XIII) and methane (Table XIV). As in the case of water, the hydrogen 2p polarisation functions do not appear to contribute to the coupling constants significantly in either of these molecules. However, their inclusion causes a substantial lowering of the total energy in each
case, and in order to maintain a balanced basis set these functions were not excluded from subsequent calculations. The hydrogen s-orbital scaling factor dependence of the coupling constants is very weak in both NH$_3$ and CH$_4$ for the same reason as in H$_2$O.

The bond length dependence of the NMR couplings in NH$_3$ and CH$_4$ has not previously been reported at the ab initio level, and the results of the present calculations indicate moderately large variations in CH$_4$, but a small effect in NH$_3$. The most dramatic changes occur with the inversion of NH$_3$ where $J$(H-H) changes sign at the top of the barrier, as found in recent CI calculations [102]; $J$(N-H) also varies greatly with the out-of-plane angle. The inversion barrier of NH$_3$ is calculated to be 0.0087 Hartrees, close to another recent SCF value of 0.0090 Hartrees [14], and in good agreement with the experimental value of 0.0092 Hartrees [138]. Allowing for the above variations with molecular geometry, the results obtained for $J$(N-H) and $J$(C-H) are rather encouraging, and the experimental value of $J$(H-H) in NH$_3$ is also bracketed by the theoretical results, if, as expected, its sign is negative. The agreement for $J$(H-H) in CH$_4$ is somewhat disappointing; the calculated values are approximately twice the magnitude of the experimental value.

The calculation of $J$(H-F) in hydrogen fluoride has been the subject of a number of ab initio investigations [37,40,42,92,94,95], but in only one case was the geometry dependence of $J$(H-F) studied [94], and the inclusion of the electron-orbital and spin-dipolar terms has also received scant attention [92]. The calculations on H$_2$O, NH$_3$ and CH$_4$ described above were extended to HF by considering all three coupling mechanisms and examining the geometry dependence of each term. The stability of each term to the inclusion of polarisation functions and to a decrease in the (s-p) basis set size has also been studied, and the results of the calculations
are presented in Table XV. Using the \([5s3p1d/3s1p]\) basis set, the total coupling constant is in excellent agreement with the experimentally-determined value, after optimisation of the hydrogen s-orbital scale factor. The Fermi contact term is found to be quite sensitive to the scale factor, and also to be responsible for most of the large variation of \(J(H-F)\) with bond length. This result is consistent with the strong bond length dependence found in \textit{ab initio} Sum-Over-States calculations of \(J(H-F)\) in HF where only the contact interaction was considered [94]. The relative magnitudes of the three terms as calculated here are also in agreement with those of an earlier non-empirical study [92]: i.e. Fermi contact > Orbital > Spin-dipolar.

The basis set dependence of the orbital and spin-dipolar terms has not yet been systematically examined at the \textit{ab initio} level. However, previous calculations on \(\text{CH}_3\text{F}\) [65] and HF [92] using basis sets of approximately minimal to double-zeta quality indicate that at this level there are substantial variations in both terms. The \([5s3p1d/3s1p]\) basis set used in the present calculations has therefore been extended in two ways to investigate this possibility. Initially, the number of hydrogen-centred s-orbitals was increased from three to four; secondly, the single Gaussian 3d orbitals on fluorine (\(\alpha = 0.84\)) were replaced by a two Gaussian expansion (\(\xi = 2.50\)) according to Dunning's prescription [136]. Neither of these extensions had a significant effect upon any of the three terms and accordingly the numerical results have not been included in Table XV.

It may therefore be tentatively proposed that the \([5s3p1d/3s1p]\) basis set represents a stable choice for the reliable calculation of directly-bonded \(X-H\) coupling constants by the SCFPM. It is to be hoped that future work will indicate that the SCF perturbation method can usefully be applied to directly-bonded coupling constants in small but chemically interesting molecules, for example: phosphoranes, boranes and fluorinated alkanes.
<table>
<thead>
<tr>
<th>$R(H-H)$</th>
<th>BASIS</th>
<th>TOTAL ENERGY</th>
<th>CONTACT (DUCHFP)</th>
<th>CONTACT (SCFPM)</th>
<th>EXPT.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.40</td>
<td>1s(STO-3G)</td>
<td>-1.121913</td>
<td>173</td>
<td>538</td>
<td>279.7</td>
</tr>
<tr>
<td></td>
<td>1s(STO-6G)</td>
<td>-1.127969</td>
<td>279</td>
<td>865</td>
<td>[90]</td>
</tr>
<tr>
<td></td>
<td>1s(STO-10G)</td>
<td>-1.128075</td>
<td>311</td>
<td>963</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1s(STO-6G)</td>
<td>-1.128219</td>
<td>239</td>
<td>789</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1s(STO-6G)</td>
<td>-1.128915</td>
<td>241</td>
<td>764</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+2s(STO-6G)</td>
<td>-1.129013</td>
<td>350</td>
<td>771</td>
<td></td>
</tr>
</tbody>
</table>

[$\xi(1s) = 1.2; \, \xi(2s) = \xi(2p) = 1.0$]

<table>
<thead>
<tr>
<th>$R(H-H)$</th>
<th>BASIS</th>
<th>TOTAL ENERGY</th>
<th>CONTACT (DUCHFP)</th>
<th>CONTACT (SCFPM)</th>
<th>EXPT.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.40</td>
<td>1s(STO-10G)</td>
<td>-1.128130</td>
<td>307.5</td>
<td>953.0</td>
<td></td>
</tr>
<tr>
<td>1.39</td>
<td>-1.128198</td>
<td>307.7</td>
<td>943.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.38</td>
<td>-1.128215</td>
<td>307.9</td>
<td>933.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.37</td>
<td>-1.128180</td>
<td>308.1</td>
<td>924.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

($\xi(1s) = 1.197 [42]$)

**TABLE I**

DUCHFP and SCFPM results for the Fermi contact contribution to nuclear spin-coupling in the hydrogen molecule (in Hertz).

Total energies are in Hartrees and bond lengths in Bohrs.
<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>BASIS</th>
<th>GEOMETRY</th>
<th>ORBITAL EXONENTS</th>
<th>TOTAL ENERGY</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH₄⁻</td>
<td>SCFAO</td>
<td>R = 2.35</td>
<td>H: $\xi(1s) = 1.15$</td>
<td>-26.952093</td>
<td>a</td>
</tr>
<tr>
<td>BH₄⁻</td>
<td>STO-6G</td>
<td>R = 2.37</td>
<td>H: $\xi(1s) = 1.04$</td>
<td>-26.913899</td>
<td>[109]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\theta = 109.45$</td>
<td>B: $\xi(1s) = 4.69$, $\xi(2s) = 1.43$, $\xi(2p) = 1.39$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>SCFAO</td>
<td>R = 2.05</td>
<td>H: $\xi(1s) = 1.40$</td>
<td>-40.172719</td>
<td>[110]</td>
</tr>
<tr>
<td>CH₄</td>
<td>STO-6G</td>
<td>R = 2.0665</td>
<td>H: $\xi(1s) = 1.17$</td>
<td>-40.102801</td>
<td>[111]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\theta = 109.45$</td>
<td>C: $\xi(1s) = 5.68$, $\xi(2s) = \xi(2p) = 1.76$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>SCFAO</td>
<td>R = 1.95</td>
<td>H: $\xi(1s) = 1.60$</td>
<td>-56.512226</td>
<td>[112]</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>STO-6G</td>
<td>R = 1.95</td>
<td>H: $\xi(1s) = 1.30$</td>
<td>-56.419246</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\theta = 109.45$</td>
<td>N: $\xi(1s) = 6.67$, $\xi(2s) = 2.08$, $\xi(2p) = 2.04$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td>SCFAO</td>
<td>R = 1.9162</td>
<td>H: $\xi(1s) = 1.40$</td>
<td>-56.148006</td>
<td>c</td>
</tr>
<tr>
<td>NH₃</td>
<td>STO-6G</td>
<td>R = 1.9162</td>
<td>H: $\xi(1s) = 1.234$</td>
<td>-55.989056</td>
<td>[113]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\theta = 106.73$</td>
<td>N: $\xi(1s) = 6.672$, $\xi(2s) = 1.966$, $\xi(2p) = 1.931$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>SCFAO</td>
<td>R = 1.8111</td>
<td>H: $\xi(1s) = 1.40$</td>
<td>-75.982935</td>
<td>[114]</td>
</tr>
<tr>
<td>H₂O</td>
<td>STO-6G</td>
<td>R = 1.8111</td>
<td>H: $\xi(1s) = 1.27$</td>
<td>-75.680523</td>
<td>[115]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\theta = 104.45$</td>
<td>O: $\xi(1s) = 7.66$, $\xi(2s) = 2.25$, $\xi(2p) = 2.21$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF</td>
<td>SCFAO</td>
<td>R = 1.7328</td>
<td>H: $\xi(1s) = 1.50$</td>
<td>-100.009119</td>
<td>c</td>
</tr>
<tr>
<td>HF</td>
<td>STO-6G</td>
<td>R = 1.7328</td>
<td>H: $\xi(1s) = 1.5163$</td>
<td>-99.501905</td>
<td>[116]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>F: $\xi(1s) = 8.6533$, $\xi(2s) = 2.5551$, $\xi(2p) = 2.5498$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOLECULE</td>
<td>BASIS</td>
<td>GEOMETRY</td>
<td>ORBITAL EXONENTS</td>
<td>TOTAL ENERGY</td>
<td>REF.</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>---------------------</td>
<td>------------------</td>
<td>--------------</td>
<td>------</td>
</tr>
<tr>
<td>CH₃F</td>
<td>SCFAO</td>
<td>R(C-H) = 2.10</td>
<td>H: ξ(1s) = 1.40</td>
<td>-138.964149</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R(C-F) = 2.618</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>tetrahedral</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃F</td>
<td>STO-6G</td>
<td>R(C-H) = 2.10</td>
<td>H: ξ(1s) = 1.18</td>
<td>-138.476812</td>
<td>[97]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R(C-F) = 2.168</td>
<td>C: ξ(1s) = 5.67, ξ(2s) = ξ(2p) = 1.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>F: ξ(1s) = 8.65, ξ(2s) = ξ(2p) = 2.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>tetrahedral</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂CO</td>
<td>SCFAO</td>
<td>R(C-O) = 2.2864</td>
<td>H: ξ(1s) = 1.40</td>
<td>-113.716000</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R(C-H) = 2.1164</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>θ(HCH) = 118.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂CO</td>
<td>STO-6G</td>
<td>R(C-O) = 2.2864</td>
<td>H: ξ(1s) = 1.20</td>
<td>-113.422676</td>
<td>[117]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R(C-H) = 2.1164</td>
<td>C: ξ(1s) = 5.7, ξ(2s) = ξ(2p) = 1.625</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>θ(HCH) = 118.0</td>
<td>O: ξ(1s) = 7.7, ξ(2s) = ξ(2p) = 2.275</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Bond lengths are in Bohrs, bond angles in degrees and total energies in Hartrees)

a R(B-H) and H: ξ(1s) were optimized together.

b Optimal ξ-values were estimated from similar molecules in the same basis.

c H: ξ(1s) was optimized at the experimental geometry.
TABLE III
SCFPM results for the coupling constants in some polyatomic molecules using optimized minimal SCFAO basis sets (in Hertz).

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>A-B</th>
<th>CONTACT</th>
<th>ORBITAL</th>
<th>DIPOLAR</th>
<th>TOTAL</th>
<th>EXPT.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH₄⁻</td>
<td>B-H</td>
<td>155.0</td>
<td>-0.5</td>
<td>0.1</td>
<td>154.6</td>
<td>± 81.5</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>-48.7</td>
<td>0.2</td>
<td>0.1</td>
<td>-48.4</td>
<td>-</td>
</tr>
<tr>
<td>CH₄</td>
<td>C-H</td>
<td>223.5</td>
<td>-0.1</td>
<td>0.0</td>
<td>223.4</td>
<td>+125</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>-65.3</td>
<td>0.5</td>
<td>0.2</td>
<td>-64.6</td>
<td>-12.4</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>N-H</td>
<td>93.3</td>
<td>0.3</td>
<td>0.0</td>
<td>93.6</td>
<td>± 52.3</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>-63.6</td>
<td>0.7</td>
<td>0.3</td>
<td>-62.6</td>
<td>-</td>
</tr>
<tr>
<td>NH₃</td>
<td>N-H</td>
<td>77.8</td>
<td>0.4</td>
<td>-0.2</td>
<td>78.0</td>
<td>± 43.6</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>-52.4</td>
<td>1.0</td>
<td>0.4</td>
<td>-51.0</td>
<td>± 10.4</td>
</tr>
<tr>
<td>H₂O</td>
<td>O-H</td>
<td>-92.7</td>
<td>-5.6</td>
<td>1.5</td>
<td>-96.8</td>
<td>± 79.0</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>-42.9</td>
<td>1.9</td>
<td>0.6</td>
<td>-40.4</td>
<td>± 7.2</td>
</tr>
<tr>
<td>HF</td>
<td>F-H</td>
<td>150.8</td>
<td>174.9</td>
<td>-26.9</td>
<td>298.8</td>
<td>+530</td>
</tr>
<tr>
<td>CH₃F</td>
<td>C-F</td>
<td>-352.4</td>
<td>40.1</td>
<td>28.2</td>
<td>-264.1</td>
<td>-161.9</td>
</tr>
<tr>
<td></td>
<td>C-H</td>
<td>246.6</td>
<td>-0.7</td>
<td>0.2</td>
<td>246.1</td>
<td>+148.8</td>
</tr>
<tr>
<td></td>
<td>F-H</td>
<td>81.1</td>
<td>18.2</td>
<td>-4.8</td>
<td>88.5</td>
<td>+40.5</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>-62.2</td>
<td>0.4</td>
<td>0.3</td>
<td>-61.5</td>
<td>-9.6</td>
</tr>
<tr>
<td>H₂CO</td>
<td>C-O</td>
<td>D</td>
<td>37.6</td>
<td>D</td>
<td>-</td>
<td>± 172</td>
</tr>
<tr>
<td></td>
<td>C-H</td>
<td>D</td>
<td>-1.8</td>
<td>D</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>O-H</td>
<td>D</td>
<td>6.6</td>
<td>D</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>D</td>
<td>0.4</td>
<td>D</td>
<td>-</td>
<td>± 40.2</td>
</tr>
</tbody>
</table>

[D = divergent]
TABLE IV

SCFPM results for the coupling constants in some polyatomic molecules using optimized minimal STO basis sets (in Hertz).

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>A-B</th>
<th>CONTACT</th>
<th>ORBITAL</th>
<th>DIPOLAR</th>
<th>TOTAL</th>
<th>EXPT.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH₄⁻</td>
<td>B-H</td>
<td>187.5</td>
<td>-0.4</td>
<td>0.1</td>
<td>187.2</td>
<td>± 81.5</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>-26.1</td>
<td>0.3</td>
<td>0.2</td>
<td>-25.6</td>
<td>-</td>
</tr>
<tr>
<td>CH₄</td>
<td>C-H</td>
<td>249.7</td>
<td>-0.1</td>
<td>0.0</td>
<td>249.6</td>
<td>+125</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>-34.1</td>
<td>0.8</td>
<td>0.0</td>
<td>-33.3</td>
<td>-12.4</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>N-H</td>
<td>116.3</td>
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<td>0.0</td>
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<td>± 52.3</td>
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</tr>
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<td>N-H</td>
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<td>± 43.6</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
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<td>0.6</td>
<td>-35.3</td>
<td>± 10.4</td>
</tr>
<tr>
<td>H₂O</td>
<td>O-H</td>
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<td>-5.2</td>
<td>± 79.0</td>
</tr>
<tr>
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<td>-741.4</td>
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<td>-161.9</td>
</tr>
<tr>
<td></td>
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<td>0.0</td>
<td>309.9</td>
<td>+148.8</td>
</tr>
<tr>
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<td>F-H</td>
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<td>-4.0</td>
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<td>+ 46.3</td>
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<tr>
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<td>- 9.6</td>
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<td>D</td>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>C-H</td>
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<td>D</td>
<td>- ± 172</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O-H</td>
<td>D</td>
<td>5.8</td>
<td>D</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>D</td>
<td>0.4</td>
<td>D</td>
<td>- ± 40.2</td>
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</table>

[D = divergent]
TABLE V

DUCHFPM results for the coupling constants in some polyatomic molecules using optimized minimal SCFAO basis sets (in Hertz).

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<thead>
<tr>
<th>MOLECULE</th>
<th>A-B</th>
<th>CONTACT</th>
<th>ORBITAL</th>
<th>DIPOLAR</th>
<th>TOTAL</th>
<th>EXPT.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH₄⁻</td>
<td>B-H</td>
<td>49.8</td>
<td>-0.3</td>
<td>0.1</td>
<td>49.6 ± 81.5</td>
<td>[118]</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>1.0</td>
<td>0.2</td>
<td>0.0</td>
<td>1.2</td>
<td>-</td>
</tr>
<tr>
<td>CH₄</td>
<td>C-H</td>
<td>80.8</td>
<td>-0.1</td>
<td>0.1</td>
<td>80.8 +125</td>
<td>[119]</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>0.8</td>
<td>0.4</td>
<td>0.1</td>
<td>1.3</td>
<td>-12.4</td>
</tr>
<tr>
<td>NH₄⁺</td>
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<td>0.2</td>
<td>0.1</td>
<td>35.5 ± 52.3</td>
<td>[121]</td>
</tr>
<tr>
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<td>H-H</td>
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<td>0.5</td>
<td>0.1</td>
<td>1.6</td>
<td>-</td>
</tr>
<tr>
<td>NH₃</td>
<td>N-H</td>
<td>27.3</td>
<td>0.3</td>
<td>0.0</td>
<td>27.6 ± 43.6</td>
<td>[122]</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>2.9</td>
<td>0.6</td>
<td>0.1</td>
<td>3.6 ± 10.4</td>
<td>[122]</td>
</tr>
<tr>
<td>H₂O</td>
<td>O-H</td>
<td>-34.7</td>
<td>-3.2</td>
<td>0.4</td>
<td>-37.5 ± 79.0</td>
<td>[123]</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>1.5</td>
<td>1.0</td>
<td>0.2</td>
<td>2.7 ± 7.2</td>
<td>[124]</td>
</tr>
<tr>
<td>HF</td>
<td>F-H</td>
<td>106.1</td>
<td>96.3</td>
<td>-8.9</td>
<td>193.5 +530</td>
<td>[93]</td>
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<td>7.3</td>
<td>-114.2 -161.9</td>
<td>[125]</td>
</tr>
<tr>
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<td>C-H</td>
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<td>0.3</td>
<td>84.8 +148.8</td>
<td>[125]</td>
</tr>
<tr>
<td></td>
<td>F-H</td>
<td>7.5</td>
<td>7.4</td>
<td>-1.1</td>
<td>13.8 +46.3</td>
<td>[125]</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>2.4</td>
<td>0.3</td>
<td>0.0</td>
<td>2.7 - 9.6</td>
<td>[126]</td>
</tr>
<tr>
<td>H₂CO</td>
<td>C-O</td>
<td>5.2</td>
<td>9.6</td>
<td>-0.4</td>
<td>14.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C-H</td>
<td>101.7</td>
<td>-0.2</td>
<td>0.2</td>
<td>101.7 ± 172</td>
<td>[127]</td>
</tr>
<tr>
<td></td>
<td>O-H</td>
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<td>1.6</td>
<td>0.0</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>19.7</td>
<td>0.4</td>
<td>0.1</td>
<td>20.2 ± 40.2</td>
<td>[128]</td>
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TABLE VI

DUCHFPM results for the coupling constants in some polyatomic molecules using optimized minimal STO basis sets (in Hertz).

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>A-B</th>
<th>CONTACT</th>
<th>ORBITAL</th>
<th>DIPOLAR</th>
<th>TOTAL</th>
<th>EXPT.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH$_4^-$</td>
<td>B-H</td>
<td>53.9</td>
<td>-0.3</td>
<td>0.2</td>
<td>53.8  ± 81.5</td>
<td>[118]</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>1.1</td>
<td>0.2</td>
<td>0.0</td>
<td>1.3</td>
<td>-</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>C-H</td>
<td>67.3</td>
<td>0.0</td>
<td>0.3</td>
<td>67.6  +125</td>
<td>[119]</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>0.9</td>
<td>0.1</td>
<td>0.1</td>
<td>1.1   -12.4</td>
<td>[120]</td>
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<td>NH$_4^+$</td>
<td>N-H</td>
<td>31.3</td>
<td>0.2</td>
<td>0.1</td>
<td>31.6  ± 52.3</td>
<td>[121]</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>0.5</td>
<td>0.7</td>
<td>0.2</td>
<td>1.4</td>
<td>-</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>N-H</td>
<td>18.1</td>
<td>0.2</td>
<td>0.0</td>
<td>18.3  ± 43.6</td>
<td>[122]</td>
</tr>
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<td></td>
<td>H-H</td>
<td>2.4</td>
<td>0.9</td>
<td>0.2</td>
<td>3.3   ± 10.4</td>
<td>[122]</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>O-H</td>
<td>-5.7</td>
<td>-2.6</td>
<td>0.2</td>
<td>-8.1  ± 79.0</td>
<td>[123]</td>
</tr>
<tr>
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<td>H-H</td>
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<td>1.7</td>
<td>0.2</td>
<td>3.1   ± 7.2</td>
<td>[124]</td>
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<tr>
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<td>F-H</td>
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<td>98.1</td>
<td>-6.4</td>
<td>-94.6 ± 530</td>
<td>[ 93]</td>
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<td>3.9</td>
<td>-177.6 -161.9</td>
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<td>C-H</td>
<td>83.6</td>
<td>-0.1</td>
<td>0.2</td>
<td>83.7  +148.8</td>
<td>[125]</td>
</tr>
<tr>
<td></td>
<td>F-H</td>
<td>2.7</td>
<td>4.6</td>
<td>-0.7</td>
<td>6.6   + 46.3</td>
<td>[123]</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>2.1</td>
<td>0.4</td>
<td>0.1</td>
<td>2.6   - 9.6</td>
<td>[126]</td>
</tr>
<tr>
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<td>16.6</td>
<td>-</td>
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<tr>
<td></td>
<td>C-H</td>
<td>88.2</td>
<td>0.1</td>
<td>0.2</td>
<td>88.5  ± 172</td>
<td>[127]</td>
</tr>
<tr>
<td></td>
<td>O-H</td>
<td>-0.9</td>
<td>1.3</td>
<td>0.1</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>19.4</td>
<td>0.4</td>
<td>0.1</td>
<td>19.9  ± 40.2</td>
<td>[128]</td>
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### SCFP results for the symmetric stretch in CH₄ using optimised minimal SCFAO basis sets (in Hertz).

Bond lengths are in Bohrs.
<table>
<thead>
<tr>
<th>R(C-H)</th>
<th>A-B</th>
<th>CONTACT</th>
<th>ORBITAL</th>
<th>DIPOlar</th>
<th>TOTAL</th>
<th>EXPT.</th>
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<tbody>
<tr>
<td>1.95</td>
<td>C-H</td>
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<td>81.2</td>
<td>+125</td>
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<tr>
<td></td>
<td>H-H</td>
<td>0.2</td>
<td>0.5</td>
<td>0.1</td>
<td>0.8</td>
<td>-12.4</td>
</tr>
<tr>
<td>2.00</td>
<td>C-H</td>
<td>80.9</td>
<td>-0.1</td>
<td>0.2</td>
<td>81.0</td>
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<tr>
<td></td>
<td>H-H</td>
<td>0.5</td>
<td>0.4</td>
<td>0.1</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>2.05</td>
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<td>-0.1</td>
<td>0.1</td>
<td>80.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>0.8</td>
<td>0.4</td>
<td>0.1</td>
<td>1.3</td>
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</tr>
<tr>
<td>2.10</td>
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<td>76.2</td>
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</tr>
<tr>
<td></td>
<td>H-H</td>
<td>1.0</td>
<td>0.4</td>
<td>0.1</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>2.15</td>
<td>C-H</td>
<td>70.9</td>
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<td>0.2</td>
<td>71.0</td>
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</tr>
<tr>
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<td>H-H</td>
<td>1.1</td>
<td>0.4</td>
<td>0.1</td>
<td>1.6</td>
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</table>

DUCHEPP results for the symmetric stretch in CH₄ using optimised minimal SCF AO basis sets (in Hertz).

Bond lengths are in Bohrs.
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<tr>
<th>MOLECULE</th>
<th>BASIS</th>
<th>GEOMETRY</th>
<th>ORBITAL EXONENTS</th>
<th>TOTAL ENERGY</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>DZ</td>
<td>R = 2.067</td>
<td>H: $\xi(1s) = 1.4$, $\xi(1s') = 1.9$</td>
<td>-40.173419</td>
<td>[104]</td>
</tr>
<tr>
<td></td>
<td>STO-6G</td>
<td>$\theta = 109.45$ C: $\xi(1s) = 5.23090$, $\xi(1s') = 7.96897$</td>
<td></td>
<td></td>
<td>[105]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\xi(2s) = 1.16782$, $\xi(2s') = 1.82031$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\xi(2p) = 1.25572$, $\xi(2p') = 2.72625$</td>
<td></td>
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</tr>
<tr>
<td>NH₃</td>
<td>DZ</td>
<td>R = 1.9162</td>
<td>H: $\xi(1s) = 1.15$, $\xi(1s') = 1.4$</td>
<td>-56.152643</td>
<td>[104]</td>
</tr>
<tr>
<td></td>
<td>STO-6G</td>
<td>$\theta = 106.73$ N: $\xi(1s) = 6.11863$, $\xi(1s') = 8.93843$</td>
<td></td>
<td></td>
<td>[105]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\xi(2s) = 1.39327$, $\xi(2s') = 2.22157$</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\xi(2p) = 1.50585$, $\xi(2p') = 3.26741$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>DZ</td>
<td>R = 1.8111</td>
<td>H: $\xi(1s) = 1.4$, $\xi(1s') = 1.65$</td>
<td>-75.984892</td>
<td>[104]</td>
</tr>
<tr>
<td></td>
<td>STO-6G</td>
<td>$\theta = 104.45$ O: $\xi(1s) = 7.06227$, $\xi(1s') = 10.10850$</td>
<td></td>
<td></td>
<td>[105]</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$\xi(2s) = 1.62705$, $\xi(2s') = 2.26158$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\xi(2p) = 1.65372$, $\xi(2p') = 3.68127$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Bond lengths are in Bohr, bond angles in degrees and total energies in Hartree)

**TABLE IX**  
Molecular geometries, basis sets and total energies for the double-zeta calculations.
TABLE X
DUCHEPMM and SCFPM results for the Fermi-contact contributions to the NMR coupling constants in CH$_4$, NH$_3$ and H$_2$O using DZ STO-6G basis sets (in Hertz).

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>A-B</th>
<th>CONTACT (DUCHEPMM)</th>
<th>CONTACT (SCFPM)</th>
<th>EXPT.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>C-H</td>
<td>34.3</td>
<td>118.2</td>
<td>± 125 [119]</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>0.6</td>
<td>-18.6</td>
<td>-12.4 [120]</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>N-H</td>
<td>16.0</td>
<td>44.9</td>
<td>± 43.6 [122]</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>-2.9</td>
<td>-30.7</td>
<td>± 10.4 [122]</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>O-H</td>
<td>-32.5</td>
<td>-66.6</td>
<td>± 79.0 [123]</td>
</tr>
<tr>
<td></td>
<td>H-H</td>
<td>-2.2</td>
<td>-24.0</td>
<td>± 7.2 [124]</td>
</tr>
</tbody>
</table>
TABLE XI

Basis Set Dependence of the Fermi-Contact Coupling Constants in H₂O

<table>
<thead>
<tr>
<th>BASIS</th>
<th>ξ₅₅</th>
<th>TOTAL ENERGY</th>
<th>J(O-H)</th>
<th>J(H-H)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Hartree)</td>
<td>(Hertz)</td>
<td></td>
</tr>
<tr>
<td>[10s6p/5s]</td>
<td>1.49</td>
<td>-76.021227</td>
<td>72.8</td>
<td>22.5</td>
</tr>
<tr>
<td>[10s6p1d/5s]</td>
<td></td>
<td>-76.050544</td>
<td>81.5</td>
<td>23.3</td>
</tr>
<tr>
<td>[10s6p/5s1p]</td>
<td>b</td>
<td>-76.047424</td>
<td>77.0</td>
<td>20.7</td>
</tr>
<tr>
<td>[10s6p1d/5s1p]</td>
<td>a,b</td>
<td>-76.058633</td>
<td>81.9</td>
<td>22.4</td>
</tr>
<tr>
<td>[5s3p/3s]</td>
<td>1.49</td>
<td>-76.020262</td>
<td>72.6</td>
<td>24.0</td>
</tr>
<tr>
<td>[5s3p1d/3s1p]</td>
<td>c</td>
<td>-76.055634</td>
<td>79.5</td>
<td>23.8</td>
</tr>
<tr>
<td>[4s2p/2s]</td>
<td>1.20</td>
<td>-76.007870</td>
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<td>23.2</td>
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<tr>
<td>[4s2p1d/2s1p]</td>
<td>c</td>
<td>-76.035128</td>
<td>82.0</td>
<td>30.9</td>
</tr>
</tbody>
</table>

EXPT ± 79.0 ± 7.2

R = 1.8111 Bohr, θ = 104.45°;

a  the 3d orbitals are 2-Gaussian expansions with ξ = 2.01 [136];

b  ξ(2pH) = 2.35 [136];

c  α(3d) = 0.74, α(2p) = 1.1 [139]; ξ₅₅ optimised in H₂O [134,135]
TABLE XII

Geometrical and Scaling Factor Dependence of the Coupling Constants in H₂O

<table>
<thead>
<tr>
<th>R₀H (Bohr)</th>
<th>θ(HOH)°</th>
<th>ξₗ</th>
<th>TOTAL ENERGY (Hartree)</th>
<th>J(O-H)</th>
<th>J(H-H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8111</td>
<td>104.45</td>
<td>1.29</td>
<td>-76.055488</td>
<td>-81.2</td>
<td>-24.0</td>
</tr>
<tr>
<td>1.49</td>
<td></td>
<td></td>
<td>-76.055634</td>
<td>-79.5</td>
<td>-23.8</td>
</tr>
<tr>
<td>1.69</td>
<td></td>
<td></td>
<td>-76.055414</td>
<td>-80.9</td>
<td>-23.4</td>
</tr>
<tr>
<td>1.8111</td>
<td>99.45</td>
<td>1.49</td>
<td>-76.054398</td>
<td>-73.2</td>
<td>-28.3</td>
</tr>
<tr>
<td>104.45</td>
<td></td>
<td></td>
<td>-76.055634</td>
<td>-79.5</td>
<td>-23.8</td>
</tr>
<tr>
<td>109.45</td>
<td></td>
<td></td>
<td>-76.055519</td>
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<td>1.7611</td>
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<td>1.49</td>
<td>-76.055803</td>
<td>-85.5</td>
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<td></td>
<td>-76.052650</td>
<td>-73.2</td>
<td>-25.5</td>
</tr>
</tbody>
</table>

EXPT ± 79.0 ± 7.2

Basis = [5s3p1d/3s1p]; α(3d) = 0.74, α(2p) = 1.1 [139]
TABLE XIII

Geometrical and Basis Set Dependence of Coupling Constants in NH₃

<table>
<thead>
<tr>
<th>BASIS</th>
<th>ε₉</th>
<th>R₉H (Bohr)</th>
<th>θ(HNH)°</th>
<th>TOTAL ENERGY (Hartree)</th>
<th>J(N-H) (Hertz)</th>
<th>J(H-H) (Hertz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[5s3p/3s]</td>
<td>1.2</td>
<td>1.9124</td>
<td>106.7</td>
<td>-56.183200</td>
<td>52.3</td>
<td>- 26.2</td>
</tr>
<tr>
<td>[5s3pld/3s]</td>
<td></td>
<td></td>
<td></td>
<td>-56.207683</td>
<td>50.4</td>
<td>- 25.9</td>
</tr>
<tr>
<td>[5s3p/3slp]</td>
<td></td>
<td></td>
<td></td>
<td>-56.207317</td>
<td>50.4</td>
<td>- 23.7</td>
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<tr>
<td>[5s3pld/3slp]</td>
<td></td>
<td></td>
<td></td>
<td>-56.215885</td>
<td>49.7</td>
<td>- 24.4</td>
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<tr>
<td>[5s3pld/3slp]</td>
<td>1.4</td>
<td>1.9124</td>
<td>106.7</td>
<td>-56.215896</td>
<td>50.1</td>
<td>- 24.1</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td></td>
<td></td>
<td>-56.215906</td>
<td>49.9</td>
<td>- 24.3</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td></td>
<td></td>
<td>-56.215885</td>
<td>49.7</td>
<td>- 24.4</td>
</tr>
<tr>
<td>[5s3pld/3slp]</td>
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<td>1.9691</td>
<td>106.7</td>
<td>-56.212035</td>
<td>49.6</td>
<td>- 25.6</td>
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<tr>
<td></td>
<td>1.9124</td>
<td></td>
<td></td>
<td>-56.215906</td>
<td>49.9</td>
<td>- 24.3</td>
</tr>
<tr>
<td></td>
<td>1.8557</td>
<td></td>
<td></td>
<td>-56.215223</td>
<td>50.0</td>
<td>- 23.4</td>
</tr>
<tr>
<td>[5s3pld/3slp]</td>
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<td>1.9124</td>
<td>120.0</td>
<td>-56.207190</td>
<td>80.2</td>
<td>+  1.8</td>
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<tr>
<td></td>
<td>106.7</td>
<td></td>
<td></td>
<td>-56.215906</td>
<td>49.9</td>
<td>- 24.3</td>
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<tr>
<td></td>
<td>90.0</td>
<td></td>
<td></td>
<td>-56.194756</td>
<td>33.0</td>
<td>- 35.1</td>
</tr>
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</table>

EXPT ± 43.6 ± 10.4

α(3d) = 0.75, α(2p) = 1.1 [139]
TABLE XIV

Geometrical and Basis Set Dependence of Coupling Constants in CH₄

<table>
<thead>
<tr>
<th>BASIS</th>
<th>( \xi_H )</th>
<th>( R_{CH} ) (Bohr)</th>
<th>( \theta \text{(HCH)} )°</th>
<th>TOTAL ENERGY (Hartree)</th>
<th>J(C-H) (Hertz)</th>
<th>J(H-H) (Hertz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[5s3p/3s]</td>
<td>1.2</td>
<td>2.0504</td>
<td>109.45</td>
<td>-40.189873</td>
<td>154.3</td>
<td>- 28.4</td>
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<td>[5s3p1d/3s]</td>
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<td></td>
<td></td>
<td>-40.204953</td>
<td>149.6</td>
<td>- 26.7</td>
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<tr>
<td>[5s3p/3s1p]</td>
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<td></td>
<td>-40.206629</td>
<td>148.3</td>
<td>- 25.6</td>
</tr>
<tr>
<td>[5s3p1d/3s1p]</td>
<td></td>
<td></td>
<td></td>
<td>-40.212292</td>
<td>147.1</td>
<td>- 25.5</td>
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<td>[5s3p1d/3s1p]</td>
<td>1.0</td>
<td>2.0504</td>
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<td>-40.212198</td>
<td>143.3</td>
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<td>1.1</td>
<td></td>
<td></td>
<td>-40.212303</td>
<td>145.6</td>
<td>- 25.4</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td></td>
<td></td>
<td>-40.212292</td>
<td>147.1</td>
<td>- 25.5</td>
</tr>
<tr>
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<td>2.1071</td>
<td>109.45</td>
<td>-40.209583</td>
<td>156.6</td>
<td>- 26.2</td>
</tr>
<tr>
<td></td>
<td>2.0504</td>
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<td>-40.212303</td>
<td>145.6</td>
<td>- 25.4</td>
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<td></td>
<td>1.9937</td>
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<td></td>
<td>-40.210207</td>
<td>135.3</td>
<td>- 24.7</td>
</tr>
</tbody>
</table>

EXPT +125 - 12.4

\( \alpha(3d) = 0.73, \alpha(2p) = 1.2 \) [139]
<table>
<thead>
<tr>
<th>BASIS (Bohr)</th>
<th>RHF (Hartree)</th>
<th>TOTAL ENERGY (Hertz)</th>
<th>CONTACT</th>
<th>ORBITAL</th>
<th>DIPOLAR</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 [5s3p1d/3s1p]</td>
<td>1.7328</td>
<td>-100.060166</td>
<td>398.3</td>
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<td>1.4</td>
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<td>-17.2</td>
<td>554.2</td>
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<tr>
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<td>356.6</td>
<td>195.0</td>
<td>-17.7</td>
<td>533.9</td>
<td></td>
</tr>
<tr>
<td>1.7</td>
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<td>192.7</td>
<td>-18.0</td>
<td>533.6</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
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<td>539.1</td>
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</tr>
<tr>
<td>1.7 [5s3p/3s]</td>
<td>1.7328</td>
<td>-100.037025</td>
<td>242.4</td>
<td>182.4</td>
<td>-22.0</td>
<td>403.8</td>
</tr>
<tr>
<td>[5s3p1d/3s]</td>
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<td>367.0</td>
<td>183.8</td>
<td>-19.3</td>
<td>531.5</td>
<td></td>
</tr>
<tr>
<td>[5s3p/3s1p]</td>
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<td>191.1</td>
<td>-20.5</td>
<td>481.1</td>
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</tr>
<tr>
<td>[5s3p1d/3s1p]</td>
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<td>358.9</td>
<td>192.7</td>
<td>-18.0</td>
<td>533.6</td>
<td></td>
</tr>
<tr>
<td>1.7 [5s3p1d/3s1p]</td>
<td>1.6828</td>
<td>-100.060423</td>
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<td>200.4</td>
<td>-13.6</td>
<td>609.6</td>
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<td>358.9</td>
<td>192.7</td>
<td>-18.0</td>
<td>533.6</td>
<td></td>
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<tr>
<td>1.7828</td>
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<td>299.0</td>
<td>185.2</td>
<td>-21.3</td>
<td>462.9</td>
<td></td>
</tr>
<tr>
<td>1.7 [4s2p/2s]</td>
<td>1.7328</td>
<td>-100.020557</td>
<td>361.6</td>
<td>182.2</td>
<td>-19.8</td>
<td>524.0</td>
</tr>
<tr>
<td>[4s2p1d/2s1p]</td>
<td>-100.046865</td>
<td>485.7</td>
<td>178.4</td>
<td>-18.9</td>
<td>645.2</td>
<td></td>
</tr>
</tbody>
</table>

EXPT +530

\[ \alpha(3d) = 0.84, \alpha(2p) = 1.0 \, [139] \]
6. **Conclusions**

The work presented here indicates that Hartree-Fock Perturbation methods such as the Self-Consistent Field Perturbation Method, used in conjunction with extended basis sets of at least double zeta quality, may be able to yield reliable values for directly-bonded NMR coupling constants in molecules of chemical interest. However, it is likely that for molecules with \( \pi \)-systems and a very small singlet-triplet separation that convergence problems may be encountered. The importance of the orbital and spin-dipolar contributions to the coupling constant in hydrogen fluoride has been demonstrated, and the geometry dependence of the coupling constants in methane, ammonia, water and hydrogen fluoride has been shown to be significant.

In the light of the large-scale calculations for geminal H-H coupling constants by Roos and co-workers [14,102], it is clear that electron correlation is very important here. Roos et alia have been able to approach the experimental values by using a zero-order wavefunction correlated by inclusion of all singly and doubly excited singlets, and a first order wavefunction expanded in all singly and doubly excited triplets, using the canonical SCF occupied and virtual orbitals. This treatment is unfortunately impractical to extend to medium size molecules. It is also likely that some intramolecular motions, such as the inversion of ammonia, may modify the calculated couplings [102]. Solvent effects on NMR coupling constants are relatively small and have been studied by Barfield & Johnston [131-133] at the INDO level with some success. However, the importance of including electron correlation remains the greatest barrier to progress in calculating NMR coupling constants generally, and is likely to restrict the amount of useful data which theoreticians can provide on many chemically interesting molecules.
Appendix: Physical Interpretation of the SCF Perturbation Method

In the SCFFM, the applied one-electron perturbation causes a change in the electron distribution of the molecule and this in turn leads to a first order response in the Hartree-Fock field which depends in a self-consistent way on the perturbed electron distribution. The iterative process thus ensures that the resulting first order wavefunction refers to an SCF perturbed state.

However, the question may be raised as to how the triplet states induced by a Fermi contact perturbation can interact with the unperturbed singlet ground state via the $r_1 z^1$ operator, since all such matrix elements are zero. Similar comments apply to the triplet states induced by the spin-dipolar perturbation, and also to the imaginary excited singlets induced by the electron-orbital perturbation. One solution would be to completely uncouple the perturbed Hartree-Fock equations (i.e. Dalgarno uncoupling), but this approach has the disadvantage that it is not independent of the choice of virtual orbitals for the calculation. For instance, defining a Modified Hartree-Fock (MHF) operator containing a pseudopotential operator projected onto the virtual orbital subspace, sets of Improved Virtual Orbitals (IVO) may be generated [129,130] which are physically more suitable for (e.g. singlet or triplet) excitations. If the set of IVOs corresponding to triplet excitations from the highest occupied MO are generated, as recommended by Huzinaga [130], then the contact couplings in methane using the minimal SCFAO basis set become:

$J(C-H) = 159.9 \text{ Hz} \quad J(H-H) = -20.75 \text{ Hz}$

in contrast to the values

$J(C-H) = 80.8 \text{ Hz} \quad J(H-H) = 0.8 \text{ Hz}$

obtained with the canonical virtual orbitals (Table V).
[80] M. F. Guest, private communication.
[81] The Laplace Transform is easily obtained from Euler's integral.


PART TWO

The Calculation of
Electron-nuclear Hyperfine Coupling Constants
by the Unrestricted Hartree-Fock Method
with Spin Annihilation
CONTENTS

SECTION 1. Introduction.

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SECTION 3. The UHF Method with Spin Annihilation.

SECTION 4. The Use of Gaussian Functions in Molecular Calculations.

SECTION 5. The Calculation of Hyperfine Coupling Constants.

SECTION 6. Vibronic Contributions to Hyperfine Coupling Constants.

SECTION 7. The Structure of the Borane Radical Anion BH$_3^-$.

SECTION 8. The Structure of the Diborane Radical Anion B$_2$H$_6^-$.

SECTION 9. The Amine Borane Radicals BH$_3$NM$_3^-$ and BH$_3$NM$_2$.


SECTION 11. The Determination of Bond Angles from ESR Data.

SECTION 12. The Identification of the N$_3^0$ or N$_3^{2-}$ Radical

Bibliography.
1. Introduction

The electron spin resonance (ESR) experiment is capable of furnishing valuable information about the distribution of unpaired electrons in radicals through the electron-nuclear hyperfine coupling constants (hfcc). In favourable cases the coupling constants can be resolved into isotropic and anisotropic components, providing useful insights into the nature of the bonding and the overall structure of the radical.

The theoretician can aid the experimentalist in the task of identifying new radicals and elucidating their electronic and molecular structures by performing calculations for the hyperfine coupling constants of possible species in various conformations. The effects of molecular vibrations and lattice environments on the observed hyperfine properties of radicals may be clarified by comparison with calculations on the isolated rigid species. It may also be possible to examine theoretically some of the relations used by experimentalists to link hyperfine coupling constants to other molecular properties such as bond angles and electronegativity differences.

The calculation of hyperfine coupling constants provides one method for assessing the adequacy of computed wavefunctions, since a good description of the wavefunction close to the nuclei is essential. Thus significant discrepancies between calculated and experimental values may indicate deficiencies in the basis set used or in the theoretical framework adopted.

The foregoing remarks are intended to underline the importance of the calculation of hyperfine coupling constants by reliable methods. In the present work, the ab initio Unrestricted Hartree-Fock method in the LCAO-MO approximation with spin annihilation and minimal Gaussian basis sets of atomic SCF orbitals has been applied to some small doublet state radicals of current experimental and theoretical interest. This approach has been shown to yield valuable results for the chemical understanding of these radicals.
2. The Unrestricted Hartree-Fock (UHF) Method

The UHF method is rather suitable for the calculation of spin densities in radicals since it employs the concept of different orbitals for different spins (DODS) within the framework of the single determinantal (SD) wavefunction. This incorporates into the calculation the desirable feature of electron spin polarization, a correlation effect which is responsible for the non-zero spin densities observed at the nuclei of rigid π-radicals.

The normalized UHF Slater determinant is [1]:

\[ \Psi_{\text{UHF}} = (n!)^{-\frac{1}{2}} \det |\psi_1(1)\alpha(1) \ldots \psi_p(p)\alpha(p) \phi_1(p+1)\beta(p+1) \ldots \phi_q(p+q)\beta(p+q)| \]

Here, the \( p \) \( \alpha \)-spin electrons occupy the set of molecular orbitals (MO's) \( \{ \psi \} \) and the \( q \) \( \beta \)-spin electrons occupy the set of MO's \( \{ \phi \} \). The total number of electrons is \( n \), so that

\[ n = p + q, \]

and, for doublet state radicals,

\[ p = q + 1. \]

Without loss of generality each set of one-electron functions may be considered orthonormal:

\[ \int \psi_i^* \psi_j \, d\tau = \delta_{ij} = \int \phi_i^* \phi_j \, d\tau \]

Amos & Hall [2] have shown that the more nearly orthogonal "corresponding orbitals" with the property:

\[ \int X_i^* n_j \, d\tau = T_i \delta_{ij} \quad (0 \leq T_i \leq 1) \]

may be generated by unitary transformations of \( \psi_i \) and \( \phi_j \). A further orthonormal combination gives the completely orthonormal UHF natural orbitals.
In order to determine the optimal orbitals, they may be expanded as a linear combination of atomic orbitals (LCAO-MO) using a set of \( m \geq n \) basis orbitals \( \{ \omega \} \) centred at the various atomic nuclei:

\[
\psi_j = \sum_{i=1}^{m} a_{ij} \omega_i \\
\phi_j = \sum_{i=1}^{m} b_{ij} \omega_i
\]  

(4)

The \( \{ \omega \} \) themselves are constructed from primitive functions \( \{ \chi \} \), which are usually either Slater-type orbitals (STO) or Gaussian-type functions (GTF).

\[
\omega_i = \sum_j d_{ij} \chi_j
\]

(5)

Using the UHF wavefunction (1), the UHF electronic energy is defined as:

\[
E_{\text{UHF}} = \int \psi_{\text{UHF}}^* H \psi_{\text{UHF}} \, dt
\]

where the non-relativistic Hamiltonian operator for the electronic energy is

\[
H = \sum_{i=1}^{n} h(i) + \sum_{i=1}^{n} \sum_{j<i}^{n} g(i,j)
\]

(6)

Here, \( h(i) = -\frac{\hbar}{2m} \nabla_i^2 - \sum_{\nu=1}^{N} \frac{Z_{\nu}}{r_{i\nu}} \)

(7)

is the one-electron part of the operator, describing both the kinetic energy of each electron and the electrostatic attraction of each electron by the \( N \) nuclei of charge \( Z_{\nu} \), and \( g(i,j) = \frac{1}{r_{ij}} \)

is the two-electron part, describing the interelectronic interactions. In
the Born-Oppenheimer approximation, the nuclei are treated as classical stationary point charges and the internuclear electrostatic repulsion term

\[ V = \sum_{\mu=1}^{N} \sum_{\nu<\mu} Z_{\mu} Z_{\nu} / R_{\mu \nu} \]  

(8)
does not appear in \( H \) and is evaluated separately.

Defining the overlap matrix of the basis functions

\[ S_{ij} = \int \omega_i^* \omega_j \, d\tau \]  

(9)

and the unrestricted bond order matrices for the \( \alpha \) and \( \beta \) electrons respectively

\[ P_{ij} = \sum_{k=1}^{P} a_{ik}^* a_{jk} \quad Q_{ij} = \sum_{k=1}^{Q} b_{ik}^* b_{jk} \]  

(10)

or

\[ P = AA^+ \quad Q = BB^+ \]  

(11)

then

\[ (PS)^2 = PS \quad (QS)^2 = QS \]  

(12)

and

\[ \text{Tr}(PS) = p \quad \text{Tr}(QS) = q \]  

(13)
due to the orthonormality of the molecular orbitals:

\[ A^+SA = I = B^+SB . \]  

(14)

The UHF energy can now be written as

\[ E_{\text{UHF}} = \int \psi^*_\text{UHF} H \psi^*_{\text{UHF}} \, d\tau \]  

\[ = \text{Tr}(PF^\alpha) + \text{Tr}(QF^\beta) - \frac{1}{2}\text{Tr}(PG^\alpha) - \frac{1}{2}\text{Tr}(QG^\beta) \]  

(15)

where

\[ F^\alpha = h + G^\alpha \]  

(16)

\[ F^\beta = h + G^\beta \]

and

\[ h_{ij} = \int \omega_i^* \left[ -\frac{i}{2} \nabla^2 + \sum_{\nu=1}^{N} \frac{Z_{\nu}}{R_{i\nu}} \right] \omega_j \, d\tau \]  

(17)
\[ G_{ij}^\alpha = \sum_{k,l} \left[ [P_{k1}Q_{k1}] \langle ik | j1 \rangle - P_{k1} \langle ik | l1 \rangle \right] = J_{ij} - K_{ij}^\alpha \]  
\[ G_{ij}^\beta = \sum_{k,l} \left[ [P_{k1}Q_{k1}] \langle ik | j1 \rangle - Q_{k1} \langle ik | l1 \rangle \right] = J_{ij} - K_{ij}^\beta \]  
and \[ \langle ij | kl \rangle = \int \omega_i^*(1) \omega_j^*(2) \left( \frac{1}{r_{12}} \right) \omega_k(1) \omega_l(2) \, d\tau_1 \, d\tau_2 \]  

The Coulomb matrix \( J \) accounts for the electrostatic repulsions between all pairs of electrons, while the exchange matrix \( K \) represents the non-classical exchange attractions of pairs of electrons with parallel spins in different orbitals (Fermi correlation).

Optimization of \( \Psi_{UHF} \) to minimize the energy \( E_{UHF} \) entails the determination of the form of the MOs at the energy minimum, by variation of the coefficients in \( A \) and \( B \). Application of the variational condition for a stationary energy subject to the orthonormality constraints on the molecular orbitals may be formulated as two sets of coupled one-electron pseudo-eigenvalue equations:

\[ F^\alpha A = S A \epsilon^\alpha \]
\[ F^\beta B = S B \epsilon^\beta \]  

These UHF equations describe the motion of each electron in the effective average Coulomb and exchange fields of all the other electrons and the nuclei. Standard eigenvalue form may be attained by orthogonalisation of the basis set and the equations may then be solved by diagonalisation of the Fock matrices \( F^\alpha \) and \( F^\beta \), yielding eigenvectors and eigenvalues. The stationary energy will be a minimum if the electrons occupy the eigenvectors corresponding to the \( p \) lowest \( \alpha \)-eigenvalues and the \( q \) lowest \( \beta \)-eigenvalues, and the UHF energy may be written:
\[ E_{\text{UHF}} = \sum_{i=1}^{p} \epsilon_{ii}^\alpha + \sum_{i=1}^{q} \epsilon_{ii}^\beta - \text{Tr}(P^\alpha) - \text{Tr}(Q^\beta) \]  

(21)

where the \( \epsilon^\alpha \) and \( \epsilon^\beta \) matrices are diagonal. However, since \( P^\alpha \) and \( P^\beta \) are functions of \( A \) and \( B \), it is necessary to solve the equations iteratively until \( A \) and \( B \) become self-consistent, when \( \psi_{\text{UHF}} \) is known as the self-consistent field (SCF) UHF wavefunction. Matrices \( A \) and \( B \) contain the SCF \( \alpha \)- and \( \beta \)-spin molecular orbitals and \( \epsilon^\alpha \) and \( \epsilon^\beta \) contain the SCF \( \alpha \)- and \( \beta \)-spin orbital energies.

From the SCF UHF wavefunction, the expectation values of the charge and spin density operators

\[ q(r) = \sum_{i=1}^{n} \delta(r-r_i) \]

and

\[ \rho(r) = \sum_{i=1}^{n} 2S_{zi} \delta(r-r_i) \]

are given by [3]:

\[ <q(r)> = \sum_{i,j}^{m} (P_{ij} + Q_{ij}) \omega_i^* (r) \omega_j (r) \]  

(22)

and

\[ <\rho(r)> = \sum_{i,j}^{m} (P_{ij} - Q_{ij}) \omega_i^* (r) \omega_j (r) \]  

(23)

where \( r_i \) is the position of electron \( i \), \( \delta \) is the Dirac delta function and \( S_{zi} \) is the operator for the z-component of the spin of electron \( i \).
3. **The UHF Method with Spin Annihilation**

Fundamental theoretical objections may be levelled at the UHF method on the grounds that while the wavefunction is an eigenfunction of the $S_z$ operator it is not in general an eigenfunction of the $S^2$ operator. This deficiency arises from the fact that the $\alpha$- and $\beta$-spin electrons are permitted to occupy different spatial orbitals, and it is generally found to result in overestimates of the calculated spin properties. An explanation for the deficiency has been given by Meyer [4] who pointed out that a major source of error which can cause an enlargement of the effective spin density by 100% is the implied coupling between polarization interactions and part of the pair correlations in the expansion of $\psi_{UHF}$ up to second order. Further, the analysis by Nakatsuji et al [5] of the UHF wavefunction in terms of configuration interaction language yielded the conclusion that the correlation effects included in $\psi_{UHF}$ are extremely limited and are mainly due to one type of singly excited configuration.

A partial solution to the problem of overestimated spin densities was suggested by Löwdin [6] who proposed the use of projection operators. The UHF wavefunction may be written as a linear combination of components of various multiplicities:

$$\psi_{UHF} = \sum_{k=0}^{q} C_{s+k} \phi_{s+k}$$

(24)

where $s = \frac{1}{2}(p-q)$ is the spin state required and the $\phi_{s+k}$ are pure spin states:

$$S^2\phi_{s+k} = (s+k)(s+k+1) \phi_{s+k}.$$ 

The projection operator

$$A_k = S^2 - k(k+1)$$

(25)
when applied to $\Psi_{\text{UHF}}$ will annihilate the component of multiplicity $(2k+1)$ in $\Psi_{\text{UHF}}$. The process may be applied to $\Psi_{\text{UHF}}$ repeatedly to remove all the unwanted components. Thus an operator of the form:

$$O_s = \prod_{k=s+1}^{s+q} \frac{(S^2-k(k+1))}{(s(s+1)-k(k+1))}$$  \hspace{1cm} (26)

may be used to select the required pure spin state of multiplicity $(2s+1)$. A serious objection to the so-called Projected UHF (PUHF) method [7,8] is that the projection is performed after the variation. Therefore the PUHF wavefunction does not minimize the molecular energy and its suitability for spin density calculations has been seriously questioned [9].

A more satisfactory procedure is to apply the variational method to the wavefunction $O_s \Psi_{\text{UHF}}$ as recommended by Löwdin [10]. However this wavefunction is a linear combination of many determinants and this makes the Extended Hartree-Fock (EHF) method of variation after projection an extremely difficult procedure. Several authors including Harriman and Sando [11,12], Goddard [13-15] and Kaldor [16-18] have however developed successful approaches to the problem. Even so, Meyer has pointed out that optimisation of the projected UHF wavefunction may not be desirable because this function also treats pair correlation effects incorrectly [4].

The difficulties inherent in the practical application of $O_s$ led Amos and Hall [2] to suggest the use of the single annihilator $A_{s+1}$ instead of $O_s$. This approximation may be justified by the demonstration that the major unwanted component in $\Psi_{\text{UHF}}$ is that with spin $(s+1)$, the states of higher multiplicity decreasing rapidly in importance [2,19]. It has been shown that this approximation may however break down as the multiplicity of the required state or the total number of electrons increases [5,19].

Although the wavefunction is now simplified to $A_{s+1} \Psi_{\text{UHF}}$ the complexities
involved in the variational procedure are prohibitive for most practical applications. For this reason the less rigorously sound procedure of applying the annihilator \( A_{s+1} \) to the wavefunction which minimises the UHF energy is generally used.

The energy after annihilation of the (s+1) spin state is given by

\[
E_{\text{UHFAA}} = \frac{\langle A_{s+1}|H|A_{s+1}\psi_{\text{UHF}} \rangle}{\langle A_{s+1}\psi_{\text{UHF}}|A_{s+1}\psi_{\text{UHF}} \rangle} \tag{27}
\]

As the \( S^2 \) operator commutes with the spinless Hamiltonian, Equation (27) becomes:

\[
E_{\text{UHFAA}} = \frac{\langle \psi_{\text{UHF}}|H|A^2_{s+1}\psi_{\text{UHF}} \rangle}{\langle \psi_{\text{UHF}}|A^2_{s+1}\psi_{\text{UHF}} \rangle} \tag{28}
\]

If the approximation that \( A_{s+1} \) is idempotent is assumed then Equation (28) simplifies to [2,3]:

\[
E_{\text{UHFAA}} = \frac{\langle \psi_{\text{UHF}}|H|A_{s+1}\psi_{\text{UHF}} \rangle}{\langle \psi_{\text{UHF}}|A_{s+1}\psi_{\text{UHF}} \rangle} \tag{29}
\]

which may be more fully expressed as [20]:

\[
E_{\text{UHFAA}} = E_{\text{UHF}} - x^{-1}[\text{Tr}((PSQSP+QSPQ-QSPO\text{QSP})h) + \sum_{stuv} (PSQSP+QSPQ-QSPO\text{QSP})_{st}(P+Q)_{uv}\langle st|uv \rangle - \sum_{stuv} ((PSQSP)_stP_{uv}+(QSPQ)_stQ_{uv} - (PSQ+QSP)_st(P+Q)_{uv}P_{stQ_{uv}} + (PSQ)_st(QSP)_{uv}\langle su|vt \rangle ] \tag{30}
\]

where \( x = \frac{1}{4}(p-q)^2 + \frac{1}{4}(p+q) - (s+1)(s+2) - \text{Tr}(PSQS) \)
The charge and spin density functions are given by [3]:

\[
\langle q(r) \rangle = \sum_{u,v} (J_{uv} + K_{uv}) \omega_u^*(r) \omega_v(r) \quad (31)
\]

\[
\langle \rho(r) \rangle = \sum_{u,v} (J_{uv} - K_{uv}) \omega_u^*(r) \omega_v(r) \quad (32)
\]

where the matrix \( J \) may be written

\[
M^2 J = [A^2 + pq - q + (3 - 2A - n + 2Tr(PSQS))] Tr(PSQS) - 2Tr(PSQSPQS) \]

\[
+ [p - Tr(PSQS)] Q
\]

\[
+ QSPSQ + [n - 3 + 2A - 4Tr(PSQS)] PSQP
\]

\[
+ [1 - p - A + 2Tr(PSQS)] [PSQ + QSP]
\]

\[
- 2[PSQPSQ + QSPSQP] + 4PSQSPQS \quad (33)
\]

\[
A = q - 2(s+1)
\]

and

\[
M^2 = A^2 + pq + [2 - 2A - n + 2Tr(PSQS)] Tr(PSQS) - 2Tr(PSQSPQS)
\]

is the normalisation factor. The matrix \( K \) is given by a similar expression with \( P \) and \( p \) interchanged with \( Q \) and \( q \) respectively. It should be noted that while \( S^2 \) commutes with \( q(r) \), \( S^2 \) and \( \rho(r) \) do not commute and, therefore, the spin density expectation value is derived from

\[
\langle \rho(r) \rangle = \frac{\langle A_{s+1} \Psi_{UHF} | \rho(r) | A_{s+1} \Psi_{UHF} \rangle}{\langle A_{s+1} \Psi_{UHF} | A_{s+1} \Psi_{UHF} \rangle}. \quad (34)
\]

Although a number of objections have been raised against the UHF method after single annihilation [9,21] it has been found to give an adequate description of the spin properties of radicals for most chemical purposes, unless the expectation value of the \( S^2 \) operator is still unreasonably large.
after annihilation [22]. When coupled with the straightforwardness of application and the retention of a conceptually simple physical model it is considered to be a valuable tool for practical application to radicals of chemical interest.

4. The Use of Gaussian Functions in Molecular Calculations

In ab initio Hartree-Fock calculations on molecules, various kinds of integral have to be evaluated but by far the most numerous are the two-electron integrals:

\[ \int \omega_1^*(1) \omega_j^*(2) [1/r_{12}] \omega_k(1) \omega_l(2) d\tau_1 d\tau_2. \]

With m basis functions there are \(-m^4/8\) such integrals after allowing for the symmetry of the \(r_{12}\) operator, and while molecular symmetry may considerably reduce this number the two-electron integral evaluation is usually the most time-consuming step of a calculation. The choice of basis functions for a calculation will therefore be influenced both by the need for a good approximation to the wavefunction and also by the limited computing time available. In calculations of spin properties, the quality of the wavefunction, especially close to the nuclei, is particularly important.

The Slater type orbital (STO) may be written as:

\[ \chi(n,\xi,r,\theta,\phi) = N(n,\xi) r^{n-1} \exp(-\xi r) Y_{lm}(\theta,\phi) \]

where 

- \(N(n,\xi)\) is the normalisation constant
- \(n\) is a positive integer
- \(Y_{lm}(\theta,\phi)\) are normalised spherical harmonics.
The STO forms an adequate representation of the atomic function, particularly in the bonding region, but the multi-centre two-electron integrals are particularly difficult to evaluate, generally requiring numerical integration, which proves to be a considerable disadvantage. Nevertheless, a large number of ab initio calculations on molecules have been performed using both minimal and extended basis sets of STOs.

The Gaussian type function (GTF) may be written as:

\[
X(n, \alpha, r, \theta, \phi) = N(n, \alpha) r^{n-1} \exp(-\alpha r^2) Y_{lm}(\theta, \phi)
\]  

(36)

where the notation is similar to that used above for the STO. The advantage of using GTFs was first pointed out by Boys [23]. They have the important property that for a multi-centre integral over Gaussians a transformation can be found which reduces the integral to a one-centre problem. As a result, relatively straightforward analytical formulae can be obtained for all the integrals required in molecular calculations, and this has led to the extensive usage of Gaussians in quantum chemistry. The advantage gained by the ease of integral evaluation is however somewhat offset by the inferior description of an atomic function given by the GTF compared to the STO. This deficiency results in the need to use a larger number of Gaussians and thus the number of integrals to be evaluated is increased.

In this work, the atomic basis functions are represented by linear combinations of GTFs [24]:

\[
\omega_i = \sum_j d_j X_j
\]  

(5)

The use of such "contractions" of Gaussians not only reduces the number of molecular integrals to be stored, but also provides one way of compensating for the poorer description by Gaussians of atomic orbitals and their cusp properties within a reasonably small basis set. In general, contractions
of five to ten Gaussians are found to be sufficient for first row elements.

The parameters of the Gaussian contractions, $\alpha_j$ and $d_j$, are usually
chosen by one of two methods. In one approach, the orbitals are optimised
by minimisation of the atomic SCF energy [25-31]. The resulting atomic
SCF orbitals may be used in molecular calculations, although such orbitals
are undoubtedly not optimal for the molecular systems to which they are
applied. However optimisation of the basis set in the molecule requires
an enormous effort for all but the simplest systems. Another approach
involves least-squares fitting of Gaussian expansions to Slater type
orbitals [32-37]. An unfortunate aspect of both methods is the problem
of multiple local minima, which can become particularly troublesome as the
number of parameters increases. No guarantee can be given that the true
minimum has been reached, but empirical checks can be performed, for
example by scanning around the minimum position or by using a different
starting point.

In the least-squares fitting of Gaussian expansions to ionic SCF
orbitals expressed as linear combinations of STOs referred to in Section
7, the error function:

$$
\varepsilon = \int (\omega_G - \omega_s)^2 \, d\tau
$$

was minimised with respect to the parameters $\alpha_j$ and $d_j$ in the Gaussian
expansion of the radial part of an orbital:

$$
\omega_G = \sum_j d_j r^{n-1} \exp(-\alpha_j r^2)
$$

subject to the normalisation condition

$$
\int \omega_G^2 \, d\tau = 1 .
$$

$\omega_s$ represents one of the standard functions of Clementi [38] expressed as
A regression method, programmed in ALGOL 60 [39], was used in an attempt to reduce the likelihood of chance minimisation into a local minimum. Crudely the error function is evaluated many times over varying ranges of the parameters $d_j$ and $a_j$ such that $e$ is always reduced. Despite the considerable computational effort expended in an attempt to find the true minimum, no such guarantee can be given.

5. The Calculation of Hyperfine Coupling Constants

The spin Hamiltonian involving electron-nuclear spin-coupling in a molecule may be expressed as:

$$H = g_e \beta_e \sum_i \sum_N g_N \beta_N S_i . T_N . I_N$$

(39)

where $S_i$ is the spin of the $i^{th}$ electron

$I_N$ is the spin of the $N^{th}$ nucleus

$g_e$ is the electronic g-factor

$g_N$ is the nuclear g-factor

$\beta_e$ is the Bohr magneton

$\beta_N$ is the nuclear magneton

and $T_N$ is the hyperfine coupling tensor for nucleus $N$ which is of diagonal form in the principal axis representation. The tensor $T_N$ can be separated into two components:

$$T_N = \frac{8}{3} \pi \delta(r_N) I + T'_N$$

(40)

where $I$ is the unit tensor, $T'_N$ is a traceless tensor representing the anisotropic contribution to $T_N$, and $(8\pi/3)\delta(r_N)$ represents the isotropic
contribution. Hence

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$$

where

$$\mathcal{H}_1 = \frac{8\pi}{3} g_\beta e \sum_i \sum_N g_{N_i} \delta(r_N) \, S_i \cdot I_N$$  \hspace{1cm} (41)$$

$$\mathcal{H}_2 = g_\beta e \sum_i \sum_N g_{N_i} S_i \cdot T_N' \cdot I_N$$  \hspace{1cm} (42)$$

The Fermi contact term $\mathcal{H}_1$ represents the energy of the nuclear moments in the magnetic fields produced at the nuclei by the electric currents associated with the electrons. The contact interaction can only occur when the electron has a finite probability of being at the nucleus, and so the isotropic coupling constant gives an indication of the s-orbital character of the electron. The isotropic hyperfine coupling constant for nucleus $N$ may be expressed as:

$$a(N) = \frac{8\pi}{3} g_\beta e g_{Ni} \rho(r_N)$$  \hspace{1cm} (43)$$

where $\rho(r_N)$ is the spin density function at nucleus $N$.

The anisotropic or dipolar term may be written as

$$\mathcal{H}_2 = -g_\beta e \sum_i \sum_N g_{N_i} \left[ \frac{S_i \cdot I_N}{r_N^3} - \frac{3(S_i \cdot r_N) (I_N \cdot r_N)}{r_N^5} \right]$$  \hspace{1cm} (44)$$

and represents the quantum mechanical equivalent of classical dipolar coupling between the electronic and nuclear magnetic moments. In situations where molecular tumbling or molecular collisions are sufficiently rapid, the anisotropic tensor is averaged to zero. The elements of $T_N'$ may be written:

$$T_N'(kl) = (r_N^2 \delta_{kl} - 3kl)/r_N^5$$  \hspace{1cm} (45)$$
where \( k, l = x_N, y_N \) or \( z_N \) and writing the matrix of integrals of \( T_{N'}^{(kl)} \) over the basis functions \( \omega_i \):

\[
[H_N^{(kl)}]_{ij} = \int \omega_i^* T_{N'}^{(kl)} \omega_j \, d\tau ,
\]

(46)

then the anisotropic hyperfine coupling tensor for nucleus \( N \):

\[
B_{kl}^{(N)} = -g_\text{e}_\text{e}_N^2 g_\text{e}_N^2 \text{Tr} [H_N^{(kl)}(P-Q)]
\]

(47)

where \( (P-Q) \) is the spin density matrix describing the spin distribution of the unpaired electron. \( B(N) \) can be diagonalised to yield the anisotropic components \( B_X(N), B_Y(N) \) and \( B_Z(N) \) along the principal axes \( X, Y \) and \( Z \). Anisotropic coupling constants give an indication of the \textit{p} (or \textit{d}) -orbital character of the unpaired electron.

In addition, the anisotropic hyperfine coupling constant

\[
A_i^{(N)} = a(N) + B_{i}^{(N)} \quad i = X, Y \text{ or } Z
\]

is often used.

6. Vibronic Contributions to Hyperfine Coupling Constants

In some radicals a marked dependence of the hyperfine couplings on temperature has been noted. This effect is believed to arise from a vibrational contribution augmenting the hyperfine coupling constant of the rigid radical [40]. This vibrational effect is generally considered to be relatively small except in radicals where only an indirect coupling mechanism is operative in the rigid system but where direct coupling is introduced by a particular molecular vibration, for example, the methyl radical [40,41]. Such radicals usually have the unpaired electron virtually
localised in a p- or d-type orbital and so the effect on the anisotropic coupling constants will be small. Thus only vibrational corrections to the isotropic coupling constants will be considered.

The estimation of the vibrational contributions to hyperfine coupling constants introduces no new principles into \textit{ab initio} calculations [42]. It involves the calculation of total energies and hyperfine coupling constants at non-equilibrium nuclear configurations. Beveridge and Miller [43] have considered the theoretical basis for estimating these contributions using the INDO method.

It is assumed that the zero-point energy vibrational modes execute simple harmonic motion:

\[
\psi_{\text{vib}} = (\alpha/\pi)^{1/4} \exp(-\alpha x^2/2) \tag{48}
\]

where \(x\) is the displacement from the equilibrium configuration along a normal co-ordinate, and

\[
\alpha = 2 \mu E_{\text{vib}}^0 \tag{49}
\]

where \(\mu\) is the reduced mass and \(E_{\text{vib}}^0\) is the zero-point energy for the vibration:

\[
E_{\text{vib}} = (v+1)(k/\mu)^{1/2} \quad v = 0,1,2 \ldots \tag{50}
\]

\(k\) being the force constant of the vibration defined by

\[
E = E_0 + \frac{1}{2} kx^2 \tag{51}
\]

\(E_0\) and \(E\) are the UHF energies at zero and non-zero displacements respectively.

The general variation of the isotropic hyperfine coupling constant, \(a\), with \(x\) is
\[ a = \sum_{n=0}^{\infty} C_n x^n \]  

(52)

If it is assumed that terms with \( n > 2 \) can be neglected, and noting that for an harmonic oscillator terms with odd powers of \( x \) disappear, then Equation (52) reduces to:

\[ a = C_0 + C_2 x^2 \]  

(53)

where \( C_0 \) is the coupling constant calculated at the equilibrium nuclear configuration. Then \( \langle a \rangle \), the vibrationally corrected hyperfine coupling constant, is the mean value of the calculated hyperfine coupling constants over the amplitude of the normal co-ordinate sampled during the execution of the zero-point vibration, as is given by

\[ \langle a \rangle = \langle \psi_{\text{vib}} | a | \psi_{\text{vib}} \rangle = C_0 + C_2/(2\alpha) \]  

(54)

The estimates obtained from Equation (54) may not be satisfactory in situations where the simple harmonic approximation is unreasonable, for example with large displacements or small force constants.

7. The Structure of the Borane Radical Anion \( \text{BH}_3^- \)

The \textit{ab initio} UHF method in the LCAO-MO approximation with spin annihilation [2] has met with considerable success in reproducing experimentally determined hyperfine coupling constants for small radicals of chemical interest. In particular, its reliability when used with minimal basis sets of SCF atomic orbitals has been tested in the isoelectronic series of radicals, \( \text{NH}_3^+ \), \( \text{CH}_3 \), and \( \text{BH}_3^- \) [42,44]. It was found that this isoelectronic series exhibits a marked gradation in optimized hydrogen
atomic orbital exponents, with values of $\xi_H$ equal to 1.15, 1.40 and 1.60 for $BH_3^-$, $CH_3$ and $NH_3^+$ respectively, which has been rationalized in terms of an excess charge effect [45,46].

While agreement with experiment was good for the ammonia radical cation, $NH_3^+$ [42] and satisfactory for the methyl radical, $CH_3$ [44], the borane radical anion, $BH_3^-$ was calculated to be bent by 9 degrees with an associated very large isotropic hyperfine coupling constant $a(^{11}B)$ [44], in contrast to that inferred from experiment [47,48]. The E.S.R. spectra assigned to the borane radical anion were characteristic of only isotropic hyperfine interactions which were independent of temperature between 80 K and 300 K and were similar in magnitude to the analogous hyperfine coupling constants of $CH_3$ and $NH_3^+$, giving similar U-values [49]. Since electronegativity considerations, reiterated by Pauling [50], lead to the prediction that $BH_3^-$ would be bent [51] in contrast to $CH_3$ and $NH_3^+$, it was suggested that the apparent planarity of $BH_3^-$ inferred from the e.s.r. data might be caused by environmental effects from the interaction of the radical anion with its host lattice, and various cationic environments for the radical were simulated [44]. In fact, no physically realistic environment used achieved the required planarity, though in some cases a tendency in the right direction was noted.

In an effort to obtain a chemically satisfactory description of the $BH_3^-$ radical, further ab initio UHF calculations have been performed with basis sets containing orbitals appropriate for the boron anion, $B^-$. Such an approach was initially suggested by the result of a Mulliken population analysis [52] in the previous calculations on $BH_3^-$ [44] where atomic SCF orbitals were used. The analysis indicated that virtually the whole net negative charge of the radical resides on the boron atom, so that the inclusion of orbitals for the boron anion in the basis set was considered
appropriate.

Previous calculations were performed with (9s,5p) Gaussian expansions of atomic SCF orbitals obtained by Huzinaga [29]. To facilitate comparison, (9s,5p) Gaussian expansions for B$^-$ were obtained by least-squares fitting [53] to Clementi's Slater expansions of the SCF orbitals for B$^-$ ($^3P$) [38]. These orbitals are given in Table I and are labelled SCFLS (self-consistent field least-squares). To check the suitability of SCFLS type orbitals for molecular calculations, (9s,5p) Gaussian expansions for the boron atom were obtained similarly from Clementi's SCF orbitals for B($^3P$) and were employed in calculations on BH$_3^-$ with the result that the optimised bond length, bending angle and hydrogen orbital exponent were identical with those obtained previously [44], while the total energy after annihilation was slightly higher (by 0.021 Hartrees), as expected.

Initially, the BH$_3^-$ radical was re-optimised using the set of anionic SCFLS orbitals at boron (Table II). The resulting structure is now a planar one, with R(B-H) increased from 2.35 to 2.45 Bohrs and $\xi_H$ from 1.15 to 1.25 due presumably to the greater spatial extension of the boron anion. The isotropic hyperfine coupling constants calculated for the rigid radical at the energy minimum are modified by inclusion of the estimated [42] normal zero-point vibrational corrections, to $a(^{11}B) = 37.2$ G, $a(^1H) = -10.0$ G, with an estimated force constant $k = 0.0075 \tau^{-2}$. Inclusion of the environment of six unit positive charges with lithium 2s atomic orbitals (unit cell 8.22 Bohrs), which induced a decrease in the bending angle in the earlier calculations [44], causes a decrease in the out-of-plane force constant in this case, as may be seen from Table II. The calculations are however unsatisfactory in that the optimised total energy for the isolated radical is significantly
higher (by 0.218 Hartrees) than that found previously using atomic SCF orbitals for boron. Evidently the boron anion orbitals give an improved description of the structurally important regions in the radical but are less successful than the atomic boron orbitals in describing the energetically important regions.

In an attempt to clarify the rôle of the B\textsuperscript{-} orbitals in determining the structure of BH\textsubscript{3}\textsuperscript{-}, a single calculation was performed on the planar radical with an extended basis set consisting of both the atomic and anionic sets of boron orbitals as well as the usual 1s functions for hydrogen, \( \xi_H = 1.15 \). Analysis of the resulting molecular orbital coefficients leads to the qualitative conclusion that while the atomic boron orbitals are involved in the core and B-H bonding regions of the radical, the non-bonding \( \pi \)-MO which accommodates the unpaired electron is represented almost exclusively by the more diffuse anionic 2p-function with the appropriate orientation.

In order to put this conclusion to the test, further \textit{ab initio} UHF calculations were performed on BH\textsubscript{3}\textsuperscript{-} using atomic orbitals at boron except for the 2p orbital perpendicular to the molecular plane for which the appropriate anionic 2p function was used, as indicated in the calculation above. Since the core and B-H \( \sigma \)-bonding orbitals remain unchanged from the previous calculations \cite{44}, where optimised values of \( R(B-H) = 2.35 \) Bohrs and \( \xi_H = 1.15 \) were determined, re-optimisation of these parameters was not considered to be necessary. The results of these calculations at various angles of bending show that the BH\textsubscript{3}\textsuperscript{-} radical is now calculated to be planar as inferred experimentally, and that the total energy after annihilation is lowered from -26.3241 \cite{44} to -26.3389 Hartrees. The estimated \cite{42} force constant for the zero-point normal vibrational mode is smaller than those found previously for CH\textsubscript{3} and NH\textsubscript{3}\textsuperscript{+},
as expected:

\[ k(BH_3^-) = 0.0255 \tau^{-2} \]
\[ k(CH_3) = 0.0405 \tau^{-2} \]
\[ k(NH_3^+) = 0.1136 \tau^{-2} \]

and the isotropic hyperfine coupling constants calculated for the rigid radical: \( a(^{11}B) = 16.68 \text{ G} \), \( a(^1H) = -14.90 \text{ G} \), are modified by inclusion of the zero-point out-of-plane vibrational corrections, to:

\[ a(^{11}B) = 34.4 \text{ G} \]
\[ a(^1H) = -12.8 \text{ G} \]

in satisfactory agreement with the experimental values [48] of

\[ a(^{11}B) = (+) 20.7 \text{ G} \]
\[ a(^1H) = (-) 15.1 \text{ G}. \]

The geometry change from pyramidal to planar in BH$_3^-$ can be understood qualitatively in terms of the repulsive effect of the unpaired (non-bonding) electron. The volume requirement of a lone pair of electrons has been demonstrated to be less than that of a covalently bound proton [54] in organic conformational analyses, and recent \textit{ab initio} calculations with localised molecular orbitals [55] show that the centroid of charge for a lone pair is always closer to the atom than for a bonding electron pair. A similar situation arises with the single non-bonding electron in BH$_3$: in the previous calculations the unpaired electron was held relatively close to the boron nucleus, causing considerable interelectronic repulsion with the B-H \( \sigma \)-bonding electrons. This could only be relieved by bending the molecular framework so that the bonds were directed away from the non-bonding electron in a pyramidal conformation.
tion. In the present calculations the more diffuse character of the anionic non-bonding orbital permits the unpaired electron to be held further away from the boron nucleus. Consequently the interelectronic repulsion with the bonding electrons is reduced and the radical remains planar. This interpretation receives support from an analysis of the total molecular energy of the BH$_3^-$ radical which reveals that in the previous calculations the interelectronic repulsion component decreased appreciably on bending, whereas in the present calculations bending causes a sharp increase in this component. The interelectronic repulsion energy appears to exert a decisive influence on the balance between the nuclear repulsion energy and the total electronic energy in these calculations on BH$_3^-$.

Having postulated the dependence of the molecular geometry and hyperfine properties of BH$_3^-$ on the spatial extension of the unpaired molecular orbital, it was of considerable interest to make a systematic study of the molecular geometry as a function of the unpaired orbital size. To this end, further ab initio UHF calculations with spin annihilation were performed on both the planar and the 2 degrees bent conformations of BH$_3^-$ over a range of compositions for the unpaired MO defined by:

$$\psi_\pi = N[\omega(2p^a) + \beta\omega(2p^-_\pi)]$$

(55)

with $$0 \leq \alpha \leq 1$$

and $$\beta = \pm(1 - \alpha),$$

where $\omega(2p^a)$ and $\omega(2p^-_\pi)$ refer respectively to the atomic and anionic boron 2p orbitals of $\pi$-symmetry. The results of the calculations are presented in Figure 1. The total energy of the planar conformation and a qualitative estimate for the 'radius' of the unpaired MO, given by the axial distance at which the radial distribution function is a maximum, are both plotted
against the parameter $\beta$. It will be seen that while the 'radius' is larger than circa 3.7 Bohrs the BH$_3^-$ radical remains planar, but for smaller values a pyramidal structure is favoured. The energy minimum occurs at a 'radius' rather larger than that of a purely anionic orbital ($\alpha = 0$) and corresponds to a planar geometry, as inferred experimentally. These results appear to support the electron-repulsion explanation given above.

In an attempt to determine the optimal form for the unpaired MO a single calculation was performed on the planar radical with both the atomic and anionic boron 2$p_\pi$ orbitals included in the basis set. The resulting orbital was predominantly anionic in character with coefficients $\alpha = 0.17$, $\beta = -1.16$. Using an unpaired orbital of this form calculations were then performed on the radical at three angles of bending to permit an estimation of the out-of-plane zero-point force constant. The results are included in Table III and it will be seen that the vibrationally corrected hyperfine couplings:

$$a^{(11}\text{B}) = 30.0 \text{ G}$$
$$a^{(1}\text{H}) = -12.1 \text{ G},$$

are in slightly improved agreement with the experimental values.

Extension to CH$_3$ and NH$_3^+$

The results of previous ab initio UHF calculations on CH$_3$ were satisfactory [44], and the agreement was good in the case of NH$_3^+$ [42]. However it was of considerable interest to discover whether significant improvements to the calculated hyperfine couplings could be obtained by optimisation of the unpaired electron orbital in a manner similar to that just described for BH$_3^-$. 

-98-
Gaussian expansions for the SCFLS 2p orbitals of C\(^+\)(\(^2\)P), C\(^-\)(\(^4\)S), N\(^+\)(\(^3\)P) and N\(^-\)(\(^3\)P) were constructed as described in the case of boron. These orbitals are included in Table I. Calculations with the atomic, anionic and cationic 2p\(_\pi\) orbitals included in the basis set indicate that the non-bonding \(\pi\)-orbital in both radicals is predominantly atomic in character. By contrast with BH\(_3^-\), the unpaired MO in CH\(_3\) contains relatively small proportions (< 20%) of the cationic and anionic functions, and these proportions are smaller still (< 12%) in the case of NH\(_3^+\). The results of the calculations on CH\(_3\) and NH\(_3^+\) are included in Table III. The vibrationally corrected isotropic hyperfine coupling constants for CH\(_3\) are seen to be in slightly improved agreement with experiment, due principally to the increased magnitude of the zero-point out-of-plane force constant. The total energy is also slightly lowered (by 0.0011 Hartrees) and the value of \(a(\text{\(^{13}\)C}) = 26\) G calculated for the rigid methyl radical is in good agreement with Fessenden's experimental estimate of 28 G [41].

The hyperfine couplings calculated for the ammonia radical cation differ little from the results of previous \textit{ab initio} UHF calculations, as is to be expected since the earlier results were already in good agreement with the experimental values. (The vibrational corrections to the isotropic hyperfine couplings in NH\(_3^+\) given in [42] are slightly in error and have been amended for their inclusion in Table III.) The energy lowering in this radical amounts to 0.0006 Hartrees.

Inspection of Table III reveals that the calculated central atom U-values are all of the correct magnitude but that the experimentally observed order is not reproduced correctly. Specifically, while the theoretical value for U(\(^{14}\)N) is relatively close, both U(\(^{13}\)C) and U(\(^{11}\)B) are calculated to be too large. This phenomenon is attributable to environmental effects, and such effects are likely to be greatly magnified in this series of
radicals owing to the importance of the out-of-plane vibration. The usual molecular interaction forces arising from a neutral host lattice are expected to increase the force constants of a trapped radical compared with the corresponding isolated radical. Thus the methyl radical trapped on Vycor glass or in a krypton matrix should have a higher out-of-plane force constant and a smaller value for \( U(^{13}\text{C}) \) than that calculated here for the isolated species. Superimposed upon this effect will be additional interactions if the lattice and the radical are both charged, as is the case for \( \text{BH}_3^- \) formed in trimethylammonium borohydride, and for \( \text{NH}_3^+ \) in ammonium perchlorate. Thus if the lattice environment around \( \text{BH}_3^- \) increases still further the out-of-plane force constant then the observed value of \( U(^{11}\text{B}) \) will be smaller than that calculated here for the isolated \( \text{BH}_3^- \) radical. In the case of \( \text{NH}_3^+ \), both types of interaction with the lattice environment are expected to be small, due to the relatively large out-of-plane force constant in the isolated species, and to the relatively unpolarisable nature of the electronic charge cloud. The calculated value of \( U(^{14}\text{N}) \) is therefore expected to be reasonably close to the observed value.

The consideration of molecular environment given above may also be used to understand the temperature independence of the width of the \( \text{BH}_3^- \) ESR spectrum [48]. If the out-of-plane force constant is suitably large due to environmental effects, then for small displacements from planarity the results in Table III show that the absolute magnitudes of \( a(^{11}\text{B}) \) and \( a(^1\text{H}) \) change in opposite directions, such that the spectrum width:

\[
3|a(^{11}\text{B})| + 3|a(^1\text{H})|
\]

may remain approximately constant over a large temperature range.

It may be concluded that the results of the \textit{ab initio} UHF calculations
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<th>Gaussian exponent</th>
<th>Expansion coefficient</th>
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TABLE II: Results for the borane radical anion using SCF LS B^- (^3P) orbitals.

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* - with environment of 6 unit positive charges and Li 2s orbitals (unit cell = 8.22 a.u.)
FIGURE 1. The Geometry of BH$_3^-$ as a Function of the Spatial Extension of the Unpaired Orbital.
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<th>TOTAL ENERGY (ASA)</th>
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**TABLE III:** Hyperfine Properties of BH₃⁻, CH₃ and NH₃⁺ using optimised μ-orbitals.
with spin annihilation for the hyperfine coupling constants and molecular structures of the isoelectronic radicals BH₃⁻, CH₃ and NH₃⁺ are in satisfactory agreement with the experimentally inferred values, and also provide useful information about the effects of molecular environment on the hyperfine coupling constants in the ESR spectra of these radicals.

8. The Structure of the Diborane Radical Anion B₂H₆⁻

The electronic structures and molecular geometries of ethane and diborane have been the subject of extensive ab initio SCFMO calculations. However, much less attention has been paid to the intermediate thirteen valence electron radicals C₂H₆⁺ and B₂H₆⁻. Pople and co-workers [56,57] have recently performed ab initio UHF calculations on the ethane cation involving a thorough geometry search and they concluded that this radical remains in a staggered (D₃d) conformation similar to ethane, rather than moving to, or towards, the bridged (D₂h) diborane structure. The radical was calculated to have a longer C-C bond than ethane due to the ionization of a 3a₁g C-C σ-bonding electron, and the methyl groups were found to be flattened out almost to planarity.

Unfortunately, very little experimental evidence regarding the structure of C₂H₆⁺ is available for comparison with these theoretical predictions. In fact, quite the most potentially useful experimental information is provided by the ESR spectrum of the isoelectronic B₂H₆⁻ radical [58], which was prepared by electron addition to diborane and matrix isolation in argon at 4 K. However no attempt was made to use the results as an aid to understanding the structure of the anion. The ESR spectrum of B₂D₆⁻ yielded the parameters:
\[ A_{//}^{(11B)} = 24.5 \pm 0.5 \text{ G} \]
\[ A_{\perp}^{(11B)} = 0 \pm 2.5 \text{ G} \]

whence \[ a_{\text{iso}}^{(11B)} = 8.2 \pm 2 \text{ G} \]
and \[ B_{//}^{(11B)} = 16.3 \pm 2 \text{ G} \]

Due to the poor resolution of the ESR spectrum for \( B_2H_6^- \), the proton coupling can only be gauged approximately. It appears that the proton coupling is nearly isotropic, with

\[ A_{//}^{(1H)} \approx A_{\perp}^{(1H)} = 0 \pm 15 \text{ G} \]

and using a Du Pont Curve Resolver a reasonable fit was obtained for \( a_{\text{iso}}^{(1H)} = 7 \text{ G} \), assuming either five or seven equally spaced lines.

There are two reasonable extreme structures for this anion: one is that calculated for \( C_2H_6^+ \) [56], namely the staggered form with \( D_{3d} \) symmetry and a single B-B \( \sigma \)-electron; the other is the symmetrically bridged \( D_{2h} \) structure of the parent molecule.

An approach to the former structure may be made by considering the interaction between a BH\(_3^-\) radical and a BH\(_3\) molecule. BH\(_3\) is certainly a trigonal planar species and the results of ESR studies [47,48] and the latest UHF calculations (Section 7) on BH\(_3^-\) support a trigonal planar structure for this radical. Thus the \( D_{3d} \) adduct should also have near local planarity at each BH\(_3\) unit, and to a first approximation the ESR spectrum should be close to that for two BH\(_3^-\) units with hyperfine parameters just half those of a single unit. From the isotropic coupling constants of BH\(_3^-\) [48]:

\[ a_{\text{iso}}^{(11B)} = 20.7 \text{ G} \]
\[ a_{\text{iso}}^{(1H)} = 15.1 \text{ G} \]

the values predicted for \( B_2H_6^- \) are:
Both values are close to the experimental results for $B_2H_6^-$. Furthermore, dividing the experimental $2B$ value of 16.3 G by the theoretical atomic $2B^o$ value of 38 G [59] gives a $\pi$-spin density at each boron atom of circa 43 per cent, which means that, within the error of this calculation, the unpaired electron is effectively shared between the two $2p_z$ atomic orbitals of boron, as required by this model. The nearly isotropic proton coupling can be rationalised if the $BH_3$ units rotate about the $D_{3d}$ ($z$) axis, and the values of $A_x$ and $A_y$ average fortuitously to a value very close to $A_z$, which is approximately equal to $a_{iso}(^1H)$. Thus every facet of the results is well accommodated by this simple model.

The alternative bridged ($D_{2h}$) model for $B_2H_6^-$ also appears to be acceptable, however. Here, the extra electron is accommodated in the outer $1b_{2g}$ orbital of the parent $B_2H_6$ molecule. This is an antibonding combination of the $2p_z$ boron orbitals, so the experimental $^{11}B$ hyperfine tensor is again well accommodated. The isotropic coupling to the four in-plane protons will again be expected to fall in the region of half the value for $BH_3^-$, but the bridging protons should exhibit a different coupling although this should also be small since they lie in a nodal plane of the $1b_{2g}$ orbital.

It may be concluded from the above discussion that the bridged model is a possible structure but rather less probable than the staggered model. Thus, when the excess electron is initially accepted by $B_2H_6$ into the $1b_{2g}$ orbital, a distortion from $D_{2h}$ symmetry occurs to minimise the strongly antibonding effect of the extra electron. As this distortion proceeds, the energies of the $b$ and $a$ orbitals switch over so that the half-filled level becomes $a_g$, transforming ultimately into the $3a_{1g}$ level of the
staggered $D_{3d}$ molecule.

In order to probe these alternative structures more rigorously, *ab initio* UHF calculations with spin annihilation have been performed on the bridged ($D_{2h}$), staggered ($D_{3d}$) and eclipsed ($D_{3h}$) structures for $B_2H_6^-$ suggested by the qualitative discussion above [60]. Recent calculations on $BH_3^-$ (Section 7) predicted isotropic coupling constants quite close to those observed, but the use of an anionic SCF $2p_\pi$ orbital was necessitated in order to correctly describe the localisation of the negative charge on the boron atom, and to reproduce the experimentally deduced planar geometry. In $B_2H_6^-$ however, the negative charge must be shared at least between the two boron atoms and the need for such anionic orbitals should consequently be greatly reduced.

The basis set used was the (9s,5p/6s) Gaussian expansions of atomic SCF orbitals, due to Huzinaga [29], which was also used in the calculations on $BH_3^-$ (Section 7). The hydrogen $1s$ atomic orbital exponent was chosen as 1.2 (close to the optimised value of 1.15 found for $BH_3^-$ [44]), and the B-B bond length was set at 3.50 Bohrs, slightly longer than in $B_2H_6$ (3.345 Bohrs) to accommodate the extra electron entering the $1b_{2g}$ antibonding MO. For all terminal protons, $R(B-H) = 2.40$ Bohrs (close to the optimised value of 2.35 Bohrs in $BH_3^-$ [44]), and for the bridging protons a bridge angle of $83^\circ$ was used (as in $B_2H_6$) giving a bond length of $R(B-H) = 2.641$ Bohrs. The energies and isotropic coupling constants were calculated from the UHF wavefunction after annihilation of the contaminating quartet spin state, using the ATOMOL 2 program [61].

The isotropic hyperfine coupling constants are calculated to be:

(i) $D_{2h}$ structure (bridged):

$a(^{11}B) = 14.25$ G; $a(^1H)(bridge) = -29.36$ G; $a(^1H)(terminal) = -15.06$ G
(ii) $D_{3h}$ structure (eclipsed):

$$a^{(11)B} = 8.60 \text{ G}; \ a^{(1)H} = -7.12 \text{ G}$$

(iii) $D_{3d}$ structure (staggered):

$$a^{(11)B} = 8.86 \text{ G}; \ a^{(1)H} = -7.50 \text{ G}$$

It is interesting to note from Figure 2 that the unpaired electron in the $1b_{2g}$ MO of the $D_{2h}$ structure is unbounded. In all other respects the diagram is exactly as was predicted qualitatively. UHF theory clearly differentiates between the bridged structure and the structures with threefold symmetry. The agreement with experiment for the latter structures is very good, and confirms the conclusions arrived at qualitatively. The total energies are in the expected order:

$$E(D_{2h}) = -52.638933 \text{ Hartrees}$$
$$E(D_{3h}) = -52.645294 \text{ Hartrees}$$
and $$E(D_{3d}) = -52.665590 \text{ Hartrees}$$

The barrier to internal rotation between the staggered and eclipsed structures is thus estimated to be 12.554 kcal/mole. However, the isotropy of the proton couplings implies that there is free rotation about the B-B bond at 4 K, and the large barrier found here may be attributed to the fact that no geometrical or orbital optimisation was performed.

The conclusion of this study is that both the thirteen valence electron radicals $C_2H_6^+$ and $B_2H_6^-$ adopt a similar structure to ethane, but with a lengthened X-X bond and flattened $XH_3$ groups. This structure is consistent with the ESR spectrum of $B_2H_6^-$. It is also of interest to note that $B_2H_5$ radicals have recently been studied by ESR of $\gamma$-irradiated $B_2H_6$, and are believed to have the $D_{2h}$ structure with one bridging hydrogen only [62]. This interpretation has
FIGURE 2. Molecular Orbital diagram for B₂H₆⁻ using the UHF SCF eigenvalues.
recently been supported by INDO calculations for the isotropic and dipolar couplings in $B_2H_5$ [63].


Although radicals derived from a wide range of alkanes have been studied by ESR spectroscopy, the isoelectronic amine borane radicals have received little or no attention. Very recently, the ESR spectra of trimethylamine borane exposed to $\gamma$-irradiation have been studied at 77 K (Species A) and after annealing above 77 K (Species B). A series of ab initio UHF calculations was performed to clarify the experimental assignments and also to investigate the structures of the observed radicals [64].

The total molecular energy and the isotropic hyperfine coupling constants $a(X)$ were calculated from the UHF wavefunction after single annihilation of the contaminating quartet spin state [3] using the ATIMOL2 program [61] and a minimal basis set of the completely contracted ($9s,5p/6s$) Gaussian expansions of atomic SCF orbitals due to Huzinaga [29].

Species A
The ESR powder spectrum comprises a quartet of broad lines of roughly equal intensity, with no further resolved features. The 58 G quartet was assigned to $a(^{11}B)$. Deuteration at boron resulted in only minor line-width changes, hence it was deduced that $a(^1H)_B = 0 \pm 4$ G. From the line-widths it was also estimated that $a(^{14}N) = 0 \pm 7$ G. These data led to the suggestion that the observed radical was $[BH_3NMe_3]^-$.

Normally this anion would be expected to dissociate:

$$BH_3-NMe_3 + e^- \rightarrow [BH_3-NMe_3]^- \rightarrow BH_3^- + NMe_3 \quad (56)$$
but the observed value of $a(^{11}\text{B})$ is nearly three times as large as in $\text{BH}_3^-$ while $a(^{1}\text{H})$ is greatly reduced (see Table IV for a numerical comparison). This could occur if the $\text{BH}_3^-$ unit were to remain non-planar with the original B-N $\sigma$-bond retained. The absence of any clear anisotropic features in the spectrum might indicate rotation within the matrix. However the broadness of the lines is likely to mean that extensive libration of the $\text{-BH}_3$ group relative to the bulky $\text{-NMe}_3$ group is responsible for the loss of resolved anisotropy.

_Ab initio_ calculations were performed on the simpler radical $[\text{BH}_3\text{NH}_3]^-$ to reduce the computational effort, since the values of $a(^{14}\text{N})$, $a(^{11}\text{B})$ and $a(^{1}\text{H})_B$ are not expected to differ greatly from those in $[\text{BH}_3\text{NMe}_3]^-$. A staggered conformation was adopted with $R(\text{B-H}) = 2.35$ Bohrs and $R(\text{N-H}) = 1.95$ Bohrs; the 1s orbital exponents of the protons attached to boron and nitrogen were set at 1.20 and 1.50 respectively. These values were derived from previous work on $\text{BH}_3^-$ [44] and $\text{NH}_3^+$ [42] using the same basis set. The conformation at nitrogen was taken to be tetrahedral since this is unlikely to be greatly modified during the formation or dissociation of the radical. The geometry at boron was permitted to become both planar and tetrahedral.

The results (Table IV) show that for values of $R(\text{B-N}) > 5$ Bohrs, the value of $a(^{14}\text{N})$ becomes suitably small, while a geometry at boron which is intermediate between tetrahedral and planar would give rise to the observed $a(^{11}\text{B})$. The corresponding value of $a(^{1}\text{H})_B$ would then be in the region of -12 to -21 G, which is rather larger than the estimated limit of $\pm 4$ G. However it should be borne in mind that neither the molecular geometry nor the hydrogen 1s orbital exponents have been optimised, and this could help to account for the discrepancy. A more important influence is probably the effect of vibrational averaging on the value of $a(^{1}\text{H})_B$. 

-112-
Earlier work on NH$_3^+$ [42] and CH$_3$ [44], and more recent results for BH$_3^-$ (Section 7), have shown that correction for the normal zero-point vibration tends to decrease the magnitude of the calculated $a(^1H)$ values and to increase the central atom $a(X)$ values. Similar considerations may well be appropriate to the present radical because of its resemblance to the isolated BH$_3^-$ radical. Essentially, the unpaired electron in [BH$_3$NH$_3$]$^-$ is calculated to reside in a B-N $\sigma^*$ MO composed of a weakly anti-bonding combination of the 2$p_z$ orbitals on boron and nitrogen. As the geometry at boron moves from planar towards tetrahedral, some boron 2$s$ character is mixed into the unpaired MO, causing an increase in $a(^{11}B)$ and a decrease in the net negative spin density at the protons.

The calculations suggest that the B-N bond has to be greatly elongated relative to the parent molecule [R(B-N) = 2.95 Bohrs in BH$_3$NH$_3$] in order to accommodate the extra $\sigma^*$ electron. Since the total energy of the system continues to decrease at double the normal molecular B-N distance, it is probable that the two halves are in fact genuinely dissociating in vacuo, and that in ESR experiments the restrictive effect of the powder environment prevents complete fragmentation. The [BH$_3$NH$_3$]$^-$ species may thus be described qualitatively in terms of a freely vibrating but non-planar BH$_3^-$ radical perturbed by a $\sigma^*$ interaction with an ammonia molecule.

In order to test the [BH$_3$NH$_3$]$^-$ assignment further, a series of ab initio UHF calculations was also performed on a possible alternative radical, [BH$_3$NH$_3$]$^+$, using the same B-H and N-H bond lengths and the same hydrogen 1$s$ orbital exponents as for [BH$_3$NH$_3$]$^-$. The geometry at boron and nitrogen and the B-N bond length were varied, but the calculated isotropic hyperfine coupling constants (Table IV) give a much poorer fit to the experimentally determined values. The agreement for [BH$_3$NH$_3$]$^-$, on the other hand, is satisfactory, and in the absence of any other reasonable structures it is concluded that the [BH$_3$NMe$_3$]$^-$ formulation for Species A is probably correct.
TABLE IV: Results of the Calculations for the Structure of Species A

<table>
<thead>
<tr>
<th>Radical</th>
<th>Geometry at B</th>
<th>R(B—N) (Bohrs)</th>
<th>Total Energy (Hartrees)</th>
<th>Isotropic Hyperfine Coupling (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$^{11}B$</td>
</tr>
<tr>
<td>$[	ext{BH}_3\text{NH}_3]^{-}$</td>
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<td>6.0</td>
<td>-82.426864</td>
<td>21.4</td>
</tr>
<tr>
<td></td>
<td>tetrahedral</td>
<td>6.0</td>
<td>-82.422816</td>
<td>109.2</td>
</tr>
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<td>tetrahedral</td>
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<td>-82.397273</td>
<td>117.8</td>
</tr>
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<td>-82.341635</td>
<td>18.5</td>
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<td>tetrahedral</td>
<td>4.0</td>
<td>-82.334366</td>
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<td>$[	ext{BH}_3\text{NH}_3]^{+}$</td>
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<td>tetrahedral</td>
<td>5.0</td>
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<td>1.4</td>
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<tr>
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<td>*planar</td>
<td>4.0</td>
<td>-82.163419</td>
<td>13.1</td>
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<tr>
<td>Species A</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>±50</td>
</tr>
<tr>
<td>$\text{BH}_3^{-}$ [48]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(+) 20.7</td>
</tr>
</tbody>
</table>

* in this calculation the geometry at N was planar
Species B

After annealing, a multiline isotropic spectrum was formed. By deuteration at boron, the value of $a(^1\text{H})_B$ was fixed at 43 G. Values of $a(^{11}\text{B}) = 12$ G and $a(^{14}\text{N}) = 18$ G were also obtained, and a set of seven features which could only arise from two equivalent methyl groups with $a(^1\text{H}) = 24$ G, fixed the structure as $\text{BH}_3\text{NMe}_2$, formed by loss of methyl from $\text{BH}_3\text{NMe}_3$.

Ab initio UHF calculations were performed on the simpler $\text{BH}_3\text{NH}_2$ radical, which is isoelectronic with the ethyl radical (Section 10), in order to reduce the computational effort. Both the staggered and eclipsed conformations were studied using a value of $R(\text{B-N}) = 2.759$ Bohrs (equal to $R(\text{C-C})$ in $\text{C}_2\text{H}_5$), and assuming trigonal planar co-ordination at nitrogen and tetrahedral co-ordination at boron. The hydrogen 1s orbital exponent was set to 1.40 for all the protons (as in $\text{C}_2\text{H}_5$), and values of $R(\text{B-H}) = 2.30$ Bohrs, $R(\text{N-H}) = 1.92$ Bohrs were adopted as realistic estimates for the system in question by comparison with the values for the $\text{BH}_3$ and $\text{NH}_3$ molecules respectively.

In Table V, the results for the staggered and eclipsed conformations are given together with a set of averaged coupling constants corresponding to rapid rotation about the B-N bond. The calculated isotropic coupling constants are in satisfactory agreement with the experimental values, and thereby confirm the experimental assignment. The large differences between the values of $a(^1\text{H})_B$ in the staggered and eclipsed conformations suggest that the interaction with the π-orbital is mainly direct and not through the σ-framework, a process which can be associated with hyperconjugation. When a B-H bond eclipses the π-orbital, the value of $a(^1\text{H})_B$ is 128.4 G, but this decreases to 2.1 G when the proton is rotated into the nodal plane of the π-orbital. Compared with the ethyl radical (Section 10) the $\text{BH}_3\text{NH}_2$
### TABLE V: Results of the Calculations on BH$_3$NH$_2$

<table>
<thead>
<tr>
<th>Radical</th>
<th>Conformation</th>
<th>Total Energy (Hartrees)</th>
<th>Isotropic Hyperfine Coupling (G) $^{11}\text{B}$</th>
<th>$^{14}\text{N}$</th>
<th>$^{1}\text{H}_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH$_3$NH$_2$</td>
<td>staggered</td>
<td>-81.898516</td>
<td>-7.0</td>
<td>12.9</td>
<td>128.4 (one)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30.6 (two)</td>
</tr>
<tr>
<td></td>
<td>eclipsed</td>
<td>-81.898501</td>
<td>-7.0</td>
<td>12.9</td>
<td>2.1 (one)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>93.5 (two)</td>
</tr>
<tr>
<td></td>
<td>averaged</td>
<td>-7.0</td>
<td>12.9</td>
<td></td>
<td>63.1</td>
</tr>
<tr>
<td>Species B</td>
<td></td>
<td>(-) 12</td>
<td>(+) 18</td>
<td>(+) 43</td>
<td></td>
</tr>
</tbody>
</table>
radical appears to exhibit a remarkably strong hyperconjugative interaction, due to the increased effective electron affinity of the radical centre.

As with other planar radical centres, for example CH$_3$, C$_2$H$_5$ and NH$_3^+$, the zero-point out-of-plane vibrational correction is expected to increase $a(^{14}\text{N})$ in BH$_3$NH$_2$, bringing the value calculated for the rigid radical into better agreement with experiment. The rather small value calculated for $a(^{11}\text{B})$ is consistent with a similar situation which arose with the methyl carbon of the ethyl radical (Section 10), and it may be conjectured that the more complex B-N bond involving hybridisation changes and inner shell polarisations may render $a(^{11}\text{B})$ more sensitive to out-of-plane motions of the amino group.

The ESR spectrum of Species B is consistent with rapid rotation about the B-N bond axis at 77 K. The rotational barrier derived from the present calculations is circa 9.4 cal/mole which is virtually insignificant, and close to the value in C$_2$H$_5$.

The results of the ab initio UHF calculations thus confirm the experimental assignment of the ESR spectrum of Species B to the radical BH$_3$NMe$_2$, and indicate that the large hyperfine coupling at the boron protons may be ascribed to hyperconjugation.

10. Hyperfine Interactions in the Ethyl Radical

In 1973, McDowell and co-workers [65] reported the ESR spectrum of the ethyl radical isolated in an argon matrix at 4.2 K and gave the first complete analysis of the anisotropic proton hyperfine interactions. Their results also provide the first experimental assessment of theoretical pre-
dictions for the anisotropic hyperfine coupling constants in the ethyl radical. While experimentalists have long recognised the importance of anisotropic coupling constants in ESR spectroscopy [59], most theoretical work has concentrated upon the calculation of isotropic coupling constants until recently [66]. Previously, several semi-empirical calculations [67-76] and one ab initio study [77] of spin densities and isotropic coupling in the ethyl radical had been performed. However only three previous calculations of anisotropic coupling in C₂H₅ were available, all of them using semi-empirical methods [78-80]. Since the ethyl radical is sufficiently small to be the subject of a non-empirical investigation, it is highly desirable to compare ab initio results for the proton anisotropic hyperfine coupling tensors with the experimentally determined parameters and with the results of semi-empirical calculations. Such a comparison would serve not only to confirm the experimental assignments but also to evaluate the reliability of ab initio and semi-empirical values for α- and β-proton anisotropic coupling constants.

Ab initio UHF calculations with annihilation of the contaminating quartet spin state [2,3] have been performed [81] on the staggered and eclipsed conformations of the ethyl radical using the completely contracted (9s,5p/6s) Gaussian expansions of atomic SCF orbitals, due to Huzinaga [29]. The hydrogen atomic orbital exponents were chosen to be 1.40 from previous optimisations on the methyl radical [44] and on methane [82] using the same basis set. The geometry was idealised; that is, the bonds were arranged tetrahedrally for the methyl group and in a trigonal plane for the methylene group. Bond lengths were taken from previous theoretical work on the ethyl radical: R(C-C) = 1.46 Å [80]; R(C-H)(methyl) = 1.09 Å; R(C-H)(methylene) = 1.079 Å [75]. The co-ordinates used for each conformation are given in Table VI. Atomic units are used throughout, except...
that coupling constants are in Gauss.

The total energy of each conformation after annihilation is:

\[ E(\text{staggered}) = -78.521205 \text{ Hartrees} \]
\[ E(\text{eclipsed}) = -78.521201 \text{ Hartrees}, \]

which corresponds to a physically insignificant internal rotation barrier of 2.6 cal/mole. Similar results have subsequently been obtained by Christoffersen and co-workers [83], Pople and co-workers [84], Berthier and co-workers [85] and Almlöf and co-workers [86], in \textit{ab initio} calculations using a variety of different basis sets. The \textit{ab initio} UHF values of 460 cal/mole and 620 cal/mole reported earlier by Pople et alia [56] were obtained after full geometry optimization.

The isotropic hyperfine coupling constants for the ethyl radical, calculated from the UHF wavefunction after spin annihilation, are given in Table VII. The agreement between theory and experiment is sufficiently good to confirm the experimental assignment unequivocally. The largest discrepancies occur with the carbon nuclei, but in the case of the methylene carbon at least, direct comparison with experiment is misleading. A similar situation arose with the methyl radical [44] for which the calculated value of \( a(^{13}\text{C}) = 27.33 \text{ G} \) was significantly smaller than the experimental value of 38 G [41]. This coupling constant is known to be temperature dependent due to out-of-plane vibrational motion of the radical and the experimental value in the rigid planar radical has been estimated to be \textit{circa} 28 G [41]. Schrader and Karplus [40] demonstrated the importance of including an out-of-plane vibrational contribution in the calculation of the coupling constant, and when this is allowed for using the \textit{ab initio} UHF method the value of \( a(^{13}\text{C}) \) is augmented to 54.64 G [44]. Thus a direct comparison of the theoretical and experimental values of \( a(^{13}\text{C}) \) for the planar methyl radical and the planar methylene group in the
ethyl radical displays such a close similarity that it may be concluded that there is a similar out-of-plane vibration and associated temperature dependence in both cases. The value calculated for $a^{(13\text{C})}$ at the methylene carbon atom is therefore considered to be appropriate for the rigid radical.

The methylene proton coupling constants are calculated to be 1.33 G less than the experimental value, which is consistent with previous results obtained for the methyl radical where a small positive vibrational correction to $a^{(1\text{H})}$ was found [44]. However, it is likely that the more complex C-C bond involving hybridisation changes and inner shell polarisations may render the $a^{(13\text{C})}$ of the methyl group more sensitive to the out-of-plane vibration of the methylene group. In view of such considerations, the agreement for the methyl $a^{(13\text{C})}$ is satisfactory, and is not critical to the ensuing discussion.

The proton isotropic hyperfine coupling constants are in good agreement with experiment. The large differences between the methyl proton couplings in the eclipsed and staggered conformations suggest that the interaction with the $\pi$-orbital of the methylene carbon is mainly direct and not through the $\sigma$-bond framework, a process which can be associated with hyperconjugation. A similar direct delocalisation of $\pi$-spin density was also found in the isoelectronic BH$_3$NH$_2$ radical (Section 9). Since the barrier to internal rotation is very small, the three methyl group protons will become equivalent by rapid free rotation about the C-C bond axis, and this averaging effect has been allowed for by taking all the eclipsed and staggered values bracketed together and finding their mean.

In the future it is possible that different conformations of the ethyl radical may be isolated, locked in lattices or matrices at very low temperatures. In addition, ethyl radicals may be produced in environments
with differing degrees of rotational freedom, as for example the methyl radical was trapped on Vycor glass [87]. In both situations it is necessary to have hyperfine data available for various conformations of the radical, and for this reason the hyperfine coupling constants for the eclipsed and staggered conformations are listed, together with those for the rotationally averaged conformation.

The present values for the isotropic hyperfine coupling constants compare most favourably with the results of subsequent ab initio calculations using the restricted Hartree-Fock method with perturbation theory [85], the UHF method with spin annihilation [86], and the UHF method using molecular fragments [83]. In particular, the value for the methylene carbon atom is calculated to be closer to that expected for a rigid trigonal planar radical centre in the present study. In general, the results reported here are somewhat closer to the experimental values than those from the other ab initio calculations.

The anisotropic coupling tensors \( B \) are given in Table VIII. Anisotropic components do not appear to be particularly sensitive to vibrational effects [66] and therefore comparison may be made directly with experiment. Besides the staggered and eclipsed values, the tensors for an averaged conformation allowing for rapid free rotation of the methyl protons about the C–C bond are also included. The evaluation of this is slightly different than for the isotropic coupling constants, due to the directional character of the tensors. In addition to averaging over the staggered and eclipsed conformations, the mirror images of these must also be included in the averaging procedure. For the eclipsed conformation the mirror image is generated by reflection in the \( xz \) plane, and for the staggered conformation by reflection in the \( yz \) plane.

McDowell et alia have shown that their ESR spectrum is consistent with
a freely rotating methylene group [65]. If this is the case then it is immaterial whether or not the methyl group is locked into the matrix, as long as interaction with the matrix environment is negligible. The results for the averaged conformation of the methyl group must now be modified, because the unique axis containing the π orbital rotates in the xy plane if the methylene group is freely rotating. If this rotation is sufficiently rapid then the ethyl radical assumes an apparent axial symmetry about the C—C bond, and

\[
B_\perp = \frac{1}{2}(B_{xx} + B_{yy}) \\
B_\parallel = B_{zz} = -2B_\perp
\]

The values for \(B_\parallel\) are immediately obtained from Table VIII and are:

- methylene group: \(B_\parallel (^{13}\text{C}) = -32.03\ \text{G}, B_\parallel (^1\text{H}) = -6.63\ \text{G}\)
- methyl group: \(B_\parallel (^{13}\text{C}) = 0.69\ \text{G}, B_\parallel (^1\text{H}) = 2.85\ \text{G}\).

In Table IX the proton coupling constants are compared with experiment and other calculations. It will be seen that the present \textit{ab initio} UHF results are in excellent agreement for the α (methylene) protons, and in moderately good agreement for the β (methyl) protons where the discrepancies can be traced back to the isotropic coupling constant entirely. The difference between \(A_\parallel\) and \(A_\perp\) for both α and β protons is well reproduced by the present calculations, but is substantially overestimated by the semi-empirical calculations. Almlöf and co-workers [86] have recently reported \textit{ab initio} UHF results for the dipolar tensors in the ethyl radical, using a Gaussian basis set of approximately double zeta quality. They do not give results for the axially symmetric radical, but the reported values for the protons are in reasonable agreement with some experimentally inferred dipolar hyperfine couplings.
<table>
<thead>
<tr>
<th>centre</th>
<th>atom</th>
<th>eclipsed</th>
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</tr>
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<tbody>
<tr>
<td></td>
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<td>y</td>
</tr>
<tr>
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<td>3</td>
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<td>4</td>
<td>C</td>
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<td>7</td>
<td>H</td>
<td>-1.682</td>
<td>-0.971</td>
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**TABLE VI:** Coordinates for the Nuclei in each Conformation of the ethyl radical

<table>
<thead>
<tr>
<th>centre</th>
<th>atom</th>
<th>eclipsed</th>
<th>staggered</th>
<th>average</th>
<th>observed</th>
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<td>x</td>
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<tr>
<td>1</td>
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<td>29.91</td>
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<tr>
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<td>-23.71</td>
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<td>(+) 26.87 [88]</td>
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**TABLE VII:** Isotropic Hyperfine Coupling Constants in the ethyl radical
TABLE VIII: Anisotropic Coupling Tensors, B. The tensors are symmetric and the reference axes are in order x, y, z.

<table>
<thead>
<tr>
<th>centre</th>
<th>atom</th>
<th>eclipsed conformation</th>
<th>staggered conformation</th>
<th>average conformation</th>
</tr>
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<td>β protons</td>
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<td>-------</td>
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<td>$A_{//}$</td>
<td>$A_{\perp}$</td>
<td>$a$</td>
</tr>
<tr>
<td>ESR (in solid argon)</td>
<td>[65]</td>
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<td>(-) 19.4</td>
<td>(-) 22.8</td>
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<tr>
<td>ESR (in liquid ethane)</td>
<td>[88]</td>
<td>-</td>
<td>-</td>
<td>(-) 22.4</td>
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<td>VB (semi-empirical)</td>
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<td>-11.8</td>
<td>-22.4</td>
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<tr>
<td>INDO-UHF</td>
<td>[80]</td>
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<td>-12.3</td>
<td>-19.1</td>
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<td>UHF (ab initio)</td>
<td>this work</td>
<td>-30.3</td>
<td>-20.4</td>
<td>-23.7</td>
</tr>
</tbody>
</table>

**TABLE IX:** Observed and Calculated Proton Hyperfine Coupling Constants in the Ethyl Radical.
11. The Determination of Bond Angles from ESR Data

Assuming the mutual orthogonality of sp\(^n\) hybrid orbitals on the central atom of a molecule, Coulson [89,90] was able to derive equations linking the central atom hybridization ratios \(\lambda_i\) with the valence angles \(\theta_{ij}\) for various molecular symmetries, based on the condition:

\[
\lambda_i \lambda_j \cos \theta_{ij} + 1 = 0
\]  
(57)

For a radical \(XY_2\) of \(C_2v\) symmetry, Coulson's equation may be written:

\[
\theta = 2 \cos^{-1} \left(\lambda^2 + 2\right)^{-\frac{1}{2}}
\]  
(58)

where \(\theta\) is the bond angle and \(\lambda\) is the hybridisation ratio of the non-bonded hybrid orbital on the central atom \(X\). That is:

\[
\lambda = \frac{C_p}{C_s}
\]  
(59)

where \(C_s\) and \(C_p\) are the respective coefficients of the valence s and p orbitals of \(X\) in the molecular orbital of the unpaired electron.

Coulson's equations have been widely used by ESR spectroscopists [59] to estimate the bond angles of radicals from ESR data when both the isotropic (\(a\)) and anisotropic (\(2B\)) hyperfine coupling constants of the central atom are known. The procedure normally adopted is to obtain the s and p spin densities at the central atom from the relations:

\[
C_s^2 = \frac{a(X)}{a^0(X)}
\]
\[
C_p^2 = \frac{2B(X)}{2B^0(X)}
\]  
(60)

where the \(a^0\) and \(2B^0\) values refer to the atom \(X\) in states where the valence s and p orbitals respectively have unit population. Such free atom values are not generally determined experimentally, but have been calculated from \textit{ab initio} SCF wavefunctions for the central atom [91]. Although the above
procedure is qualitatively reasonable, errors may be introduced if the form of the atomic orbitals close to the nucleus is significantly altered upon molecule formation. The application of Coulson's equations to real molecules must in any case be regarded as a strictly approximate approach, if only because the overlap between orbitals on atoms X and Y is neglected. However the inclusion of overlap should not seriously alter the qualitative features predicted by the equations.

Perhaps the most valuable aspect of the equations for the ESR spectroscopist, who is often concerned with the task of identification, is their generality. The absolute accuracy of predicted bond angles is usually of relatively minor importance, but if the equations are to be of any practical use then the very least to be expected is that trends in the variation of bond angle with hybridisation ratio will be reliably reproduced over a wide range of radicals. In this connection the equations have been linked with Pauling's recently reiterated electronegativity considerations [50] to study the variations in the predicted bond angle as a function of the electronegativity difference:

\[ \Delta X = X_Y - X_X \]

in \( \text{XY}_2 \) and \( \text{XY}_3 \) \( \sigma \)-radicals [59,92,93].

It is highly desirable to perform as unequivocal as possible a test on Coulson's equation (58) over a whole series of radicals of \( C_{2v} \) symmetry with a wide variety electronegativity differences and bond angles. Since experimental verification has not been forthcoming due to an inability to measure the geometry of most radicals using standard techniques, an attempt has recently been made to provide a theoretical test of the validity of Equation (58) [94]. The results of INDO calculations for the radicals \( \text{CO}_2^- \) and \( \text{BF}_2 \) over a wide range of bond angles led Owens to the conclusion
that Equation (58) is quite unreliable, even in a qualitative sense. This conclusion was later supported by Takahata et alia [95] and by Westhof and Müller [96] using similar approaches.

In order to examine the interpretation of the theoretical results which led to the conclusion that Equation (58) is qualitatively unreliable, a series of ab initio UHF calculations with spin annihilation was performed on the 17 valence electron \( \sigma \)-radicals of \( C_{2v} \) symmetry: \( \text{BF}_2 \), \( \text{BO}_2^{-} \), \( \text{CO}_2^{-} \), \( \text{NO}_2 \) and \( \text{N}_3^{2-} \) [97]. The UHFAA method has been shown to be reliable for the evaluation of hyperfine coupling constants for second row elements when used in conjunction with minimal basis sets of SCF atomic orbitals [66], and it was considered to be appropriate in this situation because a theoretical test of Equation (58) from a rather less arbitrary standpoint is desirable. In addition it is convenient because direct comparison with the INDO results can be made. Minimal basis sets of SCF atomic orbitals were used in the \((9s,5p)\) Gaussian expansions of Huzinaga [29] and bond lengths \( R(X-Y) \) were taken from previous theoretical and experimental work on the radicals. In the case of \( \text{BO}_2^{2-} \) a suitable bond length was selected as no previous studies on this species were known.

The results of the calculations are presented in Table X and the major results are summarised graphically in Figure 3 where values of \( \lambda^2 \) calculated by the experimentalist's procedure are plotted against the bond angles used in the UHF calculations on each radical. The curve corresponding to Equation (58) is also included in Figure 3. The similarity of the curves for the radicals in Figure 3 with those obtained by Owens [94] shows that both the INDO and ab initio UHF methods lead to qualitatively similar results and therefore need not be discussed separately. The fact that the "individual" curves do not follow Equation (58) closely caused Owens to call into question the validity of Coulson's equation. However, it may be
argued that Equation (58) should not necessarily apply to all possible bond angles of C$_{2v}$ triatomic molecules. Coulson's equation is certainly quite general and in this respect it differs markedly from both the INDO and \textit{ab initio} UHF methods which are molecule dependent and employ a minimum energy criterion to determine the optimal description of a real molecule. Thus, within a given theoretical framework there is just one bond angle which minimises the energy of an isolated, unperturbed molecule. It is suggested therefore that each "individual" curve provides one point, corresponding to the equilibrium bond angle for the radical in question, which should come close to falling on the curve predicted by Coulson's equation. These points are identified by $\bigodot$ in Figure 3 and it can be seen that they lie remarkably close to the curve for Equation (58) considering that the bond lengths were selected rather than optimised with respect to the total energies of the radicals. Since the chosen bond lengths are believed to be nearly optimal at the equilibrium bond angles of the radicals, the points of minimum energy should correspond closely to real radicals. The results show therefore that real XY$_2$ $\sigma$-radicals follow Equation (58) remarkably well and ESR spectroscopists are only concerned with real radicals.

It should be pointed out that for real systems the ESR data often pertain to radicals in perturbing environments such as lattices and matrices. Such perturbations are known to modify the ESR parameters of radicals, especially of radical ions, and will clearly alter the bond angles predicted by Coulson's equations. However the curves in Figure 3 should not be used to study environmental effects because the Hamiltonian operator used in these calculations did not contain terms to represent any environmental interactions. Such interactions with a lattice take the form of crystal fields which modify the electron distribution in the radical...
as well as simple steric constraints which alter the geometry.

Unfortunately, the bond angle has only been unequivocally determined by other experimental methods for one of the radicals studied here, namely gaseous NO$_2$ where a value of 134.1° was found [101] by microwave techniques. Using the hyperfine parameters determined in the gas phase [98]:

\[
\begin{align*}
    a(\mathbf{^{14}N}) &= 52.6 \text{ G} \\
    2B(\mathbf{^{14}N}) &= 14.2 \text{ G}
\end{align*}
\]

in Equation (58) yields a predicted bond angle of 133.3° in excellent agreement. This result strongly supports the conclusion that Coulson's equation is reliable enough to be used by ESR spectroscopists for estimating bond angles.

In Table XI the trends in bond angle and central atom hyperfine properties with decreasing electronegativity difference $\Delta X$ are displayed for the five isoelectronic radicals. These results refer to the calculations closest to the optimum bond angle of each radical. The bond angles predicted by Coulson's equation are in remarkably good agreement with those actually used, as noted earlier. Also included in Table XI are estimates of the optimum value of the bond angle for each radical, based on the total energies listed in Table X.

The trends shown in Table XI reflect closely the trends found from ESR data, which have been rationalised [59] using straightforward electronegativity arguments [50]: As $\Delta X$ increases, the unpaired $\sigma^*$ electron in C$_2$v $XY_2$ radicals resides more and more on the least electronegative atom (i.e. X) and therefore the total (p+s) spin density on X increases. However, with increasing $\Delta X$ the X–Y bonding electrons become more polarised towards Y, causing the bonding orbitals at X to gain p character and lose s character. This in turn causes a decrease in the bond angle and in the
FIGURE 3. The Variation of $\lambda^2$ with bond angle for five iso-electronic radicals.
<table>
<thead>
<tr>
<th>TABLE X: Variation of hyperfine parameters with bond angle for five iso-electronic $C_2v$ radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BF$_2$ Radical</strong> (R = 2.50) [99]</td>
</tr>
<tr>
<td>$\theta$</td>
</tr>
<tr>
<td>Energy</td>
</tr>
<tr>
<td>a(X)</td>
</tr>
<tr>
<td>2B(X)</td>
</tr>
<tr>
<td>$\lambda^2$</td>
</tr>
<tr>
<td><strong>BO$_2^-$ Radical</strong> (R = 2.505)</td>
</tr>
<tr>
<td>$\theta$</td>
</tr>
<tr>
<td>Energy</td>
</tr>
<tr>
<td>a(X)</td>
</tr>
<tr>
<td>2B(X)</td>
</tr>
<tr>
<td>$\lambda^2$</td>
</tr>
<tr>
<td><strong>CO$_2^-$ Radical</strong> (R = 2.3810) [100]</td>
</tr>
<tr>
<td>$\theta$</td>
</tr>
<tr>
<td>a(X)</td>
</tr>
<tr>
<td>2B(X)</td>
</tr>
<tr>
<td>$\lambda^2$</td>
</tr>
<tr>
<td><strong>NO$_2$ Radical</strong> (R = 2.2620) [101]</td>
</tr>
<tr>
<td>$\theta$</td>
</tr>
<tr>
<td>Energy</td>
</tr>
<tr>
<td>a(X)</td>
</tr>
<tr>
<td>2B(X)</td>
</tr>
<tr>
<td>$\lambda^2$</td>
</tr>
<tr>
<td><strong>N$_2^-$ Radical</strong> (R = 2.3622) [102]</td>
</tr>
<tr>
<td>$\theta$</td>
</tr>
<tr>
<td>Energy</td>
</tr>
<tr>
<td>a(X)</td>
</tr>
<tr>
<td>2B(X)</td>
</tr>
<tr>
<td>$\lambda^2$</td>
</tr>
</tbody>
</table>

(Angles in degrees; bond lengths in Bohrs; energies in Hartrees; coupling constants in Gauss.)
TABLE XI: Trends in the properties of five iso-electronic $C_2v$ radicals near their equilibrium bond angles

<table>
<thead>
<tr>
<th>Radical</th>
<th>BF$_2$</th>
<th>BO$_2^-$</th>
<th>CO$_2^-$</th>
<th>NO$_2$</th>
<th>N$_3^-$</th>
</tr>
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<tbody>
<tr>
<td>$\Delta X$</td>
<td>1.94</td>
<td>1.40</td>
<td>0.89</td>
<td>0.40</td>
<td>0.00</td>
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<tr>
<td>Estimated $\theta$</td>
<td>121</td>
<td>131</td>
<td>134</td>
<td>135</td>
<td>151</td>
</tr>
<tr>
<td>Actual $\theta$</td>
<td>120</td>
<td>130</td>
<td>134</td>
<td>134.25</td>
<td>150</td>
</tr>
<tr>
<td>$\alpha(X)$</td>
<td>237.6</td>
<td>97.9</td>
<td>126.8</td>
<td>37.4</td>
<td>17.8</td>
</tr>
<tr>
<td>$2\beta(X)$</td>
<td>17.9</td>
<td>16.6</td>
<td>32.3</td>
<td>15.8</td>
<td>16.9</td>
</tr>
<tr>
<td>$C_0^2 + C_2^2$</td>
<td>0.802</td>
<td>0.571</td>
<td>0.602</td>
<td>0.532</td>
<td>0.529</td>
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<tr>
<td>$C_0^2/C_2^2$</td>
<td>1.44</td>
<td>3.23</td>
<td>4.36</td>
<td>6.86</td>
<td>15.41</td>
</tr>
<tr>
<td>Predicted $\theta$ (Eq. 58)</td>
<td>114.7</td>
<td>128.1</td>
<td>133.5</td>
<td>140.7</td>
<td>152.3</td>
</tr>
</tbody>
</table>

(Angles in degrees, coupling constants in Gauss)
hybridisation (p:s) ratio of the non-bonding orbital on X.

It may be concluded that \textit{ab initio} UHF calculations support the continued use of Coulson's equation as a reliable means of estimating bond angles in triatomic radicals from ESR data. The calculations also reproduce experimentally observed trends in bond angle and central atom spin densities associated with variations in electronegativity difference along an iso-electronic series of radicals.

12. The Identification of the \( \text{N}_3^0 \) or \( \text{N}_3^2^- \) Radical

In 1970, Marinkas [103] reported the ESR spectrum of a radical in uv-irradiated barium azide crystals, which he identified as \( \text{N}_3^2^- \). Two years later Neilson and Symons [104] also reported the detection of this species by ESR of \( \gamma \)-irradiated potassium azide. However, on the basis of INDO calculations of the isotropic hyperfine coupling constants for both the \( \text{N}_3^2^- \) and \( \text{N}_3^0 \) radicals, Adams and Owens [102] concluded that the observed radical was in fact \( \text{N}_3^0 \), which had not previously been detected by ESR spectroscopy [105]. They used the INDO values for the isotropic couplings in each radical to select the sign combination for the experimental anisotropic couplings which gave the best agreement for each radical, and this led them to prefer the \( \text{N}_3^0 \) description. In fact, the agreement between experiment and the INDO results for \( \text{N}_3^2^- \) was also acceptable [102].

In order to attempt to resolve the identification of the radical, \textit{ab initio} UHF calculations with spin annihilation were carried out for the isotropic and anisotropic hyperfine coupling constants of both \( \text{N}_3^2^- \) and \( \text{N}_3^0 \) [106]. In the first instance a minimal basis set of Slater type orbitals in the STO-3G expansion was used with the average molecular scaling factors
proposed for nitrogen [35]. The geometry adopted for \( N_3^2^- \) of \( R(N-N) = 2.3622 \) Bohrs and \( \theta = 161^\circ \) was that obtained from the INDO calculations by optimization [102]. For \( N_3^9 \), ab initio restricted Hartree-Fock open shell calculations have yielded a linear asymmetric structure at the energy minimum with \( R = 2.16 \) and \( R^' = 2.345 \) Bohrs, while the optimised symmetric structure was found to be \( R = R^' = 2.225 \) Bohrs [107].

Later it became possible to repeat the above calculations on the CDC 7600 computer at U.M.R.C.C. using a minimal basis set of the \((9s,5p)\) type atomic SCF orbitals for nitrogen obtained by Huzinaga [29]. This basis set is expected to represent the electron distribution in the region of the nuclei more accurately than the STO-3G basis, and should lead to more reliable results for the calculated hyperfine coupling constants. Apart from the improved basis set, the only difference between the two sets of calculations was the bond angle of \( N_3^9 \) for which a value of \( \theta = 150^\circ \) was adopted, since this is close to the optimal value in the \((9s,5p)\) SCF AO basis set (Section 11).

The results of both sets of calculations are collected in Table XII, together with the INDO [102] and experimental [103] results. It must be mentioned here that the results given in Table I of [106] for the asymmetric \( N_3^9 \) radical are not correct because the wavefunction had not been properly optimized. The correct results for the asymmetric \( N_3^9 \) radical have since been obtained and are included in Table XII.

The results of the ab initio UHF calculations indicate clearly that the choice of signs for the components of the central nitrogen atom hyperfine tensor made by Adams and Owens \((A_x = -15.7, A_y = +19.6, A_z = -28.0 \ G [102])\) is quite unsuitable for either \( N_3^9 \) or \( N_3^2^- \). If, however, all components of the hyperfine tensor are taken to be positive, then \( a = +21.1 \ G \) and there is generally good agreement with the calculated hyperfine couplings.
for the central atom of $N_3^\cdot$. The alternative is to take all components of
the hyperfine tensor to be negative, but the agreement with the calculated
hyperfine couplings for the central atom of $N_3^\circ$ is less good because the
relative magnitudes of $A_x$ and $A_y$ are not correct. Thus the central atom
results favour $N_3^2$. The results for the terminal nitrogen atoms are less
conclusive in that reasonable agreement can be obtained for either radical.

However, the identification of the observed radical as $N_3^2$ rather
than $N_3^\circ$ receives further support from a comparison of the hyperfine couplings
at the central and terminal nitrogen atoms. The $N_3^\circ$ radical is linear and
its unpaired electron is in a degenerate $\pi_g$ orbital confined to the terminal
nitrogen atoms by a nodal plane through the central atom. Thus spin
density will appear at the central atom only indirectly via spin polarisation
of the remaining $\sigma$ and $\pi$ electrons, and the hyperfine coupling at the
central nitrogen atom will be smaller in magnitude than at the terminal
nitrogen atoms. The UHF calculations on $N_3^\circ$ (Table XII) confirm this con­
clusion, but the experimental situation is quite different, with the
central atom hyperfine coupling observed to be approximately twice as
large as that for the terminal atoms. The $N_3^2$ radical, on the other hand,
is considerably bent and its unpaired electron is in the $6a_1$ molecular
orbital which includes important $s$ and $p_\sigma$ contributions from the central
atom (cf. the isoelectronic NO$_2$ radical). Thus the hyperfine coupling at
the central atom in $N_3^2$ is calculated to be larger in magnitude than that
at the terminal nitrogens by a factor which is consistently close to two,
in excellent accord with the experimental results (Table XII).

Taken together, this means that the $N_3^2$ postulate gives satisfactory
agreement with experiment while the $N_3^\circ$ model should be rejected. One
important conclusion of this comparative study is that it is unwise to rely
solely on computed isotropic couplings when attempting to identify unknown
radicals from their ESR single crystal spectra. Owens and Adams [108] subsequently reported INDO calculations of the unpaired p spin densities for N$_3^0$ and N$_3^-$, and concluded, by comparison with the experimental values [103], that their results in fact supported the N$_3^-$ assignment.

There have been three other calculations on the N$_3$ radical [107-109]. The best energy of -163.10 Hartrees was obtained by Archibald and Sabin who performed an extensive geometry search. McCain and Palke using the ab initio open shell restricted Hartree-Fock method obtained an energy of -162.494 Hartrees, and a p spin density of 0.511 for the terminal nitrogen atoms. Metrenin [109] performed INDO calculations including the azide lattice field, but no numerical results are given in the Russian abstract of the paper. Further calculations on N$_3^-$ have very recently been reported by Chuvylkin et alia [110] in which hyperfine coupling constants and g-tensors were calculated by the INDO method at several geometries, and these results appear to confirm the identification of the radical in irradiated azides as N$_3^-$. 

-137-
TABLE XII: Energies (Hartrees) and Hyperfine Coupling Constants (Gauss) for the $N_3^0$ and $N_3^2^-$ Radicals

<table>
<thead>
<tr>
<th>Radical</th>
<th>Basis</th>
<th>Method</th>
<th>Energy</th>
<th>$a_{iso}$</th>
<th>$A_y$</th>
<th>$A_z$</th>
<th>$A_x$</th>
<th>Central Nitrogen Atom</th>
<th>$a_{iso}$</th>
<th>$A_y$</th>
<th>$A_z$</th>
<th>$A_x$</th>
<th>Terminal Nitrogen Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_3^0$</td>
<td>INDO</td>
<td>-</td>
<td>-8.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>STO-3G</td>
<td>UHFAA</td>
<td>-161.106509</td>
<td>-5.9</td>
<td>-2.5</td>
<td>-9.0</td>
<td>-6.1</td>
<td>2.5</td>
<td>-4.1</td>
<td>16.4</td>
<td>-4.2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SCFOA</td>
<td>UHFAA</td>
<td>-162.974523</td>
<td>-7.0</td>
<td>-3.3</td>
<td>-10.9</td>
<td>-6.8</td>
<td>3.5</td>
<td>-6.0</td>
<td>22.1</td>
<td>-5.6</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$N_3^0$</td>
<td>STO-3G</td>
<td>UHFAA</td>
<td>-161.131064</td>
<td>-7.0</td>
<td>-4.0</td>
<td>-9.8</td>
<td>-7.3</td>
<td>(i) 5.4</td>
<td>-7.0</td>
<td>18.8</td>
<td>4.4</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(asym)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(ii) -0.2</td>
<td>-1.9</td>
<td>9.4</td>
<td>-8.1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SCFOA</td>
<td>UHFAA</td>
<td>-163.006337</td>
<td>-8.5</td>
<td>-5.2</td>
<td>-11.8</td>
<td>-8.5</td>
<td>(i) 8.0</td>
<td>-9.1</td>
<td>25.3</td>
<td>7.7</td>
<td>-</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(ii) -0.6</td>
<td>-2.3</td>
<td>12.2</td>
<td>-11.7</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>UHFAA</td>
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<td>11.3</td>
<td>5.3</td>
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<td></td>
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<td>$Ba(N_3)_2$</td>
<td>centre</td>
<td>ESR</td>
<td></td>
<td>(21.1)</td>
<td>(+)19.6</td>
<td>(+)28.0</td>
<td>(+)15.7</td>
<td>(0.1)</td>
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<td>(+)14.0</td>
<td>(-)6.2</td>
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(i) long bond, (ii) short bond; signs and $a_{iso}$ values in parentheses are the assignments deduced from the present study.
FIGURE 4. Co-ordinate representation for the $N_3^0$ and $N_3^{2-}$ Radicals.
BIBLIOGRAPHY


In Part I infinitesimal self-consistent field Hartree-Fock perturbation theory is applied to the calculation of the Fermi contact, electron orbital and spin-dipolar contributions to indirect nuclear spin-spin coupling constants in some small closed-shell molecules from \textit{ab initio} LCAO-MO SCF wavefunctions. The dependence of the calculated values upon the size of Gaussian basis set employed and upon variations in molecular geometry is examined. The circumstances under which the method may be expected to yield results sufficiently reliable for most chemical purposes are indicated.

In Part II the \textit{ab initio} Unrestricted Hartree-Fock method with single spin annihilation is used in the LCAO-MO approximation with minimal Gaussian basis sets of atomic SCF orbitals to evaluate the isotropic and anisotropic electron-nuclear hyperfine coupling constants in some small doublet state free radicals of current experimental interest. This approach is applied to the identification of new radical species and to the elucidation of their molecular structures. In addition, the method is used to check the experimental assignments of hyperfine coupling constants deduced from ESR spectra and to investigate the reliability of Coulson's equation for the estimation of bond angles in triatomic ABA radicals.
ERRATA

Page 35, Equation (4.10). The L.H.S. should read: $v_{t_1t_2t_3}$.

Page 127, Line 22. After "variety" insert "of".

Page 137, Line 1. The final item on the line should be: [111].

Page 145. Add: