AB INITIO CALCULATIONS OF HYperfine COUPLING CONSTANTS.

A Thesis presented for the degree of
Doctor of Philosophy
in the Faculty of Science of Leicester University.

by

N.A. Smith.

November, 1971

The University
Leicester
STATEMENT.

The work described in this thesis, unless otherwise acknowledged in the text, has been carried out by the author in the Department of Chemistry of the University of Leicester between October 1968 and September 1971. The work has not been presented, and is not being concurrently presented, for any other degree.

Signed

Nigel A. Smith

November, 1971
ACKNOWLEDGEMENTS.

The author wishes to offer his thanks to:

Dr T.A. Claxton for his supervision and constant advice on the work presented in this thesis.

Prof. M.C.R. Symons for his helpful discussions.

Dr D. McWilliams, Dr B. Weiner and M. Godfrey for their tolerance and advice.

Dr J. Thompson and the staff of the University of Leicester Computing Laboratory for making facilities available for computations.

The Science Research Council for providing a grant.
CONTENTS

THEORY: The Use of the Ab Initio Unrestricted Hartree Fock Method in the Determination of Spin Density Distributions.

Introduction. 1
I. The Unrestricted Hartree Fock Method. 2
II. The Use of Annihilation and Projection Operators. 5
III. Application of Gaussians to Molecular Calculations. 8
IIIa. Construction of Gaussian Basis Sets. 10
IIIb. The Double Basis Approach. 13
IV. Optimisation in Ab Initio Calculations. 15
V. Methods of Minimising the UHF Energy. 17
  1) The Matrix Diagonalisation Method. 17
  2) Steepest Descents Method. 18
  3) The Conjugate Gradient Method. 20
VI. Restriction of Spin Contamination. 25
VII. The Calculation of Hyperfine Coupling Constants. 27
VIIa. Analytical Formulae for Anisotropic Integrals. 30
VIIb. Vibronic Contributions to the Hyperfine Constants. 35
Conclusions. 36

CHAPTER 1: Comparison of Minimisation Procedures for UHF Wavefunctions.

Introduction. 39
Results and Discussion. 42
Conclusions. 45
CHAPTER 5: Double Basis Calculations on Large Molecular Systems.

Introduction. 127
Method. 128
Results and Discussion. 130
The Pyrazine Molecule. 130
The Pyrazine Anion. 134
The Monoprotonated Pyrazine Radical. 139
Conclusions. 142

REFERENCES. 144
THEORY
Introduction

The Electron-Spin Resonance Experiment provides information associated with the manner in which unpaired electrons are distributed in a system. Analysis of the data obtained sometimes permits insight into the structure of the system investigated. The data derived is generally expressed in terms of hyperfine coupling constants associated with the nuclei which form the radical. In favourable cases this information can be separated into an isotropic and an anisotropic contribution, supplying valuable indications on the nature of the bonding and the overall structure of the radical.

The large amount of experimental data available has motivated many theoretical studies designed to predict the spin density distribution in radical species. The majority of these are semi-empirical while few calculations on a non-empirical level have appeared aimed at the explanation of observed hyperfine coupling constants. Although many studies have appeared in the literature concerning the prediction of isotropic hyperfine coupling constants, calculations designed to give anisotropic hyperfine coupling constants are few and generally incomplete.

These deficiencies motivated a study of spin density distributions from a Gaussian based ab initio viewpoint. The term ab initio implies no approximation above the Hartree Fock (separation of the many electron problem into a series of one electron problems) with the linear combination of atomic
orbitals approximation generally assumed and the atomic orbitals represented, in practice, by Slater or Gaussian type functions; all electrons are considered explicitly and all integrals evaluated exactly. The form of the wavefunction used and the manner in which it is constructed and minimised are described in the following sections. General analytical formulae for the integrals associated with the anisotropic hyperfine coupling constants are derived over Gaussian functions. A brief discussion of the effects of vibronic contributions on spin properties concludes this theoretical section. The application of the techniques elaborated are then presented.

I. The Unrestricted Hartree Fock Method

Various forms of the wavefunction for an open-shell system have been considered. The Unrestricted Hartree Fock (UHF) function has the advantage of retaining many of the analytical features of the Restricted Hartree Fock method by the simple extension of unpairing the electrons. By permitting the $\alpha$ and $\beta$ electrons to occupy different spatial orbitals correlation is implicitly incorporated into the wavefunction.

For an $N$ electron system of $p$ $\alpha$ electrons and $q$ $\beta$ electrons ($p>q$) the UHF wavefunction $\Psi_{\text{UHF}}$ takes the single determinantal form,

$$\Psi_{\text{UHF}}=(N!)^{-1/2}\det\begin{bmatrix}\psi(1)\alpha(1)\cdots\psi(p)\alpha(p)\varphi(p+1)\beta(p+1)\cdots\varphi(N)\beta(N)\end{bmatrix}$$

Without loss of generality the one electron
functions of the $\alpha$ electrons $\psi_i$ and of the $\beta$ electrons $\varphi_i$ may be considered as orthonormal amongst themselves

$$\int \psi_i^* \psi_j \, d\tau = \int \varphi_i^* \varphi_j \, d\tau = \delta_{ij}$$

A further reduction of the number of integrals which have to be considered results from the use of the "corresponding orbitals" suggested by Amos and Hall. These have the property,

$$\int \psi_i^* \varphi_j \, d\tau = T_i \delta_{ij}; \quad 0 \leq T_i \leq 1 \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdOTS
The UHF energy $E_{\text{UHF}}$ may now be written as,

$$E_{\text{UHF}} = \text{Tr}(PP^\alpha) + \text{Tr}(QP^\beta) - \frac{1}{2} \text{Tr}(PG^\alpha) - \frac{1}{2} \text{Tr}(QG^\beta) \quad \ldots \ldots \quad (6)$$

where

$$P^\alpha = h + G^\alpha \quad \ldots \ldots \ldots \quad (7)$$

$$P^\beta = h + G^\beta$$

$h$ is the one electron matrix with elements,

$$h_{ij} = \int \omega_i^*(r) \frac{1}{2} \nabla^2 \frac{1}{|r - \tau|} \omega_j d\tau \quad \ldots \ldots \ldots \quad (8)$$

and $G^\alpha$ and $G^\beta$ are the two electron matrices defined by,

$$G^\alpha_{ij} = \sum_{k,l} [ (P_{kl} + Q_{kl}) \langle ik | jl \rangle - P_{kl} \langle ik | lj \rangle ] \quad \ldots \ldots \ldots \quad (9)$$

$$G^\beta_{ij} = \sum_{k,l} [ (P_{kl} + Q_{kl}) \langle ik | jl \rangle - Q_{kl} \langle ik | lj \rangle ]$$

$$\langle ik | jl \rangle = \int \omega_i^*(l) \omega_j^*(2) \frac{1}{|r_{1,2}|} w_k(l) w_l(2) d\tau_1 d\tau_2 \quad \ldots \ldots \ldots \quad (10)$$

The energy may be minimised by the variation of the coefficients in $A$ and $B$ or, equivalently, of the bond order matrices $P$ and $Q$. Methods which are applicable to the minimisation problem will be considered in a later section.

The expectation values of the charge density operator,

$$q(r) = \sum_{i=1}^{N} \delta(r-r_i)$$

and the spin density operator,

$$\rho(r) = \sum_{i=1}^{N} 2S_{z_i} \delta(r-r_i)$$

over the atomic basis functions $\omega_i$ are given by,

$$q(r) = \sum_{\mu,\nu} \left( P_{\mu\nu} + Q_{\mu\nu} \right) \omega^*_\mu(r) \omega^*_\nu(r) \quad \ldots \ldots \ldots \quad (11)$$

$$\rho(r) = \sum_{\mu,\nu} \left( P_{\mu\nu} - Q_{\mu\nu} \right) \omega^*_\mu(r) \omega^*_\nu(r)$$
II: The Use of Annihilation and Projection Operators

Fundamental theoretical objections may be raised against the UHP method on the grounds that, although the wavefunction is an eigenfunction of the $S_z$ operator, it is not, in general, an eigenfunction of the $\hat{S}^2$ operator. The deficiency is found to result in overestimates of the calculated spin properties.

Lowdin\(^4\) has suggested a solution to this problem by the use of projection operators. The UHF wavefunction is a mixture of components of various multiplicities and may be written formally as,

$$\Psi_{\text{UHF}} = \sum_{k=0}^{\infty} c_{s+k} \phi_{s+k}$$

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

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

The projection operator,

$$A_k = \frac{\hat{S}^2 - k(k+1)}{s(s+1) - k(k+1)}$$

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

$$Q_s = \prod_{k=s+1}^{\infty} \left[ \frac{(\hat{S}^2 - k(k+1))/(s(s+1) - k(k+1))}{(s(s+1) - k(k+1))} \right]$$

may be used to select the required pure spin state of multiplicity $(2s+1)$.

In the Extended Hartree Fock method the variational procedure is applied to the wavefunction $Q_s \tilde{\Psi}_{\text{UHF}}$. This is an extremely difficult procedure, but Harriman et al\(^6\) have developed a successful approach.
The difficulties inherent in the practical application of $Q_s$ led Amos and Hall\textsuperscript{2} to suggest the use of the single annihilator $A_{s+1}$ rather than $Q_s$. The justification for this approximation results from the demonstration that the major unwanted component in $\Psi_{UHF}$ is that with spin $(s+1)$, the states of higher multiplicity decreasing rapidly in importance\textsuperscript{2,5}. 

Although the wavefunction is now simplified to $A_{s+1}\Psi_{UHF}$ the complexities involved in the variational procedure are prohibitive. For this reason the annihilator $A_{s+1}$ is generally applied to the wavefunction which minimises the energy in the Unrestricted Hartree Fock approximation. Generally a lower energy is obtained, but no rigorous proof of the necessity of this is available.

The energy after annihilation of the $(s+1)$ spin state $E_{UHFAA}$ is given by,

$$E_{UHFAA} = \frac{\langle A_{s+1}\Psi_{UHF} | H | A_{s+1}\Psi_{UHF} \rangle}{\langle A_{s+1}\Psi_{UHF} | A_{s+1}\Psi_{UHF} \rangle} \quad \ldots \ldots (14)$$

or,

$$E_{UHFAA} = \frac{\langle \Psi_{UHF} | H | A_{s+1}^2 \Psi_{UHF} \rangle}{\langle \Psi_{UHF} | A_{s+1}^2 \Psi_{UHF} \rangle} \quad \ldots \ldots (15)$$

where the second result, equation (15), is given as $S^2$ commutes with the spinless Hamiltonian. Equation (15) may be reduced further if the approximation that $A_{s+1}$ is idempotent is used, so that

$$E_{UHFAA} = \frac{\langle \Psi_{UHF} | H | A_{s+1}\Psi_{UHF} \rangle}{\langle \Psi_{UHF} | A_{s+1}\Psi_{UHF} \rangle} \quad \ldots \ldots (16)$$

$E_{UHFAA}$ may then be more fully expressed as\textsuperscript{1,1},
\[
E_{\text{UHF}} = E_{\text{UHF}} - x^{-1} \left[ \text{Tr}((\text{PSQ} \text{SP} + \text{SPQ} \text{SQ} - \text{PSQ} - \text{QSP})_{P+Q})_{uv} <su|tv> \
+ \sum_{\text{Stuv}} (\text{PSQ} \text{SP} + \text{SPQ} \text{SQ} - \text{PSQ} - \text{QSP})_{st}(\text{P+Q})_{uv} <su|tv> \
- \sum_{\text{Stuv}} ((\text{PSQ} \text{SP})_{st} P_{uv} + (\text{QSP} \text{SQ})_{st} Q_{uv} \
- (\text{PSQ} + \text{QSP})_{st}(\text{P+Q})_{uv} + P_{st} Q_{uv} \
+ (\text{PSQ})_{st}(\text{QSP})_{uv} <su|tv> \right] \quad (17)
\]

where,
\[
x = \frac{1}{2}(p-q)^2 + \frac{1}{2}(p+q) - (s+1)(s+2) - \text{Tr}(\text{PSQ})
\]
and \( E_{\text{UHF}} \) is the UHF energy.

The charge and spin density functions are given by,
\[
q(r) = \sum_{uv} (J_{uv} + X_{uv}) \omega_u^*(r) \omega_v(r) \quad (18)
\]
\[
p(r) = \sum_{uv} (J_{uv} - X_{uv}) \omega_u^*(r) \omega_v(r)
\]

where
\[
M_J = [A^2 + pq -q + (3-2A-N+2\text{Tr}(\text{PSQ})) \text{Tr}(\text{PSQS})] \
- 2\text{Tr}(\text{PSQSPQS})] P + [p - \text{Tr}(\text{PSQS})] Q \
+ \text{QSPSQ} + [N-3+2A-4\text{Tr}(\text{PSQ})] \text{PSSP} \
+ [1-p-A+2\text{Tr}(\text{PSQ})][\text{PSQ} + \text{QSP}] \
- 2[\text{PSQSPQS} + \text{QSPQSP}] + 4\text{PSQPSQSPQSP}
\]

and
\[
A = q - 2(s+1) \
M = A^2 + pq + [2-2A-N+2\text{Tr}(\text{PSQ})] \text{Tr}(\text{PSQS}) \
- 2\text{Tr}(\text{PSQSPQS})
\]

\( \mathcal{K} \) is given by a similar expression to that for \( J \) with the \( P \) and \( p \) interchanged with the \( Q \) and \( q \). As the \( \mathcal{S}^2 \) and the \( q(r) \) operators do not commute the expectation value is from
\[
p(r) = \frac{<A_{s+vUHF} | q(r) | A_{s+vUHF}>}{<A_{s+vUHF} | A_{s+vUHF}>}
\]
All theoretical procedures designed to evaluate the wavefunctions of molecules of chemical interest are unsatisfactory if electron correlation is dominant. In open shell cases this is particularly apparent and it is necessary, if an objective is chemical, to use a practical method which has been shown to work. Although a number of objections have been levelled against the projected UHF method, in this form, it has been found to give an adequate description of the spin properties of radicals and for that reason, combined with the simplicity of application, is considered a useful tool in the analysis of molecular properties.

III. Application of Gaussians to Molecular Calculations

In practical applications of the Unrestricted Hartree Fock method on a radical with \( m \) basis functions, \( \omega_\mathbf{i} \), a number of types of integral have to be evaluated. By far the most abundant of these are the two electron integrals of the form,

\[
\int \omega^*_\mathbf{i}(1)\omega^*_\mathbf{j}(2)[1/r_{12}]\omega_\mathbf{k}(1)\omega_\mathbf{l}(2)d\tau_1d\tau_2
\]

In fact there are \( m^4 \) such integrals and although this number may be considerably reduced by symmetry, \( m \) does not have to become very large for computation to be prohibitively long. For this reason various semi-empirical theories have been proposed and applied with varying degrees of success. Certainly the information and insight acquired by the use of semi-empirical techniques has been of great value, but an analysis of the methods of
quantum chemistry from a less arbitrary position would be informative as to the nature, and value, of the approximate wavefunctions that have been used.

With the availability of high speed computers it is now feasible to approach the problem of molecular calculations in an ab initio manner. The need for a good approximation to the wavefunction, especially close to the nucleus, is critical to the calculation of spin properties, thus supplying a rigid test of the wavefunction used.

The Slater type orbital (STO) forms an adequate representation of the atomic function, particularly in the bonding region, but has the disadvantage, for the multicentre two electron integral, of difficulty of evaluation, generally involving a numerical integration. Nevertheless, a large number of ab initio studies on molecules have been performed using STO's. Shavitt and Karplus\cite{Shavitt} have suggested the use of the Gaussian Expansion method,

\[ e^{-\frac{1}{2} \int 4a e^{-\frac{S^2}{4a} + \frac{1}{4a}r^2} d\alpha} \]

in the evaluation of the integrals over STO's. This, however, does not alleviate the need for a numerical integration.

The advantages of using Gaussian type orbitals was first pointed out by Boys\cite{Boys}. Gaussians of the form,

\[ \chi_i = r_i^n \exp(-\alpha_i r_i^2) \]

where \( n \) is an integer, have
the property that for a multicentre integral over Gaussians a transformation can be found which reduces the integral to a one centre problem. This property results in quite simple analytical formulae for the integrals involved in molecular calculations and has led to the extensive use of Gaussian functions in theoretical chemistry. The advantage gained by the ease of elucidation is somewhat offset by the inferior description give by the GTO compared to the STO. This deficiency results in the need for a larger basis set of Gaussians, and thus an increase in the number of integrals required. Fortunately this increase is more than compensated for by the ease of computation of the integrals over Gaussians and sufficiently accurate wavefunctions can be used.

IIIa. Construction of Gaussian Basis Sets

The requirement for large basis sets of GTO's in the accurate description of systems in theoretical calculations raises problems in the linear minimisation. Even for small systems the number of linear parameters to be optimised can be very large. Clementi and Davis have suggested that the Gaussian basis should be contracted, reducing the number of linear parameters by taking orbitals which are linear combinations of the Gaussian basis,

$$\omega_i = \sum_{j=1}^{n} c_j \chi_j$$

where $\chi_j$ is a Gaussian of the form
\[ \chi_j = n_j r^{n_j - 1} \exp(-\alpha_j r^2) Y_{\ell \mu}(\theta, \phi) \]

\( Y_{\ell \mu} \) are normalised spherical harmonics and \( n_j \) the normalisation factor,

\[ n_j = 2^{n_j + 1} [(2n_j - 2)!]^{-\frac{1}{2}} (2\pi)^{-\frac{1}{2}} \alpha^{-\frac{1}{2}} (2n_j + 1)/4 \]

The application of Gaussians to molecular calculations is dependent upon the use of contractions; the manner of the contraction has been subject to investigation by several workers \(^{17-20}\). In the applications of the ab initio method reported use is made throughout of complete contraction of the Gaussian functions. Thus the 1s of hydrogen is represented by a linear sum of GTO's and the 1s, 2s and 2p of carbon are represented by similar expansions.

The employment of contraction while paramount to molecular calculations does not in itself result in any reduction in the number of integrals to be calculated, although it does reduce the number of integrals to be stored. Extensive basis sets would counter the purpose of Gaussians; generally it is found that 9 to 11s type and 5 to 7p type Gaussian functions are sufficient in the description of the first row elements \(^{17,21}\). In the applications to be reported further reductions in integral calculation has been achieved by using contractions of the form,

\[ \varphi_i = \sum_{j=1}^{n} c_{ij} \chi_j \]

where the \( \varphi_i \) are the s type or p type orbitals used as a basis for the atom involved in the molecular system.

Gaussian basis sets, of various sizes, are
reported in the literature using the manner of contraction (of linear and non-linear parameters) outlined \(^{17,21-24}\). The major methods used in the optimisation of parameters are based upon the least squares or the energy criterion. The least squares approach, fitting a Gaussian expansion to Slater type orbitals, has been employed in a variety of forms by many workers \(^{25-28}\). An unfortunate aspect of the method of least squares is the problem of local minima; for large Gaussian sets the number of local minima can be particularly troublesome. Generally empirical checks can be pursued to clarify the position, for example, by scanning around the minimum position. Optimisation of the basis set by minimisation of the SCF atomic energy has proved to be the most popular procedure \(^{21,29}\). The atomic SCF bases, optimised on the energy criterion, are used as bases for molecular calculations. Undoubtedly the atomic (and least squares) bases are not optimal for the molecular systems they are applied to and for this reason attempts have been made to optimise the molecular basis in the molecular environment \(^{30}\). The enormity of the problem involved in molecular optimisation is reduced by the use of smaller basis sets. This necessity for a smaller basis leads to a poor description of the wavefunction and invalidates its use for calculations aimed at predicting spin properties, although, no doubt, insight into less sensitive properties can be obtained.

For the calculation of spin properties a good
description of the wavefunction close to the nucleus is essential. This has led to the use of the atomic Gaussian basis fitted by the energy criterion where an adequate description of the orbitals and their cusp properties is expected for a reasonable sized basis.

IIIb. The Double Basis Approach

A large number of calculations using Gaussian type orbitals have been reported. The treatment of systems such as the nucleotide bases composing the nucleic acids has now become feasible from an ab initio viewpoint. It is only natural that calculations involving large molecules, and hence a large number of basis functions, should necessitate the availability of an extremely powerful computer installation. The fact that for most workers such facilities are not available has limited the number of accurate, large scale calculations to a few centres. Even a system such as $\text{SO}_4^{2-}$, using a reasonable basis, would present a formidable problem in terms of the time required. This limitation, through restricted facilities, has motivated a search for suitable approximations on the ab initio method which, without invalidating the concept, will allow for a more general application.

The basis functions $w_1$ are approximately represented by a linear expansion of Gaussians,

$$w_1 = \sum_{j=1}^{n} c_j X_j + \delta w_1 \quad \ldots \ldots \ldots \ldots \ldots (19)$$

where as $n$ increases the truncation error $\delta w_1$ decreases. It has been
demonstrated by Cook and Palmieri\textsuperscript{34} that the expansion required for the calculation of one electron integrals to a certain accuracy is larger than that required for the calculation of two electron integrals to the same degree of accuracy. The first order correction in a general two electron integral is given by terms such as
\[ \int \delta w_1^*(1)w_j^*(2)[1/r_{12}]w_k(1)w_1(2) d\tau_1 d\tau_2 \]

The numerical value of this correction when the integral is over more than one centre will be significantly less than if it were a one centre integral. This led Cook and Palmieri to suggest a mixed basis method\textsuperscript{34} where the one electron and one centre two electron integrals are calculated over Slater type orbitals and the multicentre two electron integrals are evaluated using small expansions of Gaussian type orbitals. As the vast majority of computation is spent on the evaluation of such multicentre two electron integrals the reduction in computer time is sufficient to permit much larger systems to be studied than would otherwise be feasible.

The work of Cook and Palmieri was Slater orientated but may easily be extended to complete Gaussian orientation and the use of different Gaussian expansions in molecular calculations is differentiated from their "mixed" basis method by reference to the "double" basis method. Generally the value of $n$ in equation (19) is about four for the accurate reproduction of the one electron and one centre two electron integrals and two is sufficient for the
multicentre two electron integrals.

The problem arises over the most suitable choice of basis to be used in double basis calculations. The large expansions optimised on the energy criterion were considered best suited for the one centre and one electron integrals. However the molecular, rather than atomic, nature of the multicentre two electron integrals suggest that a fit of the small basis over the space would be preferable. The large expansions and the Slater type orbitals give an adequate description of the atomic wavefunction over all regions of space so that a least squares fit of the small basis to either of these functions would yield an expansion suitable to the requirements of the double basis method. Such small expansions are available for the first row elements.

The manner in which Gaussian type orbitals are applied to ab initio calculations, as outlined above, is well documented and no attempt at a comprehensive review is felt necessary. The sensitivity of the spin properties to the wavefunction, however, requires further discussion.

IV. Optimisation in Ab Initio Calculations

The ab initio calculation of hyperfine coupling constants derived from the Electron Spin Resonance experiment has proved to be a field much neglected. Recently some workers have taken up the challenge but the results, using various wavefunctions, are discouraging. In this work, using the
Unrestricted Hartree Fock wavefunction after annihilation, the sensitivity of the spin properties to the wavefunction have made it necessary, where possible, to further optimise the basis. The simplest way to achieve a degree of optimisation of the Gaussian basis is by varying the exponential factor

\[ \varphi_1(\xi_1) = \sum_j c_j \xi_j(a_j^*); \quad a_j^* = \xi_1 \alpha_j \]

where \( \xi_1 \) is a positive scalar representing the change of the exponential factor in the molecular species as compared to its value in the free atom. Even this approach, in conjunction with the optimisation of the geometry, will soon become too time consuming as the number of basis orbitals in the system increases. For this reason only the optimisation of the exponential factor of the 1s orbital of the hydrogen atom is considered. This approach is felt to be justified as the atomic 1s orbital of the hydrogen would be expected to be most affected by transfer to a molecular environment.

In larger systems, where optimisation of the proton exponent, and even completely or partially of the geometry, is not feasible, the best values have to be estimated from experience. This approach, of non-optimisation in some cases, is taken as any reduction of the size of the expansion sets used would more than offset the value of any optimisation achieved.
V. Methods of Minimising the UHF Energy

The use of Gaussian type orbitals is centred upon the computational efficiency achieved in the evaluation of the integrals involved in molecular calculations. However, now that the problem is defined a minimisation of the energy of the system must be effected within the framework of the approximation used, that is, the Unrestricted Hartree Fock method. Even with contraction of the basis set the number of atomic orbitals used can soon become large, and as the function to be evaluated is non-trivial any iteration cycle of minimisation must be as efficient as possible. Three approaches have been adopted to this problem; the matrix diagonalisation method \(^{37,38}\), the steepest descents method \(^{39-41}\) and the method of conjugate gradients \(^{42-45}\).

1) The Matrix Diagonalisation Method

The method of matrix diagonalisation uses the equations,

\[
\begin{align*}
F^\alpha_A &= S\varepsilon^\alpha \\
F^\beta_B &= S\varepsilon^\beta \\
\end{align*}
\]

which the orbitals must satisfy. The Fock matrices \(F^\alpha\) and \(F^\beta\) for the \(\alpha\) and \(\beta\) electrons respectively, the \(A\) and \(B\) matrices of coefficients of the molecular orbitals over the atomic orbital basis and \(S\) the overlap matrix are defined as previously (equations (1) to (9)). The \(\varepsilon^\alpha\) and \(\varepsilon^\beta\) matrices are diagonal. The energy is then given by, \(^{37,38}\)

\[
E_{\text{UHF}} = \sum_i \varepsilon^\alpha_{ii} + \sum_i \varepsilon^\beta_{ii} - \frac{1}{2} \text{Tr}(P\varepsilon^\alpha) - \frac{1}{2} \text{Tr}(Q\varepsilon^\beta) \quad (21)
\]
As the Fock matrices are functions of the matrices A and B the manner of solution must be by successive approximation. Thus $\mathbf{F}^\alpha$ and $\mathbf{F}^\beta$ are calculated from an initial approximation to A and B; the process is repeated until self consistency is achieved and hence the minimum attained.

2) The Steepest Descents Method

The method of steepest descents for the solution of the eigenvalue problem was first suggested by McWeeny for closed shell systems and later extended to the UHF method.

The method, in general terms, may be considered as follows: for a function $f(x)$ of $n$ variables, $x_1, x_2, \ldots, x_n$ or $|\mathbf{x}>$ using Dirac notation, if there is a first approximation $|\mathbf{x}_0>$ to $|\mathbf{x}>$ and the gradient of $f(x_0)$, $|\mathbf{g}_0>$ ($=|\mathbf{g}(x_0)>$), can be found, then a better approximation, $|\mathbf{x}_1>$, to $|\mathbf{x}>$ is given by

$$|\mathbf{x}_1> = |\mathbf{x}_0> - \lambda_0|\mathbf{g}_0>$$

or generally,

$$|\mathbf{x}_{i+1}> = |\mathbf{x}_i> - \lambda_i|\mathbf{g}_i> \quad \ldots \quad (22)$$

Thus an iterative cycle is formed. The positive scalar $\lambda_i$ is chosen at each iteration so that $|\mathbf{x}_{i+1}>$ is approximately the minimum in the direction $|\mathbf{g}_i>$ from $|\mathbf{x}_i>$. 

As the first order density matrix and consequently the density matrices of all other orders may be expressed in terms of $\mathbf{P}$ and $\mathbf{Q}$ only it follows that the bond order matrices are fundamental quantities of the theory and there is no requirement to calculate the orbitals, as in the matrix diagonalisation method.
Direct minimisation of the energy by variation of \( P \) and \( Q \) has been formulated by Amos for the changes

\[
P \rightarrow P + \delta P \\
Q \rightarrow Q + \delta Q
\]

subject to the conditions

\[
(PS)^2 = PS; \quad (QS)^2 = QS \\
\text{Tr}(PS) = p; \quad \text{Tr}(QS) = q
\]

Defining the matrices,

\[
P' = S^{-1}P \\
s = P'P^\alpha P \\
I = s + s^+ \\
J = s - s^+
\]

and similar expression for \( Q' \), \( t \), \( K \) and \( L \) respectively, by replacing \( P \) by \( Q \) and \( P^\alpha \) by \( P^\beta \).

Then the directions of descent are, to second order,

\[
\delta P = - \lambda^\alpha (I + \lambda^a ISJ)^{-1} (I + \lambda^a ISJ) \\
\delta Q = - \lambda^\beta (I + \lambda^b KSK)^{-1} (I + \lambda^b KSL)
\]

The inverse in equation (25) may be neglected to first order in \( \lambda^\alpha \) and \( \lambda^\beta \) to give the more approximate result,

\[
\delta P = - \lambda^\alpha (I + \lambda^a ISJ) \\
\delta Q = - \lambda^\beta (I + \lambda^b KSL)
\]

The step lengths \( \lambda^\alpha \) and \( \lambda^\beta \) are given by the expressions,

\[
[a^2 - (2a-c)(2a'-c')]\lambda^\alpha = (2a-c)b + b'd \\
[a^2 - (2a'-c')(2a-c)]\lambda^\beta = (2a'-c')b' + bd
\]

\[
a = \text{Tr}(ISJ^\alpha) \\
b = \text{Tr}(I^\alpha) \\
c = \sum_{ijk} I_{ij} I_{kl} [\langle ikjl \rangle - \langle iklj \rangle]
\]

with similar expressions.
for $a'$, $b'$ and $c'$ by replacing $I$, $J$ and $P^2$ by $K$, $L$ and $P^3$ respectively.

$$d = \sum_{ijkl} I_{ijkl} K_{kl} <ik|jl>$$

Generally the modified bond order matrices obtained are neither idempotent nor have the correct traces necessitated by the conditions (2h).

Idempotency may be restored by repeated application of

$$P = (PS)^2(3S^{-1} - 2P)$$
$$Q = (QS)^2(3S^{-1} - 2Q)$$

and the traces corrected using

$$P = P + aS^{-1}$$
$$Q = Q + bS^{-1}$$

with

$$a = (p - Tr(PS))/N$$
$$b = (q - Tr(QS))/N$$

The steepest descents process may then be continued until self consistency is achieved.

3) The Conjugate Gradient Method

In the method proposed by Fletcher for closed shell systems and extended by Sutcliffe to open shell systems for the Restricted Hartree Fock and Multiconfigurational Self Consistent Field wavefunctions an approach is adopted which is dependent upon the unconstraining of the parameters to be varied.

The m$x$ matrix $A$ must satisfy the orthonormality condition

$$A^+ S A = I$$

where $I$ is the identity matrix.
To unconstrain the minimisation problem an m×p matrix \( \mathbf{Y}^\alpha \) is defined such that

\[
\mathbf{A} = \mathbf{Y}^\alpha \mathbf{U}^\alpha
\]

(27)

where \( \mathbf{U}^\alpha \) is constructed in a manner to ensure that \( \mathbf{A} \) satisfies the condition of orthonormality.

By defining \( \mathbf{Y}^\beta \) and \( \mathbf{U}^\beta \) in a similar fashion for \( \mathbf{B} \), then the \( \mathbf{P} \) and \( \mathbf{Q} \) matrices may be calculated and hence the energy. \( \mathbf{A} \) and \( \mathbf{B} \) may be obtained by any orthonormalisation procedure to give the same energy, so that the energy, in \( \mathbf{Y}^\alpha \) and \( \mathbf{Y}^\beta \), is not unique. However, as pointed out in the steepest descents method as the bond order matrices are uniquely defined so are all other properties predicted. Thus the nature of the \( \mathbf{Y}^\alpha \) and \( \mathbf{Y}^\beta \) obtained is irrelevant and the problem of constraints may be ignored.

Following the work of Fletcher for the closed shell problem the matrices \( \mathbf{U}^\alpha \) and \( \mathbf{U}^\beta \) are defined as

\[
\mathbf{U}^\alpha = (\mathbf{Y}^\alpha \mathbf{S} \mathbf{Y}^\alpha)^{-\frac{1}{2}}
\]

(28)

\[
\mathbf{U}^\beta = (\mathbf{Y}^\beta \mathbf{S} \mathbf{Y}^\beta)^{-\frac{1}{2}}
\]

The bond order matrices may be written as

\[
\mathbf{P} = \mathbf{Y}^\alpha \mathbf{M}^\alpha \mathbf{Y}^\alpha^+
\]

(29)

\[
\mathbf{Q} = \mathbf{Y}^\beta \mathbf{M}^\beta \mathbf{Y}^\beta^+
\]

with

\[
\mathbf{M}^\alpha = \mathbf{U}^\alpha \mathbf{U}^\alpha^+ = (\mathbf{Y}^\alpha \mathbf{S} \mathbf{Y}^\alpha)^{-1}
\]

(30)

and similarly for \( \mathbf{M}^\beta \).

If a change in \( \mathbf{Y}^\alpha \) to \( \mathbf{Y}^\alpha + \delta \mathbf{Y}^\alpha \) is made then \( \mathbf{M}^\alpha \) is changed by \( \delta \mathbf{M}^\alpha \). Neglecting terms higher than first order in \( \delta \mathbf{Y}^\alpha \)
\[ M^\alpha + \delta M^\alpha = (Y^\alpha + \delta Y^\alpha + \delta Y^\alpha + Y^\alpha + S Y^\alpha )^{-1} \]
\[
= (I + M^\alpha \varepsilon^\alpha )^{-1} \]
\[
= (I - M^\alpha \varepsilon^\alpha ) \]
\[
\varepsilon^\alpha = \delta Y^\alpha \]
\[
SY^\alpha + \delta Y^\alpha + SY^\alpha . \]

Thus from (31),
\[ \delta M^\alpha = - M^\alpha \varepsilon^\alpha M^\alpha \]

The change \( \delta P \) in \( P \) can be obtained as
\[ \delta P = Y^\alpha M^\alpha SY^\alpha + \delta Y^\alpha M^\alpha Y^\alpha + \delta Y^\alpha M^\alpha \]
\[ = Y^\alpha M^\alpha SY^\alpha (I - SP) + (I - SP) \delta Y^\alpha M^\alpha Y^\alpha \]
\[ = Y^\alpha M^\alpha SY^\alpha + \delta Y^\alpha M^\alpha Y^\alpha \]
\[ \ldots (32) \]

and similar expressions may be derived for \( \delta M^\beta \) and \( \delta Q \).

The change in the energy is then,
\[ \delta E = \text{Tr} (F^\alpha \delta P) + \text{Tr} (F^\beta \delta Q), \]
\[ = 2 \text{Tr} (F^\alpha Y^\alpha M^\alpha SY^\alpha ) + \text{Tr} (F^\beta M^\beta SY^\beta ) \]
\[ = 2 [(I - SP) F^\alpha Y^\alpha M^\alpha ] : SY^\alpha + 2 [(I - SQ) F^\beta M^\beta ] : SY^\beta \]
\[ \ldots (33) \]

where the colon : represents summation over two suffices. By virtue of the relationship between the gradient \( \nabla E^\alpha \) (or \( \nabla E^\beta \)) and the increments in \( Y^\alpha \) (or \( Y^\beta \)) from equation (33),
\[ \nabla E^\alpha = 2 (I - SP) F^\alpha Y^\alpha M^\alpha \]
\[ \nabla E^\beta = 2 (I - SQ) F^\beta Y^\beta M^\beta \]
\[ \ldots \ldots \ldots \ldots (34) \]

and the complete gradient of the energy is given by the \( mx(p + q) \) partition matrix
\[ \nabla E = (\nabla E^\alpha : \nabla E^\beta) \]
and similarly,
\[ Y = (Y^\alpha : Y^\beta) \]

With the definition of the linear parameters \( Y \) and the gradient \( \nabla E \) the method of conjugate gradients...
proposed by Fletcher and Reeves \(^4\) may be used. The Fletcher and Powell method \(^3\) is excluded as the storage of the inverse Hessian matrix during computation is necessitated.

Considering a general quadratic function \(f\) of \(n\) variables in the form,

\[
f = f_0 + \langle a | x \rangle + \frac{1}{2} \langle x | G | x \rangle \tag{35}
\]

where \(G\) is the Hessian matrix of second derivatives, \(|x_i\rangle, i=0,1,2, \ldots\) are successive approximations to the minimum \(|x\rangle\). The gradient \(|g_1\rangle\) is

\[
|g_1\rangle = |a\rangle + G|x_1\rangle \tag{36}
\]

The step from \(|x_i\rangle\) to \(|x_{i+1}\rangle\) is defined in the conjugate gradient approach by

\[
\langle g_{i+1} | p_i \rangle = 0 \tag{37}
\]

\[
|x_{i+1}\rangle = |x_i\rangle + \lambda_i |p_i\rangle \tag{38}
\]

where \(\lambda_i\) is a scalar and \(|p_i\rangle\) is some specific direction from a line through \(|x_i\rangle\).

Repeated application of (38) results in

\[
|x_n\rangle = |x_{j+1}\rangle + \sum_{i=j+1}^{n-1} \lambda_i |p_i\rangle ; \quad 0 \leq j < n-1
\]

and hence

\[
|g_n\rangle = |g_{j+1}\rangle + \sum_{i=j+1}^{n-1} \lambda_i G|p_i\rangle \tag{39}
\]

By forming the product of (39) with \(|p_j\rangle\),

\[
\langle g_n | p_j \rangle = \sum_{i=j+1}^{n-1} \lambda_i \langle p_i | G | p_j \rangle \tag{40}
\]

From (40) if

\[
\langle p_i | G | p_j \rangle = 0 ; \quad i \neq j \tag{41}
\]
then
\[ \langle g_n | p_j \rangle = 0 \]
and since \(|p_0>, |p_1>, \ldots |p_{n-1}\rangle\) form a basis
\[ \langle g_n | = 0 \]
so that
\[ |x_n\rangle = |x\rangle \]

Thus quadratic convergence is achieved in a maximum of \(n\) iterations when using a set of \(G\) conjugated directions. For a non-quadratic function the same formulation is applicable but the process will be iterative rather than finite and a test of convergence is necessary.

As the function and gradient are defined numerically \(G\) is not explicitly known. In the Fletcher and Powell\(^3\) procedure \(|p_i\rangle\) is defined as
\[ |p_i\rangle = -H_i |g_i\rangle \quad \ldots \ldots \quad (42) \]
where \(H_0, H_1, \ldots\) are a sequence of symmetric positive definite matrices constructed such that as the minimum is approached \(H_i\) tends to \(G^{-1}\), the inverse Hessian matrix. The disadvantage of this method lies in the necessity to store the intermediate matrix \(H\). The procedure adopted by Fletcher avoids this by generating \(|p_0>, |p_1>, \ldots\) such that \(|p_{i+1}\rangle\) is a linear combination of \(|g_{i+1}\rangle\) and \(|p_0>, |p_1>, \ldots |p_i\rangle\) which satisfy the orthonormality condition (41)

The equations are found to reduce to
\[ |p_{i+1}\rangle = -|g_{i+1}\rangle + \beta_i |p_i\rangle \quad \ldots \ldots \quad (45) \]
where the scalar $\beta_i$ is

$$\beta_i = \langle \xi_{i+1} | \xi_{i+1}^\dagger \rangle / \langle \xi_i | \xi_i^\dagger \rangle$$

($|p_0\rangle$ is defined as $-|\xi_0\rangle$ so that initially a steepest descent is taken).

In summary $|x_{i+1}\rangle$ is given by equation (38); $|\xi_{i+1}\rangle$ and hence $|p_{i+1}\rangle$ are calculated and the cycle repeated. $\lambda_i$ in equation (38) is defined such that $|x_{i+1}\rangle$ is the minimum position in the function on a line through $|x_i\rangle$ in the direction $|p_i\rangle$.

The three approaches to minimisation, matrix diagonalisation, steepest descents and conjugate gradients, are written into a computer program in a manner which allows unrestricted interchange between any of the techniques when it is felt that such a switch will increase the rate of convergence.

VI. Restriction of Spin Contamination

The methods described are used to minimise the energy in the Unrestricted Hartree Fock formulation and then a single annihilator $A_{s+1}$ applied to the UHF wavefunction $\Psi_{UHF}$.

The energy after annihilation

$$E_{UHFAA} = \frac{\langle A_{s+1}^\dagger \Psi_{UHF} | H | A_{s+1} \Psi_{UHF} \rangle}{\langle A_{s+1}^\dagger \Psi_{UHF} | A_{s+1} \Psi_{UHF} \rangle}$$

$$= \frac{\langle \Psi_{UHF} | A_{s+1}^2 \Psi_{UHF} \rangle}{\langle \Psi_{UHF} | A_{s+1} \Psi_{UHF} \rangle} \quad \ldots \quad (44)$$

as $S^2$ commutes with the spinless Hamiltonian. Expression (44) is difficult to evaluate and for this reason it is assumed that $A_{s+1}$
is idempotent so that

$$E_{UHFAA} = \frac{\langle \Psi_{UHF} | H | A_{s+1} \Psi_{UHF} \rangle}{\langle \Psi_{UHF} | A_{s+1} \Psi_{UHF} \rangle} \quad \ldots \quad (45)$$

As the annihilation is achieved after functional minimisation, and in fact only a single annihilator is used, there is no guarantee that the errors in the method are small. Generally the necessary conditions for small errors, that all coefficients $c_{s+i}$ are small for $i \geq 2$ in the equation

$$\Psi_{UHF} = \sum_{i=0}^{q} c_{s+i} \Psi_{s+i} \quad \ldots \quad (46)$$

are satisfied and this fact is responsible for the use of the approximation. The acute sensitivity of the $\langle S^2 \rangle$ value to the coefficients can be remedied by minimising the function

$$\epsilon = \alpha E_{UHF} + (1 - \alpha) \langle S^2 \rangle_{UHF} \quad \ldots \quad (47)$$

where $\alpha$ is a scalar in the range $0 \leq \alpha \leq 1$, rather than minimising $E_{UHF}$. Experience has shown that cases do arise when the expectation value of $S^2$, even after annihilation, is unusually high. These cases are due to severe contamination from spin states of multiplicity $(2(s+i)+1)$, for $i \geq 2$, and for this reason the function (47) has been used. The improvement obtained in the expectation value of $S^2$, however, is achieved at the expense of a higher energy.
In the electron spin resonance technique the spin Hamiltonian considered is generally that involving coupling of the electrons and the nuclei and may be expressed as

$$\mathcal{H} = g_e \beta_e \sum_i \sum_N g_N \beta_N S_i \cdot T_N \cdot I_N$$ ....(48)

where $i$ and $N$ refer to the electrons and nuclei respectively and $S_i$ is the spin of the $i^{th}$ electron and $I_N$ the spin of the $N^{th}$ nucleus. $g_e$ and $g_N$ are the electronic and nuclear $g$ values, $\beta_e$ and $\beta_N$ the electronic and nuclear magnetons. $T_N$ is a hyperfine tensor which can always be reduced to diagonal form by a suitable choice of axes, these axes being referred to as the principal axes.

The tensor $T_N$ may be separated into two components

$$T_N = \frac{8 \pi}{3} \delta(r_N) I + T'_N$$ .... .......(49)

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

Thus,

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

$$\mathcal{H}_1 = \frac{8 \pi g_e \beta_e}{3} \sum_i \sum_N g_N \beta_N \delta(r_N) S_i \cdot I_N$$ .......(50)

$$\mathcal{H}_2 = g_e \beta_e \sum_i \sum_N g_N \beta_N S_i \cdot T'_N \cdot I_N$$ .......(51)

The isotropic or Fermi contact term $\mathcal{H}_1$ represents the energy of the nuclear moment in the magnetic field.
produced at the nuclei by electric currents associated with the electrons. As a contact term the interaction can only occur when the electron has finite probability of being at the nucleus, that is, for electrons with s orbital character.

The hyperfine coupling constant $a_N$, for nucleus $N$, may be defined from (50) as

$$a_N = \frac{8}{3}\gamma_N g_e \beta_e g_N \beta_N \rho(r_N)$$

$$= \frac{8}{3}\gamma_N g_e \beta_e \rho(r_N)$$

where $\gamma_N$ is the gyromagnetic ratio of nucleus $N$ and $\rho(r_N)$ is the value of the spin density function at nucleus $N$.

The anisotropic or dipolar term $\mathcal{H}_2$ may equally be defined as

$$\mathcal{H}_2 = -g_e \beta_e \sum_i \sum_N g_N \beta_N \left[ \frac{S_i \cdot I_N}{r_N^5} - \frac{3(S_i \cdot r_N)(I_N \cdot r_N)}{r_N^7} \right]$$

$\mathcal{H}_2$, representing the quantum mechanical equivalent of dipolar coupling, is the interaction between the electron and nuclear magnetic moments. For a completely spherical environment the anisotropic term averages to zero.

The elements of $T^i_N$ may be written

$$T^i_N(kl) = (r_N^2 \delta_{k_l} - 3k_l)/r_N^5$$

where $k,l = x_N, y_N$ or $z_N$

Defining the matrix $a_{kl}(N)$,

$$[a_{kl}(N)]_{rs} = \int \omega^s \omega^r T^i_N(kl) \omega^s \partial^r$$

where $\omega^r$ are the basis functions. Then the anisotropic coupling constant,
\( B_{kl}(N) \), for nucleus \( N \), is

\[
B_{kl}(N) = -g_e \beta_e N \beta_N \text{Tr}(a_{kl}(N)(P-Q)) \quad \ldots \ldots \ldots \ldots (53) \\
\]

\( k, l = x, y, z \)

where \( (P-Q) \), the difference of the bond order matrices, is the spin distribution of the odd electron.

As the anisotropic hyperfine coupling tensor \( B(N) \) can always be diagonalised the anisotropic values are reported for the diagonalised matrix as \( B_x(N), B_y(N), B_z(N) \) along the principal axes \( X, Y \) and \( Z \). In the same way that the isotropic coupling constants give an indication of \( s \) orbital character the anisotropic give an indication of \( p \) (or \( d \)) orbital character.

As hyperfine coupling constants are expressed in terms of the applied magnetic field, the quantities \( a_N \) and \( B(N) \) must be obtained in the appropriate units - generally Gauss.

By inspection of the expressions for the isotropic term and the anisotropic tensor it can be seen that the former presents a trivial problem whereas the latter is less trivial. The difficult nature of the anisotropic integrals has limited the number of theoretical studies to a very few cases.

Silverstone and Todd have recently derived analytical formulae, applicable to the calculation of the general anisotropic integral, over Slater type orbitals. This represents the first analytical analysis of the general three centre integral over a basis. For Gaussian type orbitals Kern and Karplus
have reported an expression for the integral over s
type Gaussian functions by using the Gaussian transform
method
\[ \frac{3a^2-r^2}{r^3} = \frac{a^2}{3\pi} (l/r) + \frac{4a^2}{3} \delta(r); \quad q=x,y,z \]

General analytical formulae for the anisotropic integrals over Gaussian type orbitals, however, have
not been reported.

VIIa. Analytical Formulae for Anisotropic Integrals

The analytical derivation of integrals of the form
\[ \langle a_{pq}(C) \rangle = \langle g_A | a_{pq}(C) | g_B \rangle \]
are required where
\[ g_A \] is a Gaussian centred at A (with coordinates \( A_x, A_y, A_z \))
\[ g_A = N_A a_{pq}(C) = (x_a x, y_a y, z_a z) e^{-a_A r_A^2} \]
\[ x_A = x - A_x \]
\[ r_A^2 = x_A^2 + y_A^2 + z_A^2 \]

\( N_A \) is the normalisation constant; \( l_A, m_A, n_A \) are non-negative integers. Similarly
\[ g_B = (B, a_B, l_B, m_B, n_B) \]
for a Gaussian centred on
\( B \) (with coordinates \( B_x, B_y, B_z \)) and
\[ a_{pq}(C) = \frac{3p_q - r_C^2 \delta_{pq}}{r_C^3} \]
\( p,q \) represent \( x_C, y_C \) or \( z_C \)
\( (=z-C_z) \) and centre C has coordinates \( C_x, C_y, C_z \) and \( x,y,z \)
are referred to the principal axis system.

The method used to obtain analytical expressions for the integrals relies upon the use of the identity suggested by the work of Singer,

\[
\frac{1}{r^2} = 8(3\pi^2)^{-1} \int_0^1 u^4 e^{-r^2 u^2} du = 8(3\pi^2)^{-1} \int_0^1 \frac{v^4}{(1-v^2)^2} e^{-r^2 v^2/(1-v^2)^2} dv
\]

Using this transformation the integrals may be expressed, after considerable manipulation, in the form

\[
\langle a_{pq}(c) \rangle = \Delta \left[ 3w_{pq} - w_{pq} \right] \quad \ldots \ldots \ldots (55)
\]

where \( p, q = x, y, z \) and

\[
W = W_{xx} + W_{yy} + W_{zz}
\]

\[
\Delta = \frac{8\pi}{3} (\alpha_A + \alpha_B) \exp\left( -\frac{A_B^2}{2} \alpha_A \alpha_B / (\alpha_A + \alpha_B) \right) \mathcal{N}_A \mathcal{N}_B
\]

\[
\overline{A_B}^2 = (A_x - B_x)^2 + (A_y - B_y)^2 + (A_z - B_z)^2
\]

The \( W \)'s in (55) are defined as

\[
\begin{align*}
W_{xx} &= 2V_{100} - 4CP_x V_{100} + CP_x^2 V_{000} \\
W_{yy} &= 2V_{010} - 4CP_y V_{010} + CP_y^2 V_{000} \\
W_{zz} &= 2V_{001} - 4CP_z V_{001} + CP_z^2 V_{000} \\
W_{xy} &= 4V_{110} - 2CP_x V_{010} - 2CP_y V_{100} + CP_x CP_y V_{000} \\
W_{xz} &= 4V_{101} - 2CP_x V_{001} - 2CP_x V_{100} + CP_x CP_z V_{000} \\
W_{yz} &= 4V_{011} - 2CP_y V_{001} - 2CP_y V_{010} + CP_y CP_z V_{000}
\end{align*}
\]

where, for example,

\[
CP_x = C_x - P_x
\]

\[
P_x = \alpha_A A_x + \alpha_B B_x
\]

- \( \alpha_A + \alpha_B \)
In equation (56) the V's are defined by the general expression
\[
V_{s_1s_2s_3} = \sum_{i_1r_1} s_1t_1 R_{i_1r_1}(l_A, l_B, A_x, B_x, C_x, \gamma)
\times \sum_{i_2r_2} s_2t_2 R_{i_2r_2}(m_A, m_B, A_y, B_y, C_y, \gamma)
\times \sum_{i_3r_3} s_3t_3 R_{i_3r_3}(n_A, n_B, A_z, B_z, C_z, \gamma)
\times \sum_{u=0}^{\infty} \binom{r+t}{u} \left( -1 \right)^u F_\gamma (\gamma \cdot \overline{CP}^2) \quad \ldots (57)
\]
where
\[
r = r_1 + r_2 + r_3, \quad i = i_1 + i_2 + i_3, \quad s = s_1 + s_2 + s_3
\]
\[
t = t_1 + t_2 + t_3, \quad \nu = i - 2r + u + 2 - s
\]
and the gamma function
\[
F_\gamma (g) = \int_0^1 u^2 e^{-gu^2} du
\]
The general form of the R's as given in equation (57) is
\[
\text{st} \quad R_{ir}(k_A, k_B, A_q, B_q, C_q, \gamma) = f_i(k_A, k_B, A_q, B_q, C_q)
\times \frac{i! \overline{CP}^2 \epsilon^r s e^t (2r+1)^t-s}{r! (i-2r-s)!} \quad \ldots (58)
\]
where
\[
\gamma = \alpha_A + \alpha_B
\]
\[
\epsilon = 1 / (4\gamma)
\]
\[
f_i(l, m, a, b) = \frac{i = \min (i, l)}{1 = \max (0, j-m)} \binom{l}{i} \binom{m}{j-i} a^{l-i} b^{m+i-j}
\]
In equation (57) the limit of each summation is a function of the R which is being summed. Thus, using the terminology of equation (58), i is an integer within the range s to (k_A+k_B) and r is an
integer within the range 0 to \((i-s)/2\). In the
derivation of the \(V\)'s the infinite terms which arise
in \(V^{000}_{100}, V^{000}_{010}\) and \(V^{000}_{001}\) have been neglected since in
the complete integral for \(<a_{pp}(C)>\) they cancel out exactly.

The formulae given are general for any Gaussian
type orbital. In the application of the integrals it
is convenient to have special formulae for the s- and
p-type Gaussian functions. Using the terminology of
Clementi and Davis\(^5\)

\[
W^{00}_{ij} = \int S^{00}_{i} I^{00}_{j}
\]

\[
W^{ko}_{ij} = \int [S^{ko}_{i} + S^{00}_{i} I^{ko}_{j}]
\]

\[
W^{ok}_{ij} = \int [S^{ok}_{i} + S^{00}_{i} I^{ok}_{j}]
\]

\[
W^{kl}_{ij} = \int [S^{kl}_{i} + S^{ko}_{i} I^{ol}_{j} + S^{01}_{i} I^{ko}_{j} + S^{00}_{i} I^{kl}_{j}]
\]

where

\[
I^{00} = CP_i CP_j F_2(t)
\]

\[
I^{ko} = I^{ok} = \left(\frac{1}{2S_1} (CP_i \delta_{jk} + CP_j \delta_{ik}) F_2(t)\right)
\]

\[
I^{kl} = CP_i CP_j CP_k CP_l F_4(t)
\]

\[
\frac{1}{2S_1} [(CP_i CP_j \delta_{kl} + CP_i CP_k \delta_{jl} + CP_i CP_l \delta_{jk} + CP_j CP_k \delta_{il}) F_3(t) - \frac{1}{2S_1} (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{jk} \delta_{il}) F_2(t)]
\]

\[
S^{00} = N_A N_B (\pi/(a_A + a_B))^{3/2} \exp(-a_A a_B AB^2/(a_A + a_B))
\]

\[
S^{ko} = -S^{00}(A_i - B_i) a_B/(a_A + a_B)
\]

\[
S^{ok} = -S^{00} a_B/(a_A + a_B)
\]

\[
S^{kl} = \left[\delta_{kl} - (A_i - B_i)(A_j - B_j) a_A a_B/(a_A + a_B)^2\right] S^{00}
\]
\[ CP_i = C_i - P_i \]

\[ CP^2 = (C_x - P_x)^2 + (C_y - P_y)^2 + (C_z - P_z)^2 \]

\[ P_i = (a^A_i A_i + a^B_i B_i) / (a^A_i + a^B_i) ; \quad (i, j, k, l= x, y \text{ or } z) \]

\[ \sum = \frac{8}{3} S_i \]

\[ t = S_i \frac{PC^2}{2} \]

\[ S_i = a^A_i + a^B_i \]

we have the following special formulae with

\[ W_{kl} = W_{xx} + W_{yy} + W_{zz} \]

\[ <s_A | a_{ij} (C) | s_B> = 3W_{ij}^{00} - W_{ij}^{00} \delta_{ij} \]

\[ <p_{kA} | a_{ij} (C) | s_B> = 3W_{ij}^{k0} - W_{ij}^{k0} \delta_{ij} \]

\[ <s_A | a_{ij} (C) | p_{kB}> = 3W_{ij}^{0k} - W_{ij}^{0k} \delta_{ij} \]

\[ <p_{kA} | a_{ij} (C) | p_{kB}> = 3W_{ij}^{kl} - W_{ij}^{kl} \delta_{ij} \]

The matrix \( a_{pq} (c) \) of integrals over the basis can then be used in equation (53) to give the anisotropic tensor \( B(C) \). Diagonalisation then gives \( B_x (C), B_y (C) \) and \( B_z (C) \) and the principal axes; with the calculated isotropic hyperfine coupling constant \( a_0 \) for centre \( C \) the coupling constants \( A_x (C), A_y (C) \) and \( A_z (C) \) for the complete operator defined in equation (49) may be obtained

\[ A_i (C) = a_0 + B_i (C) ; \quad i = x, y, \text{ or } z \]
VIIb. Vibronic Contributions to the Hyperfine Constants

Experimental data for the electron spin resonance technique indicates that, in some systems, there is a marked dependence on temperature. This effect is believed to be due to a vibronic contribution augmenting the hyperfine coupling constants in the system. Discrepancies between the rigid theoretical model used in the calculation and experiment suggests that some estimate of the vibronic contribution should be made when possible.

Assuming the simple case when the zero point energy vibrational modes are executing simple harmonic motion

$$\psi = (a/\pi)^k e^{-ax^2/2} \quad ............(59)$$

where $x$ is the displacement from the equilibrium configuration along a normal coordinate.

$$\alpha = 2\mu E_{\text{vib}}$$

$\mu$ is the reduced mass and $E_{\text{vib}}$ is the zero point energy for the vibration

$$E_{\text{vib}} = (v + \frac{1}{2})(k/\mu)^{\frac{1}{2}} \quad ; \quad v=0,1,2...$$

$k$ is the force constant of the vibration defined by

$$E = E_0 + \frac{1}{2}kx^2$$

$E_0$ and $E$ are the UHF energy at zero and non-zero displacement respectively.

The general variation of the hyperfine coupling constant $\alpha$ with $x$ is
If it is assumed that terms with \( n>2 \) can be neglected
\[ a = c_0 + c_1x + c_2x^2 \] \hspace{1cm} (60)
the term \( n=1 \) disappears when considering an harmonic oscillator. \( c_0 \) is the calculated coupling constant at equilibrium configuration. The observed value \( <a> \), using equation (60) and the wavefunction in (59), is given as
\[ <a> = c_0 + c_2/(2a) \] \hspace{1cm} (61)
This formula, (61), may be used to give an estimate of the vibronic contribution if the harmonic approximation is reasonable.

**Conclusions**

The Unrestricted Hartree Fock method with single spin annihilation after minimisation has been formulated in the framework of the linear combination of atomic orbitals approximation. An adequate representation of the atomic orbitals may be obtained through expansions of Gaussian type orbitals.

Objections levelled against the UHF method on the grounds that an eigenfunction of \( S^2 \) is not obtained and correlation is not correctly reproduced are not completely removed by the action of a single annihilator. However this annihilation generally results in only minor contamination of the pure spin state and, in fact, if electron correlation is dominant
none of the methods used for open shell systems are satisfactory.

The necessary condition to test the value of any method used to predict a molecular property is an accurate wavefunction. In the ab initio method this accuracy can be achieved but generally some degree of optimisation, of the basis and the molecular geometry, is required. The criterion of optimisation has rarely been applied in ab initio calculations, and it may be conjectured that, for this reason, the relative value of the methods has not been established. The UHF method with single annihilation is developed in this thesis and the results show that the approach can work and in fact give very satisfactory results in most open shell systems studied. The importance of optimisation, where feasible, is also demonstrated.
CHAPTER 1
Introduction.

The Unrestricted Hartree Fock (UHF) method is applied, in this thesis, to the explanation of the observed hyperfine coupling constants in species with an unpaired electron. Expressions for the energy and other relevant quantities of a molecular system have been derived in Sections I and II. The adoption of the ab initio approach ensures an adequate description of the electron distribution and the application of a single annihilation, after minimisation of the UHF energy, removes, although not entirely, the contamination to the pure spin state, which results since the wavefunction is not an eigenfunction of the $S^2$ operator.

The method used to minimise the UHF energy is threefold; Roothaan's repeated diagonalisation method, McWeeny's steepest descents method and a modification, for use on UHF wavefunctions, of Fletcher's conjugate gradient method; these procedures are described in Section V. The requirements of minimisation are such that the energy is the lowest possible subject to an orthonormality constraint on the molecular orbitals. An additional requirement, for practical applicability, is a reasonable rate of convergence. Sleeman has compared the effectiveness of the procedures of Roothaan and McWeeny, using the Open Shell Restricted Hartree Fock method, drawing a number of conclusions which are also applicable to the Unrestricted Hartree Fock method.

A phenomenon displayed by the Roothaan method is
oscillation, and for some functions divergence, of the energy. Sleeman has shown that extrapolation procedures which increase the rate of convergence in well-behaved cases do not necessarily remove the oscillatory behaviour of the function. Berthier and Millie\textsuperscript{56} have shown that the convergence problem in the diagonalisation method, at least for the open shell case, is associated with the sequence of occupied and virtual orbitals. By selecting the correct orbitals at each iteration no difficulties arise in the minimisation. However, the applicability of this approach is limited since, particularly for large molecular systems, how to select the right occupied orbitals is not obvious.

The method of steepest descents calculates the incremental change in the approximate density matrices along the negative gradient of the energy at the point which reduces the energy most. It is possible to estimate optimum multipliers, $\lambda$, of the gradient vector so that the density matrices are changed by these amounts. Sleeman has shown that a good starting approximation is necessary when using the McWeeny method. However, even after providing improved density matrices, for example, by initial use of the diagonalisation method, convergence can be slow. Sleeman has also demonstrated that the first order expression for the $\lambda$ multipliers can be inadequate, resulting in divergent behaviour. The method of McWeeny assumes that the variables in which the energy is defined are independent; however they are not, being restricted by the orthonormality conditions.
Generally optimum values of the multipliers, \( \lambda \), which also satisfy the orthonormality conditions cannot be found, leading to the necessity to renormalise at each iteration so that the energy may be recalculated. Since the next iteration takes into account information from the previous iteration the modification of the variables, by renormalisation, reduces the effectiveness of the minimisation.

The Fletcher method \(^2\) finds the minimum of the energy on a line through the energy gradient in the conjugate direction. The approach, unlike that of McWeeny, is able to make full use of the information from the previous iteration by working in variables which are independent. Thus, from Section V 3), the variables considered are \( Y \) where,

\[
A = YU
\]

\[\text{(1)}\]

and \( U \) is defined as

\[
U = (Y^+SY)^{-1/2}
\]

\[\text{(2)}\]

so that \( A \) satisfies the orthonormality conditions. This facet, using independent variables, allows for a much enhanced convergence over the McWeeny method as a more efficient minimisation procedure, such as the conjugate gradient method, can be used on unconstrained problems.

The modifications to the equations of Fletcher, for application to UHF wavefunctions, derived in Section V 3), were programmed in the manner suggested by Fletcher \(^4\). A comparison of the three minimisation procedures was then made using, as an example the CN
radical.

Results and Discussion.

In molecular calculations the initial approximation to the molecular orbitals, and density matrices, is obtained by the diagonalisation of the one electron Hamiltonian matrix. The convergence studies in this Chapter are concerned with the efficient means of minimising the energy from this starting point. In most cases the Roothaan method is convergent and may be used exclusively, since the iteration time is less than half that of the other two methods. Difficult cases, where the Roothaan method does not converge initially, are known and the minimum must be approached by another method.

Calculations on the CH radical have been done using a minimal basis set of SCF atomic orbitals represented by a linear combination of Gaussian type orbitals in their fully contracted form; the 9s type and 5p type of Huzinaga were used for carbon and nitrogen. The minimisation of this radical has proved difficult and therefore suggests itself as a good test case. In figure 1 and 2 the electronic energy of CN (at 2.2 and 2.0 a.u. respectively) has been plotted as a function of time, showing the convergence properties of the minimisation procedures (commencing with the orbitals obtained from the diagonalisation of the one electron Hamiltonian matrix).

For the CN radical at 2.2 a.u. the Roothaan method minimises on to two values, oscillating infinitely between them (curve (iii)) and never
Minimisation of the ON radical (bond distance 2.2 a.u.)

(i) McWeeny  (ii) Fletcher  (iii) Roothaan
(iv) Minimum energy obtained by using Roothaan's method after McWeeny's or Fletcher's method.
Minimisation of the CN radical (bond distance 2.0 a.u.)

(i) McWeeny  (ii) Fletcher  (iii) Roothaan  
(iv) At this time all minimisation methods were changed to Roothaan's method.
reaching the true minimum. The superiority of the Fletcher method is apparent in this case (curve (ii)). The poor convergence shown by the McWeeny method (curve (i)) has been associated with the inner shell molecular orbitals, which cause large variations in the excitation energies. Hillier and Saunders have suggested that this defect is corrected by their energy weighted steepest descents method. The Roothaan method is convergent for the CN radical at 2.0 a.u. (figure 2), however, the Fletcher method is initially superior.

Conclusions.

Although only one example has been examined, tentative conclusions can be drawn. The Roothaan method, with or without incorporating extrapolation procedures, is incomparably faster than any other technique near the energy minimum, and this method is reserved exclusively for that situation. The steepest descents method appears to be redundant when the conjugate gradient approach is available, since the Fletcher method enables the minimum to be approached much more efficiently. The method of minimisation suggested from the results is a combination of the Fletcher and Roothaan procedures; initial use of the former and then application of the latter, reaching the true minimum without use of McWeeny's method.
CHAPTER 2
Introduction.

The isoelectronic hydride series, BH$_3^-$, CH$_3$ and NH$_3^+$, has been the subject of many investigations. The relatively small values of the isotropic hyperfine coupling constants of the heavy atoms has led to the conclusion that the species are planar π radicals. The out-of-plane vibration is also generally considered to augment the heavy atom coupling constants, although other explanations have been suggested.

The series presents a good test of the ability of the ab initio UHF method, with spin annihilation after minimisation, to reproduce, non-empirically, observed hyperfine coupling constants, particularly those of the heavy atoms, for which it has been suggested the UHF approach is inherently inaccurate. An important aspect raised by these calculations is the importance of the interaction between the radical and its environment. It is the implied assumption of many qualitative interpretations for the rationalisation of observed hyperfine coupling constants in chemical terms that the environmental interaction is small. Whether, in fact, the interaction is small for charged species in charged environments may be indicated by theoretical calculations, where the radical is taken in isolation, as, for example, in the case of the NH$_3^+$ radical. A study of the effect of the environment on the e.s.r. spectra of trapped radicals has already been initiated from an experimental viewpoint.
Method.

The ab initio UHF method in the l.c.a.o.-m.o. approximation with spin annihilation, as described earlier (Sections I and II), was used. A minimal basis set of orbitals was represented by Gaussian expansions in their completely contracted form; 9s-type and 5p-type for nitrogen, carbon and boron and 6s-type for hydrogen as given by Huzinaga. The orbital exponent, $\alpha$, of the hydrogen atomic orbital and the bond length, $r(X-H)$, were both optimised to an accuracy of 0.05, assuming in each case the radical was planar. The results given were calculated from the UHF wavefunction after annihilation of the contaminating quartet spin state and are expressed in atomic units (a.u. where $1 \text{a.u.} = 0.529167\text{Å}$, $1 \text{a.u.} = 27.06\text{eV}$.) except for the hyperfine coupling constants which are expressed in Gauss (G).

Non-planar nuclear configurations were studied by moving the heavy atom perpendicularly out of the plane of the three fixed hydrogen atoms; no attempt was made to optimise the hydrogen orbital exponents or the bond lengths for the non-planar configurations.

The vibronic contributions to the coupling constants were estimated in the manner outlined previously (Section VIIb) assuming an harmonic oscillator, using

$$<a> = c_0 + c_2/(2\alpha) \quad \ldots \ldots \ldots (1)$$

$c_0$ is the calculated hyperfine coupling constant at equilibrium, $<a>$ the observed coupling constant,
\[ \alpha = 2\mu E \]

\( \mu \) is the reduced mass. \( E \), the zero point energy, is evaluated from the force constant \( k \) of the vibration which is calculated from the variation of the UHF energy along a normal coordinate. The coefficient \( c_2 \) is estimated from the variation of the coupling constant along a normal coordinate.

Only the \( \alpha \) stretching mode and \( \alpha' \) bending mode are considered, although the latter seems to be the only vibrational mode which can significantly affect the coupling constants. Because of the difficulties in obtaining reliable estimates of \( \alpha \) and \( c_2 \), calculations were made at various values of the angle of bending \( \Theta \) and extrapolated back to \( \Theta = 0^\circ \). In this way it was considered that some compensation would be made for the non-optimisation of the bond length and the hydrogen orbital exponent for the non-planar configurations.

Objections to the use of formula (1) may be raised for vibrations with small force constants or when the approximations give a poor representation of the coupling constant for large angles of bending. An alternative would be to use numerical integration as suggested by Beveridge and Miller,\(^6\)\(^8\)

**The Ammonium Radical Cation.**

Hyde and Freeman\(^6\)\(^6\) and Cole\(^6\)\(^5\) have observed electron spin resonance spectra for X-ray irradiated ammonium perchlorate crystals at room temperature which were interpreted to arise from the radical ion \( \text{NH}_3^+ \), with isotropic hyperfine coupling constants
Rao and Symons on $\gamma$-irradiation of ammonium perchlorate found the same radical with $a_N=19.3 \text{G}$, $a_H=25.8 \text{G}$ at 77 and 293K. Evidence that the radical was undergoing restricted rotation limited mainly to an in-plane motion suggests that the interaction with the environment may be sufficiently small for the radical to be regarded as existing in an unperturbed state.

The theoretical results for $\text{NH}_3$ are presented in Table 1. The energy after annihilation of the quartet spin state of the UHF function for the optimised planar configuration (figure 1) with hydrogen orbital exponent of 1.6 and bond length of 1.95 a.u. was calculated to be $-55.85625 \text{a.u.}$. The hyperfine coupling constants were $a_N=10.57 \text{G}$ and $a_H=-22.65 \text{G}$. The agreement between experimental and theoretical proton coupling constants is satisfactory but the theoretical nitrogen coupling constant accounts for only 55% of the experimental value. The hyperfine coupling constant of nitrogen may be depressed by an inadequate representation of the electron density at the nucleus, as well as the neglect of orbital contraction on bond formation. The magnitude of the deviation from experiment, however, suggests that consideration should be taken of the contribution of the zero point energy vibrations to the coupling constants. The vibronic contribution should considerably increase $a_N$ while leaving $a_H$ relatively unaffected.

A force constant $k=0.1136 \text{a.u.} \ (\text{a.u.}=1.544 \times 10^6 \text{gs}^{-2})$
<table>
<thead>
<tr>
<th>bond length (a.u.)</th>
<th>hydrogen orbital exponent</th>
<th>bending angle $\Theta^\circ$</th>
<th>total energy (a.u.)</th>
<th>coupling constants (G) $a_N$</th>
<th>$a_H$</th>
<th>$&lt;8^2&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.80</td>
<td>1.40</td>
<td>0</td>
<td>-55.79987</td>
<td>11.67</td>
<td>-17.76</td>
<td>750018</td>
</tr>
<tr>
<td>2.00</td>
<td>1.40</td>
<td>0</td>
<td>-55.84325</td>
<td>13.10</td>
<td>-20.40</td>
<td>750046</td>
</tr>
<tr>
<td>2.20</td>
<td>1.40</td>
<td>0</td>
<td>-55.82179</td>
<td>14.43</td>
<td>-24.22</td>
<td>750125</td>
</tr>
<tr>
<td>1.80</td>
<td>1.60</td>
<td>0</td>
<td>-55.83262</td>
<td>9.737</td>
<td>-20.86</td>
<td>750010</td>
</tr>
<tr>
<td>2.00</td>
<td>1.60</td>
<td>0</td>
<td>-55.85422</td>
<td>10.82</td>
<td>-23.36</td>
<td>750023</td>
</tr>
<tr>
<td>2.20</td>
<td>1.60</td>
<td>0</td>
<td>-55.81273</td>
<td>11.69</td>
<td>-26.92</td>
<td>750056</td>
</tr>
<tr>
<td>1.80</td>
<td>1.80</td>
<td>0</td>
<td>-55.83769</td>
<td>7.929</td>
<td>-22.56</td>
<td>750005</td>
</tr>
<tr>
<td>2.00</td>
<td>1.80</td>
<td>0</td>
<td>-55.83908</td>
<td>8.662</td>
<td>-24.58</td>
<td>750011</td>
</tr>
<tr>
<td>2.20</td>
<td>1.80</td>
<td>0</td>
<td>-55.77890</td>
<td>9.095</td>
<td>-27.32</td>
<td>750022</td>
</tr>
<tr>
<td>1.90</td>
<td>1.55</td>
<td>0</td>
<td>-55.85126</td>
<td>10.83</td>
<td>-21.39</td>
<td>750018</td>
</tr>
<tr>
<td>1.95</td>
<td>1.55</td>
<td>0</td>
<td>-55.85500</td>
<td>11.12</td>
<td>-22.06</td>
<td>750023</td>
</tr>
<tr>
<td>2.00</td>
<td>1.55</td>
<td>0</td>
<td>-55.85426</td>
<td>11.39</td>
<td>-22.79</td>
<td>750028</td>
</tr>
<tr>
<td>1.90</td>
<td>1.60</td>
<td>0</td>
<td>-55.85383</td>
<td>10.31</td>
<td>-22.00</td>
<td>750015</td>
</tr>
<tr>
<td>1.95</td>
<td>1.60</td>
<td>0</td>
<td>-55.85625</td>
<td>10.57</td>
<td>-22.65</td>
<td>750019</td>
</tr>
<tr>
<td>1.90</td>
<td>1.65</td>
<td>0</td>
<td>-55.85472</td>
<td>9.794</td>
<td>-22.51</td>
<td>750013</td>
</tr>
<tr>
<td>1.95</td>
<td>1.65</td>
<td>0</td>
<td>-55.85584</td>
<td>10.03</td>
<td>-23.13</td>
<td>750016</td>
</tr>
<tr>
<td>2.00</td>
<td>1.65</td>
<td>0</td>
<td>-55.85254</td>
<td>10.26</td>
<td>-23.82</td>
<td>750019</td>
</tr>
<tr>
<td>1.95</td>
<td>1.60</td>
<td>2.5</td>
<td>-55.85584</td>
<td>11.26</td>
<td>-22.37</td>
<td>750019</td>
</tr>
<tr>
<td>1.95</td>
<td>1.60</td>
<td>5</td>
<td>-55.85455</td>
<td>13.30</td>
<td>-21.56</td>
<td>750018</td>
</tr>
<tr>
<td>1.95</td>
<td>1.60</td>
<td>10</td>
<td>-55.84869</td>
<td>20.98</td>
<td>-18.50</td>
<td>750017</td>
</tr>
</tbody>
</table>

*marks minimum

Theoretical Results for NH$_3^+$
Summary of the calculations on the $\text{NH}_3^+$ radical; variation of the total energy after annihilation with bond length for those values of the hydrogen orbital exponent $\alpha$ as indicated.

---, estimated minimum total energy after annihilation as a function of bond length.
Variation of the nitrogen and hydrogen isotropic coupling constants with angle of bending $\Theta$. 
Variation of the nitrogen and hydrogen hyperfine coupling constants with the bond distance for those values of the hydrogen atomic orbital exponent, $\alpha$, which have been indicated. ———, estimated variation of the nitrogen and hydrogen hyperfine coupling constants with bond distance at minimum total energy.
was evaluated for the out of plane vibrational mode. This compares with \( k = 1.372 \text{a.u.} \) for the symmetric stretch vibrational mode. The value of \( c_2 \) in equation (1) was found to be 96.15 for nitrogen (see figure 2) which gives

\[
\alpha_N = 10.57 + 6.35 = 16.92 \text{G}
\]

Similarly the inclusion of the vibronic contribution for hydrogen gives \( \alpha_H = -20.02 \text{G} \) where \( c_2 \) is 39.82.

Hence the inclusion of the vibronic contribution permits 88% of the experimental coupling constant of the nitrogen to be accounted for theoretically. The almost linear variation of the hydrogen and nitrogen calculated coupling constants for the symmetrical stretching mode (figure 3) together with the high force constant, and hence large \( \alpha \) in equation (1), demonstrates that this vibration makes negligible contribution to the observed hyperfine coupling constants.

The Methyl Radical.

A number of experimental and theoretical studies are reported for the \( \text{CH}_3 \) radical. An early determination by Cole et al.\(^{62}\) of the carbon isotropic coupling constant, \( \alpha_c = 41 \text{G} \), showed, by the relative smallness of its value, that the radical is planar. Experimental values of \( \alpha_c = 38 \text{G} \) and \( \alpha_H = -23 \text{G} \)\(^{74}\) seem to be generally true in solution and matrix environments; however these hyperfine coupling constants are temperature dependent. Although calculations on \( \text{CH}_3 \) have predicted reasonable values for the proton coupling constant\(^ {75}\) the values found for the carbon are very high.\(^ {76-78}\)
Importance has been attached to the effect of the out of plane vibration on the hyperfine coupling constants, a suggestion originating from Schrader and Karplus. The temperature dependence is well explained by including the effects of this vibration. Fessenden has suggested that a rigid planar model for the methyl radical may have $a_C=28\,G$, the other $10\,G$ being due to the out of plane vibration.

The results for the calculations on $\text{CH}_3^+$ are summarised in Table 2. The optimised planar configuration has an energy of $-39.5428\,a.u.$ for a bond length of $2.05\,a.u.$ and hydrogen orbital exponent of $1.40$ (figure 4). The isotropic hyperfine coupling constants are $a_C=27.33\,G$ and $a_H=-23.39\,G$ for the rigid planar configuration. The contribution of the out of plane zero point vibration was estimated in the same way as for $\text{NH}_3^+$. The out of plane vibrational force constant was calculated to be $k=0.0405\,a.u.$ This is much less than that calculated for $\text{NH}_3^+$ ($k=0.1136\,a.u.$) thereby accounting for the marked temperature dependence shown by $\text{CH}_3^+$ but not $\text{NH}_3^+$. The symmetrical stretching vibrational force constant, $k=1.292\,a.u.$, is much higher than the out of plane force constant and makes negligible contribution to the coupling constants.

The coefficients $c_2$ were found to be $264.8$ for carbon and $35.12$ for hydrogen (see figure 5) giving increments of $27.31\,G$ and $3.96\,G$, for carbon and hydrogen respectively, to be added to the planar radical isotropic coupling constants to account for the out of plane vibration. The theoretical estimates of the
<table>
<thead>
<tr>
<th>bond length (a.u.)</th>
<th>hydrogen orbital exponent</th>
<th>bending angle $\Theta^\circ$</th>
<th>total energy (a.u.)</th>
<th>coupling constants (G)</th>
<th>$\langle S^2 \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.80</td>
<td>1.20</td>
<td>0</td>
<td>-39.42928</td>
<td>25.76</td>
<td>-15.55</td>
</tr>
<tr>
<td>2.00</td>
<td>1.20</td>
<td>0</td>
<td>-39.51166</td>
<td>31.72</td>
<td>-18.04</td>
</tr>
<tr>
<td>2.20</td>
<td>1.20</td>
<td>0</td>
<td>-39.52256</td>
<td>38.70</td>
<td>-21.69</td>
</tr>
<tr>
<td>1.80</td>
<td>1.40</td>
<td>0</td>
<td>-39.48438</td>
<td>20.80</td>
<td>-19.58</td>
</tr>
<tr>
<td>2.00</td>
<td>1.40</td>
<td>0</td>
<td>-39.54090</td>
<td>25.96</td>
<td>-22.46</td>
</tr>
<tr>
<td>2.20</td>
<td>1.40</td>
<td>0</td>
<td>-39.52824</td>
<td>31.74</td>
<td>-26.79</td>
</tr>
<tr>
<td>1.80</td>
<td>1.60</td>
<td>0</td>
<td>-39.49501</td>
<td>16.74</td>
<td>-22.15</td>
</tr>
<tr>
<td>1.90</td>
<td>1.60</td>
<td>0</td>
<td>-39.52256</td>
<td>18.87</td>
<td>-23.48</td>
</tr>
<tr>
<td>2.00</td>
<td>1.60</td>
<td>0</td>
<td>-39.52818</td>
<td>20.94</td>
<td>-25.13</td>
</tr>
<tr>
<td>2.10</td>
<td>1.60</td>
<td>0</td>
<td>-39.51700</td>
<td>23.07</td>
<td>-27.15</td>
</tr>
<tr>
<td>2.00</td>
<td>1.35</td>
<td>0</td>
<td>-39.53818</td>
<td>27.35</td>
<td>-21.52</td>
</tr>
<tr>
<td>2.05</td>
<td>1.35</td>
<td>0</td>
<td>-39.54161</td>
<td>28.78</td>
<td>-22.42</td>
</tr>
<tr>
<td>2.10</td>
<td>1.35</td>
<td>0</td>
<td>-39.54131</td>
<td>30.27</td>
<td>-23.41</td>
</tr>
<tr>
<td>2.05</td>
<td>1.40</td>
<td>0</td>
<td>-39.54284</td>
<td>27.33</td>
<td>-23.39</td>
</tr>
<tr>
<td>2.10</td>
<td>1.40</td>
<td>0</td>
<td>-39.54107</td>
<td>28.74</td>
<td>-24.42</td>
</tr>
<tr>
<td>2.00</td>
<td>1.45</td>
<td>0</td>
<td>-39.54099</td>
<td>24.63</td>
<td>-23.30</td>
</tr>
<tr>
<td>2.05</td>
<td>1.45</td>
<td>0</td>
<td>-39.54146</td>
<td>25.91</td>
<td>-24.25</td>
</tr>
<tr>
<td>2.10</td>
<td>1.45</td>
<td>0</td>
<td>-39.53824</td>
<td>27.23</td>
<td>-25.28</td>
</tr>
<tr>
<td>2.05</td>
<td>1.40</td>
<td>2</td>
<td>-39.54273</td>
<td>28.68</td>
<td>-23.21</td>
</tr>
<tr>
<td>2.05</td>
<td>1.40</td>
<td>5</td>
<td>-39.54216</td>
<td>35.44</td>
<td>-22.13</td>
</tr>
<tr>
<td>2.05</td>
<td>1.40</td>
<td>10</td>
<td>-39.53978</td>
<td>57.85</td>
<td>-18.84</td>
</tr>
</tbody>
</table>

*marks minimum

Theoretical Results for $\text{CH}_3^+$
Summary of the calculations on the CH₃ radical.
(See also caption to figure 1.)
Variation of the carbon and hydrogen isotropic hyperfine coupling constants with angle of bending $\Theta$. 
observed isotropic hyperfine coupling constants then become $a_C = 54.64 \text{G}$ and $a_H = -19.43 \text{G}$. Although the results are not in as good agreement with experiment as those for NH$_3^+$ they are still reasonable. The trend of the temperature variation of both $a_C$ and $a_H$ is correctly predicted since the effect of increased temperature is to increase the increment added to the planar radical.

The predicted variations of $a_C$ and $a_H$ with bond length (in the $a_1$ stretching mode) are given in figure 6. For a given hydrogen orbital exponent the variations parallel those of Beveridge and Miller$^{68}$ using the INDO method. If the optimum orbital exponent at each bond length is used $a_H$ becomes almost independent of the CH bond length whereas $a_C$ becomes more sensitive.

The Borohydride Anion.

Symons and Wardale$^{59}$ first briefly reported the BH$_3^-$ radical by $\gamma$-irradiation of KBH$_4$ and later elaborated on the reasons for the assignment.$^{60}$ Better spectra were obtained by Sprague and Williams$^{61}$ using tetramethylammonium borohydride over a wide temperature range. The two investigations are only in qualitative agreement in that the hyperfine coupling constants differ significantly, $a_B = 24.2 \text{G}, a_H = 16.3 \text{G}$$^{60}$ and $a_B = 20.7 \text{G}, a_H = 15.1 \text{G}$.$^{61}$ This is probably an environmental effect since the hyperfine coupling constants are independent of temperature between 84 and 300K.$^{61}$

The results of the ab initio UHF calculations
are given in Table 3. The optimum planar configuration, at a bond length of 2.35 a.u. and hydrogen orbital exponent of 1.15 (figure 7), gives hyperfine coupling constants of $a_B = 22.41G$ and $a_H = -20.15G$. Also reported in Table 3 are calculations on the bent $BH_3^-$ radical, in terms of angle of bending from planarity. The latter indicate that the stable configuration is when $BH_3^-$ is bent out of plane by about 9°, in contrast to the planar configurations calculated for $CH_3^+$ and $NH_3^+$, figure 8. A qualitative argument, stressing the differences in electronegativity of the atoms of the bond, may be used in explanation; in the case of $BH_3^-$ the electronegativity (between the boron and hydrogen) is only 0.1 and in the opposite sense to that in $CH_3^+$ and $NH_3^+$. The species is therefore predicted to be pyramidal whereas $CH_3^+$ and $NH_3^+$ are predicted to be planar. The potential barrier separating the planar and pyramidal conformations is probably too small to make them physically distinguishable, in which case the observed conformation will be planar.

For the bent geometry $a_B = 45G$, $a_H = -16.5G$, the former of which is far too large. If it is accepted that $CH_3^+$ and $NH_3^+$ are planar radicals then the similar $U$ value for $BH_3^-$ indicates that $BH_3^-$ is also planar. However, even for the planar radical the calculated $a_B (= 22.41G)$ is too large, especially when consideration is taken of the contribution the out of plane zero point energy vibration will make to the hyperfine coupling constants. It is difficult to estimate this vibronic contribution, owing to the double minimum in
### TABLE 3. Theoretical Results for BH₃⁻

<table>
<thead>
<tr>
<th>bond length (a.u.)</th>
<th>hydrogen orbital exponent</th>
<th>bending angle $\Theta^*$</th>
<th>total energy (a.u.)</th>
<th>coupling constants (G) $^B$</th>
<th>coupling constants (G) $^H$</th>
<th>$&lt;8^2&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.20</td>
<td>1.00</td>
<td>0</td>
<td>-26.28152</td>
<td>21.90</td>
<td>-13.93</td>
<td>750054</td>
</tr>
<tr>
<td>2.40</td>
<td>1.00</td>
<td>0</td>
<td>-26.30533</td>
<td>27.14</td>
<td>-15.96</td>
<td>750133</td>
</tr>
<tr>
<td>2.60</td>
<td>1.00</td>
<td>0</td>
<td>-26.30050</td>
<td>33.71</td>
<td>-18.76</td>
<td>750344</td>
</tr>
<tr>
<td>2.00</td>
<td>1.20</td>
<td>0</td>
<td>-26.27049</td>
<td>13.62</td>
<td>-17.21</td>
<td>750015</td>
</tr>
<tr>
<td>2.20</td>
<td>1.20</td>
<td>0</td>
<td>-26.31680</td>
<td>17.95</td>
<td>-19.30</td>
<td>750035</td>
</tr>
<tr>
<td>2.40</td>
<td>1.20</td>
<td>0</td>
<td>-26.31956</td>
<td>22.76</td>
<td>-22.40</td>
<td>750088</td>
</tr>
<tr>
<td>2.60</td>
<td>1.20</td>
<td>0</td>
<td>-26.29524</td>
<td>28.83</td>
<td>-26.91</td>
<td>750243</td>
</tr>
<tr>
<td>2.00</td>
<td>1.40</td>
<td>0</td>
<td>-26.26927</td>
<td>11.15</td>
<td>-20.52</td>
<td>750044</td>
</tr>
<tr>
<td>2.20</td>
<td>1.40</td>
<td>0</td>
<td>-26.29534</td>
<td>14.82</td>
<td>-23.21</td>
<td>750055</td>
</tr>
<tr>
<td>2.40</td>
<td>1.40</td>
<td>0</td>
<td>-26.27808</td>
<td>18.91</td>
<td>-27.24</td>
<td>750076</td>
</tr>
<tr>
<td>2.35</td>
<td>1.10</td>
<td>0</td>
<td>-26.32147</td>
<td>23.48</td>
<td>-18.58</td>
<td>750086</td>
</tr>
<tr>
<td>2.40</td>
<td>1.10</td>
<td>0</td>
<td>-26.32160</td>
<td>24.84</td>
<td>-19.30</td>
<td>750109</td>
</tr>
<tr>
<td>2.45</td>
<td>1.10</td>
<td>0</td>
<td>-26.32004</td>
<td>26.28</td>
<td>-20.10</td>
<td>750138</td>
</tr>
<tr>
<td>2.30</td>
<td>1.15</td>
<td>0</td>
<td>-26.32299</td>
<td>21.15</td>
<td>-19.41</td>
<td>750061</td>
</tr>
<tr>
<td>2.35</td>
<td>1.15</td>
<td>0</td>
<td>-26.32370</td>
<td>22.41</td>
<td>-20.15</td>
<td>750077 *</td>
</tr>
<tr>
<td>2.40</td>
<td>1.15</td>
<td>0</td>
<td>-26.32252</td>
<td>23.73</td>
<td>-20.96</td>
<td>750098</td>
</tr>
<tr>
<td>2.25</td>
<td>1.20</td>
<td>0</td>
<td>-26.32081</td>
<td>19.08</td>
<td>-19.97</td>
<td>750044</td>
</tr>
<tr>
<td>2.30</td>
<td>1.20</td>
<td>0</td>
<td>-26.32243</td>
<td>20.25</td>
<td>-20.70</td>
<td>750055</td>
</tr>
<tr>
<td>2.35</td>
<td>1.20</td>
<td>0</td>
<td>-26.32193</td>
<td>21.47</td>
<td>-21.51</td>
<td>750070</td>
</tr>
<tr>
<td>2.35</td>
<td>1.15</td>
<td>2</td>
<td>-26.32374</td>
<td>23.66</td>
<td>-19.94</td>
<td>750076</td>
</tr>
<tr>
<td>2.35</td>
<td>1.15</td>
<td>5</td>
<td>-26.32392</td>
<td>30.04</td>
<td>-18.87</td>
<td>750068</td>
</tr>
<tr>
<td>2.35</td>
<td>1.15</td>
<td>8</td>
<td>-26.32410</td>
<td>40.98</td>
<td>-17.11</td>
<td>750057</td>
</tr>
<tr>
<td>2.35</td>
<td>1.15</td>
<td>10</td>
<td>-26.32411</td>
<td>50.19</td>
<td>-15.72</td>
<td>750050</td>
</tr>
<tr>
<td>2.35</td>
<td>1.15</td>
<td>15</td>
<td>-26.32309</td>
<td>77.27</td>
<td>-12.11</td>
<td>750033</td>
</tr>
<tr>
<td>2.35</td>
<td>1.15</td>
<td>20</td>
<td>-26.31933</td>
<td>106.8</td>
<td>-9.167</td>
<td>750024</td>
</tr>
<tr>
<td>2.00</td>
<td>1.40</td>
<td>5</td>
<td>-26.26866</td>
<td>16.99</td>
<td>-19.71</td>
<td>750005</td>
</tr>
<tr>
<td>2.00</td>
<td>1.40</td>
<td>10</td>
<td>-26.26691</td>
<td>33.22</td>
<td>-17.66</td>
<td>750003</td>
</tr>
</tbody>
</table>

*marks minimum
Summary of the calculations on the BH⁻ radical
(See also caption to figure 1.)
the energy curve with out of plane bending, but 100G would be a conservative estimate. Also the force constant will be less than that for CH₃ so that a large temperature variation in a would be expected, which has not been observed.

The calculations which have given reasonable isotropic hyperfine coupling constants for NH₃⁺ and CH₃ should give a comparable accuracy for BH⁻. That this is not the case implies that external effects, not large for CH₃ and NH₃⁺ but dominant for BH⁻, modify the hyperfine coupling constants of the radicals. The neglect of the interaction with the environment would appear to be the most obvious source for the discrepancies.

**Comparison of the Results of the Isoelectronic Radicals.**

Some confidence in the calculations for the rigid planar radicals is given by the agreement between the theoretical a and the estimation given by Fessenden (27.33G and 28G respectively). Also it may be considered that environmental interaction, if important, places in jeopardy the validity of the force constant calculations. Taking the view that the electronic contributions are more important than the vibrational or environmental effects to the hyperfine coupling constants the trends calculated for the rigid planar radicals should reproduce the experimental trends.

The experimental proton hyperfine coupling constants increase in order BH⁻, CH₃⁺, NH₃⁺ (-16.5G, -23.0G and -25.9G) as predicted from the excess charge effect. Although the optimised hydrogen orbital exponents (1.15, 1.40, 1.60), for the planar radicals, are in the
order expected from the excess charge effect, the calculated proton coupling constants are not \((-20.15\text{G}, -23.39\text{G}, -22.65\text{G})\). Analysis of the results in Tables 1, 2, 3 shows that the apparent randomness in the proton coupling constants arises because of the influence of two opposing trends.

(i) Selecting a particular hydrogen orbital exponent, \(\alpha=1.4\), for the radicals and minimising the energy with respect to the bond length, a characteristic procedure of many semi-empirical methods, results in a trend in opposition to that observed experimentally \((-23.21\text{G}, -22.46\text{G}, -20.04\text{G})\).

(ii) By fixing the bond length and optimising the orbital exponent the excess charge effect may be examined in approximate isolation. Selecting a standard bond length of 2\(\text{a.u.}\) the hydrogen orbital exponents are \(1.2, 1.4, 1.6\) for \(\text{BH}_3, \text{CH}_3, \text{NH}_3\) respectively and the resulting proton coupling constants \((-17.32\text{G}, -22.46\text{G}, -23.36\text{G})\) are in the order observed experimentally.

The inability of the calculated rigid planar radicals to predict the experimental trend implies that other factors are dominant. This view is ramified when it is noted that the experimental \(U\) values for the heavy atoms of the radicals are 2.9 (\(^{11}\text{B}\)), 3.4 (\(^{13}\text{C}\)), 3.5 (\(^{14}\text{N}\)) whereas the predicted \(U\) values of the rigid planar radicals are 3.2, 2.4 and 1.8 respectively.

Any environmental effect will be expected to be over-emphasized in these radicals owing to the
importance of the out of plane vibration. Some justification of the calculated results may be obtained by a qualitative consideration of the environment. In a neutral host lattice the usual molecular interaction forces are expected to increase the force constants of the guest radical compared with the corresponding isolated radical. Superimposed on this effect will be an additional interaction when both lattice and radical are charged. Assuming that the positively charged environment of BH\textsubscript{3} increases still further the out of plane vibrational force constant qualitative agreement with experiment may be obtained. The overall effect for BH\textsubscript{3} would be a considerable increase in the force constant, accounting for the temperature dependence, and a smaller increase for the neutral CH\textsubscript{3}, resulting in a smaller vibronic contribution to the hyperfine coupling constants. Since NH\textsubscript{3} is relatively unpolarised, in this respect, the deduction is less critical, but the implication is that a negatively charged lattice tends to decrease the out of plane vibrational force constant, that is, the environmental effects partially cancel one another.

The calculation of the stable geometry of BH\textsubscript{3} as bent is embarrassing. The result implies that the environment must have a sufficient effect to force planarity. However, even for the optimised planar radical the heavy atom isotropic coupling constant is too large. If the view is taken that the positive environment about BH\textsubscript{3} induces a bond length and
hydrogen orbital exponent similar to \( \text{CH}_3 \) \( (\alpha=1.4, \) 
\( r(B-H)=2\text{a.u.}) \) the radical is found to be planar (see Table 3) and the hyperfine coupling constant of the boron is in good agreement with experiment.

**Conclusions.**

The interpretation of the e.s.r. spectra of \( \text{BH}_3, \) \( \text{CH}_3 \) and \( \text{NH}_3^+ \) is complicated by the out of plane zero point energy vibration which obscures an electronic interpretation. In addition there is evidence that the properties of \( \text{BH}_3^- \) are seriously affected by the environment. Although \( \text{CH}_3^- \) and \( \text{NH}_3^+ \) may be treated, theoretically, in isolation it appears that the environment of \( \text{BH}_3^- \) must be included in some manner if the calculated results are to be comparable to the experimental values.

Optimisation of the hydrogen atomic orbital exponent and the bond length have been shown to be of considerable importance and, where the practice is possible, this optimisation should be attempted if meaningful results for molecular systems are to be guaranteed.
CHAPTER 3
Introduction.

The study of unstable radicals trapped in solids can, in suitable cases, give information on the anisotropic, as well as the isotropic, contributions. Some anisotropic information can be gained from radicals trapped in glasses, inert gas matrices or in polycrystalline powders but the best results are obtained from single crystal studies. The radicals are generally regularly orientated to the crystal axis so that rotation of the crystal can give complete resolution of the anisotropic and the isotropic contributions.

The separation of the information, given by the electron spin resonance experiment, into an isotropic and an anisotropic contribution, supplies valuable indications on the nature of the bonding and the overall structure of the radical. This follows as the isotropic contribution is a measure of the valence s atomic orbital participation in the molecular orbitals and the anisotropic of the p (or d) orbital participation. Using the orthogonality relations derived by Coulson, that is assuming the concept of atomic orbitals in molecules is not seriously invalidated by molecular formation and orbital overlap may be neglected, it can be shown that hybridisation ratios and bond angles may be estimated from the experimental isotropic and anisotropic coupling constants.

The evaluation of the expectation value of the isotropic, or Fermi contact, term, between an unpaired
electron and a magnetic nucleus

\[(8\pi/3)g_e g_N^\beta_e g_N^\beta_N S \cdot I \quad \ldots \ldots \text{(1)}\]

is uncomplicated, the accuracy of the calculated isotropic hyperfine coupling constants depending on the adequacy of the description of the spin density at the nucleus. The expectation value of the anisotropic operator

\[r^{-3} g_e g_N^\beta_e g_N^\beta_N [3(I \cdot r)(S \cdot r)/r^2 - I \cdot S] \quad \ldots \ldots \text{(2)}\]

presents a less trivial problem.

The evaluation of the anisotropic term, in the l.c.a.o. approximation, is a three centre problem in the general case. The one and two centre integrals, arising over the anisotropic operator, have been analysed in several cases. Kern and Karplus have suggested using the Gaussian Transform of the field gradient operator, for example

\[\frac{3x^2 - r^2}{r^3} = \frac{\partial^2}{\partial x^2} \left(\frac{1}{r}\right) + \frac{4\pi}{3} \delta(r) \quad \ldots \ldots \text{(3)}\]

where \(\delta(r)\) is the Dirac delta function, and have deduced the general expression for the integral over \(s\) type Gaussian functions. Silverstone and Todd have recently derived analytical formulae for the three centre one electron integrals of the operator \(r^m r_{1 \perp}^m(\theta, \phi)\) with Slater type orbitals, where \(r_{1 \perp}^m\) denotes a spherical harmonic and \(n\) and \(l\) are integers.

The isotropic hyperfine coupling constants have been calculated for a large number of radicals but few calculations are reported for the anisotropic hyperfine coupling constants. The analytical formulae for
the anisotropic operator with Gaussian type orbitals, derived earlier (Section VIIa), enabled a study of the value of the ab initio UHF method, with single spin annihilation, in explaining experimental anisotropic hyperfine coupling constants. An accurate description of the electron distribution close to the nucleus is required for the calculation of the anisotropic terms as, essentially, $<r^{-3}>$ is evaluated. It would be expected that the method which has been applied to the calculation of isotropic hyperfine coupling constants, giving good agreement with experiment, should prove suitable for the evaluation of the anisotropic components of the hyperfine interaction tensor.

Results and Discussion.

In the results to be discussed $a_X$ is used to denote the isotropic hyperfine coupling constant for nucleus $X$, $B_i(X)$ to denote the corresponding component of the anisotropic tensor in the $i (x,y,z)$ direction referred to the molecular axes and

$$A_i(X)=a_X+B_i(X)$$

The anisotropic components of the hyperfine interaction tensor for every atom in the radicals NaH$^+$, $N_2$, NO, CN, HCO, HBO$^-$, HCN$^-$, $H_2$CN, $C_2H_3$, NH$_3^-$, and CH$_3$ are evaluated. A minimal basis set of orbitals was used for all the atoms involved in the calculations with each orbital corresponding to an SCF atomic orbital represented by an expansion of Gaussian functions. Specifically the 9s type and 5p type of Huzinaga$^{21}$ were used for boron, carbon, nitrogen and oxygen, the
12s type and 6p type of Veillard for sodium and the 6s type for hydrogen excluding the sodium hydride cation calculation where the hydrogen was represented by a 10s type expansion. All the calculations were performed using the Unrestricted Hartree Fock method with spin annihilation of the quartet state, as outlined previously.

The Sodium Hydride Cation.

Bloom, Eachus and Symons found that a species, formulated as the sodium hydride cation, NaH\(^+\), was formed when barium sulphate was precipitated from a solution containing sodium ions prior to \(\gamma\)-irradiation. The interaction between the sodium ion and the hydrogen atom gives rise to a proton hyperfine coupling constant greater than that for the free atom, \(a_H=511.5\text{G}\), \(a_{Na}=17.2\text{G}\). Ab initio UHF calculations supported the assignment giving calculated isotropic coupling constants, at a bond distance of 3.6 a.u., of \(a_{Na}=26.1\), \(a_H=508\text{G}\) for a hydrogen orbital exponent of one. As the value of the isotropic hyperfine coupling constant for the free hydrogen, with the 10s basis used, was calculated to be 502.1G, compared with 508G found experimentally, a greater value than the free hydrogen value was, in fact, obtained. (After suitable scaling the calculated proton value in NaH\(^+\) is 514.4G.) The reason for the unusual proton value was associated with the presence of overlap in the calculation.
The UHF calculations demonstrated that the radical cation did not have an isolated existence and for this reason optimisation of the hydrogen orbital

Insert, directly after the seventh line on Pg 73,

\[ B_{\parallel}^{(\text{Na})} = 4.2 \text{G} \]
\[ B_{\perp}^{(\text{Na})} = -2.1 \text{G} \]
\[ B_{\parallel}^{(\text{H})} = 1.7 \text{G} \]
\[ B_{\perp}^{(\text{H})} = -0.85 \text{G} \]

and, using the spin density matrix of the UHF calculation, the calculated values were, not very satisfactory. The discrepancy for the proton may be accounted for qualitatively when it is noted that the unpaired electron on the hydrogen is mainly in the 1s orbital, making no contribution to the anisotropic component of the coupling constant. This results, when a minimal basis set of orbitals is used, in the calculated coupling arising solely from the small amount of spin in the overlap region and on the sodium ion. By postulating the occurrence of a polarisation of the hydrogen orbital, as may be achieved by mixing of the 1s of the hydrogen with its 2p orbital along the molecular axis, there will be a contribution of 2B to \( B_{\parallel}^{(\text{H})} \) and \(-B\) to \( B_{\perp}^{(\text{H})} \). If B were 1.01G exact agreement with experiment would result. For an electron in a 2p atomic orbital of hydrogen the calculated value of B is 3.17G, indicating that in NaH\(^+\) there is considerable polarisation of the orbital on the proton.

The inability to optimise the hydrogen orbital
exponent led to the use of unit value for the exponent. If, as seems probable, a hydrogen orbital exponent greater than unity were more appropriate for \( \text{NaH}^+ \) an increase in both \( a_H \) and \( B \) would result allowing for a smaller calculated polarisation of the proton orbital, while still maintaining the unusually large isotropic coupling constant found for the proton.

The Nitrogen Molecule Anion.

The ease with which inorganic azides may be decomposed, both thermally and photolytically, to form centres may account for the explosive nature of this class of compounds. Some of the centres formed are analogous to those of the alkali halides, created by radiation damage, but others, such as the \( N_2^- \) radical, are particular to azide compounds. There has been some difficulty in the identification of the paramagnetic species formed from azides, caused, to some extent, by the significant dependence of the coupling constants upon the environment. A compilation of experimental coupling constants for a species assigned as \( N_2^- \), in various host lattices, is given in Table 1.

Although the environment has a marked effect a calculation should give sufficiently good agreement to indicate whether the assignment is realistic. At a bond length of 2.14 a.u. the isotropic hyperfine coupling constants are calculated to be 2.765G and the principal components of the A tensor are given in Table 1, where the z axis is coincident with the molecular
Hyperrite Coupling Constants (in GHz) for \( ^{14}N \) for various host crystallites

<table>
<thead>
<tr>
<th>( \gamma )</th>
<th>( \delta )</th>
<th>( \zeta )</th>
<th>( \eta )</th>
<th>( \chi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>6.1</td>
<td>6.1</td>
<td>21.6</td>
<td>6</td>
</tr>
<tr>
<td>5.1</td>
<td>3.6</td>
<td>21.4</td>
<td>21.6</td>
<td>6</td>
</tr>
<tr>
<td>0.7</td>
<td>5.1</td>
<td>21.3</td>
<td>21.6</td>
<td>6</td>
</tr>
<tr>
<td>1.1</td>
<td>9.6</td>
<td>20.0</td>
<td>3.5</td>
<td>6</td>
</tr>
<tr>
<td>6.1</td>
<td>5.9</td>
<td>2.1</td>
<td>6.6</td>
<td>6</td>
</tr>
<tr>
<td>4.1</td>
<td>8.8</td>
<td>12.0</td>
<td>6.5</td>
<td>6</td>
</tr>
<tr>
<td>4.1</td>
<td>4.1</td>
<td>6.9</td>
<td>8.8</td>
<td>6</td>
</tr>
<tr>
<td>8.1</td>
<td>12.1</td>
<td>25.6</td>
<td>6.6</td>
<td>6</td>
</tr>
</tbody>
</table>

This work (theoretical)

<table>
<thead>
<tr>
<th>( \delta )</th>
<th>( \epsilon )</th>
<th>( \zeta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>692</td>
<td>91</td>
<td>06</td>
</tr>
</tbody>
</table>

Table 1
axis and the unpaired electron occupies a $\pi^*$ antibonding orbital.

A fortunate feature of the UHF method is the lifting of the degeneracy of a degenerate pair of orbitals when such a pair is available for the description of one electron. As the $N_2^-$ radical has always been observed in environments which remove the degeneracy of the $\pi^*$ antibonding orbitals the results of the UHF calculation are directly applicable.

**Nitric Oxide.**

Studies of the NO radical are reported for the molecule in the gas phase, absorbed on magnesium oxide and in single crystals of hydroxylammonium chloride, after irradiation with X rays at 77K. The latter study of Ohigashi and Kurita gave the A hyperfine tensor of the nitrogen.

$$A_x(N) = 36.4 \text{G} \quad A_y(N) = 5.4 \text{G} \quad A_z(N) = 11.5 \text{G}$$

with the z axis coincident with the molecular axis. The unpaired electron was found to be in a $\pi^*$ antibonding orbital lying $2000\text{cm}^{-1}$ below the $\pi^*$ orbital, the degeneracy being lifted in a manner analogous to the isoelectronic $N_2^-$ ion. No experiment appears to have reported the isotropic hyperfine coupling constant of the nitrogen in NO so that the signs of the A tensor components is uncertain. Gallagher and Johnson have deduced approximate values of $a_N = 14.2 \text{G}$ and $B_z(N) = -20.83 \text{G}$, from the microwave spectrum of the NO ground state, suggesting that $A_z(N)$ is negative.
Using a bond length of 2.175 a.u., the unpaired electron was calculated to occupy the $\tau_x^*$ antibonding orbital. The calculated coupling constants are

- $a_N = 5.39 G$
- $B_x(N) = 26.97 G$
- $B_y(N) = -10.72 G$
- $B_z(N) = -16.25 G$
- $a_O = -2.11 G$
- $B_x(0) = -43.39 G$
- $B_y(0) = 30.08 G$
- $B_z(0) = 13.31 G$

from which,

- $A_x(N) = 32.36 G$
- $A_y(N) = -5.33 G$
- $A_z(N) = -10.86 G$

The agreement between the experimental and the theoretical coupling constants indicates that the experimental values of $A_y(N)$ and $A_z(N)$ should be taken as negative, a result consistent with $N_2^−$.

The Cyanide Radical.

Easley and Welther by trapping CN, in random orientation, in argon, kryton and neon matrices at 4K, were able to report the following magnetic properties of the species

- $a_C = 210 G$
- $B_\parallel(C) = 32 G$
- $B_\perp(C) = -16 G$
- $a_N = -4.5 G$
- $B_\parallel(N) = 11 G$
- $B_\perp(N) = -5.5 G$

Ab initio UHF calculations on the radical have given isotropic coupling constants of $a_C = 339.2 G$, $a_N = -6.182 G$, showing good agreement for the nitrogen but not for the carbon. The discrepancy found was not thought to be caused by the UHF method, a similar result was obtained with the Restricted Hartree Fock method, but rather a result of the inadequacy of the SCF atomic orbitals used as basis orbitals. Any inadequacy of the basis is exaggerated in the case
of the ON radical, where a delicate balance between the s and p ratio of the hybrid orbitals involved in the σ bond and in the non-bonding orbital on the carbon is maintained.

The excess s character calculated in the non-bonding orbital of the carbon is also reflected in the low values calculated for the anisotropic components, \( B_{\parallel}(C) = 17.15 \text{G} \) whereas the calculated value of \( B_{\parallel}(N) \) is \( 9.55 \text{G} \), in good agreement with experiment.

The HBO\(^-\), HCO, HCN\(^-\) Radicals.

The characteristically large hyperfine interaction of the proton in these radicals has interested a number of workers. The spin density matrices of the ab initio UHF calculations aimed at predicting the isotropic coupling constants of the isoelectronic radicals\(^ {107} \) were used for the evaluation of the anisotropic components. In these calculations all bond angles were assumed to be \( 120^\circ \) and for HCO a hydrogen orbital exponent of \( 1.4 \) was chosen while a value of \( 1.2 \) was taken for the anions. The BO, CO, CN bond lengths were chosen as \( 2.4, 2.3, \) and \( 2.2 \text{ a.u.} \) respectively and the CH of HCN\(^-\) was set at \( 2.0\text{a.u.} \), the others, HB and HC for HBO\(^-\) and HCO, being taken as \( 2.2\text{a.u.} \).

HCO

Experimental and theoretical hyperfine coupling constants for HCO are given in Table 2. Symons and Wardale\(^ {106} \) in their study of the radical in single crystals of formic acid were only able to find the
### Table 2: Relevant Coupling Constants (in G) for HGO

<table>
<thead>
<tr>
<th>( \lambda'' )</th>
<th>( \lambda' )</th>
<th>( \lambda )</th>
<th>( \lambda' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>148.4</td>
<td></td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>130</td>
<td>135</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td>112.5</td>
<td></td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>126</td>
<td>137</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

Note: The table includes relevant coupling constants (in G) for HGO.
relative orientations of the anisotropic components of the hyperfine tensor in the molecular plane, rendering unfeasible an estimate of the bond angle from the e.s.r. data. The theoretical anisotropic components of the hyperfine interaction tensor are given in figure 1a.

\textbf{HBO}^-

The \(\gamma\)-irradiation of alkali borohydrides at 20K gave values of the B tensors for the HBO\(^-\) radical\(^{106}\); for boron 12, \(-6, -6\)G and for hydrogen 8, \(-4, -4\)G. Calculated components of the anisotropic hyperfine tensor are given in figure 1b. The experimental results are probable poor approximations\(^{60}\) and it is sufficient that the existence of the radical HBO\(^-\) is confirmed by the calculation together with the calculated isotropic coupling constants, \(a_H=91.6\)G, \(a_B=123\)G\(^{107}\) (compared with the \(a_H=94\)G, \(a_B=101\)G found experimentally\(^{60}\)).

\textbf{HCN}^-

Ultraviolet or gamma irradiation of cyanide doped alkali halide crystals at 77K followed by briefly warming to 280K then recooling, results in the production of the HCN\(^-\) radical ion\(^{108-110}\). At 77K the spectrum is isotropic, indicating rapid rotation or reorientation of the radical. At 4K however the tumbling of the radical has been frozen out and the spectrum is completely anisotropic, permitting a full determination of the magnetic parameters\(^{110}\). This detailed magnetic data, for the HCN\(^-\) radical, allows an extremely important test to be made of the theoretical
The principal values and axes of the anisotropic components of the hyperfine coupling tensors for (i) HCO and (ii) HBO. All quantities except angles are in Gauss. The numbers close to the nuclei represent components perpendicular to the molecular plane. The arrows point to the values associated with the direction of the axis and do not represent a direction (a tensor component, not a vector component).
method used. An important aspect which arises is the
accuracy to which the orientation of the principal
axes of the anisotropic components can be determined,
particularly if no independent study of the
orientation of the radical in the crystal is available.

The theoretical and experimental anisotropic
components of the hyperfine interaction tensors are
presented in figure 2. The calculated values of \( a_H = 14.0 \cdot 3 \),
\( a_C = 74.4 \) and \( a_N = 4.92 \) for the isotropic coupling
constants agree excellently with experiment, where
an angle of 131° was estimated; \( a_H = 136.4 \), \( a_C = 74.7 \)
and \( a_N = 7 \). The agreement between theoretical and
experimental anisotropic coupling constants is also
satisfactory. There is a discrepancy between the
orientation of the calculated and the experimental
anisotropic components of the proton, suggesting that
a re-examination of the accuracy with which the
orientation has been determined may be of value.

By considering the \( \text{HCN}^- \) radical ion as a
derivative of the linear \( \text{HCN} \) molecule, formed by
bending and addition of an electron, two extreme
situations can be envisaged. Assuming homolytic
fission of the inplane \( \pi \) bond on bending, an electron
will occupy an \( \text{sp}^2 \) hybrid orbital on the carbon and
an inplane \( \text{p} \) orbital on the nitrogen. Addition of an
electron to form a pair, with the electron in either
orbital, results in the two extreme cases.
Consideration of the spin density distributions in
figure 2 (i) and (ii) indicates that both models
contribute to an appreciable extent.
The principal values and axes of the anisotropic components of the hyperfine coupling tensors for HCN. 
(i) theoretical values; (ii) experimental values. 
(See also the caption to figure 1.)
The H₂CN Radical.

Interest in H₂CN is associated with the particularly favourable conditions for hyperconjugation, arising from the planar structure of the radical, the short CN double bond and the unpaired electron being formally located in the inplane 2p orbital of the nitrogen. Experimental anisotropic parameters are reported for the nitrogen only·

\[ a_N = 9.5 \text{G} \quad \text{A}_||(N) = 34.4 \text{G} \quad \text{A}_\perp(N) = -3 \text{G} \]

The proton isotropic coupling constant \( a_H = 87.4 \text{G} \) or 92.1G, the latter from the powder spectrum, is also reported.

An ab initio UHF calculation for a bond angle of 120° and CH and CN bond length of 2.2 and 2 a.u. respectively gave isotropic couplings·

\[ a_H = 84.8 \text{G} \quad a_N = 7.2 \text{G} \quad a_C = -18.7 \text{G} \]

Using the spin density matrix of this calculation the anisotropic components were calculated and are given in figure 3. The A tensor for nitrogen is

\[ \text{A}_y(N) = 37.3 \text{G} \quad \text{A}_z(N) = -10.5 \text{G} \quad \text{A}_x(N) = -5.3 \text{G} \]

with the z axis parallel to the CN bond and the molecule in the yz plane.

The value of 87.4G for the proton hyperfine coupling constant appears to have been measured from the parallel features of the electron spin resonance experiment spectrum and if this is the case should correspond closely to \( \text{A}_||(H) \). Since \( a_H = \text{A}_||(H) - B_H(H) = 90.2 \text{G} \) better agreement with experiment, for the 91.2G proton value from the powder spectrum, is obtained.
The principal values and axes of the anisotropic components of the hyperfine coupling tensors of $\text{H}_2\text{CN}$. (See also the caption to figure 1.)
The Vinyl Radical.

The sensitivity of the sign of the $\alpha$ proton coupling constant of the vinyl, $(a_H^\alpha = \pm 13.5\, \text{G experimental})$ to the bond angle $\text{CCH}_\alpha$ has caused previous calculations to be inconclusive. No experimental data for the anisotropic interactions is available for the vinyl radical but the closely related radical DOOC-CH=CH', produced by irradiation of a single crystal of deuterated maleic acid, has been studied. For DOOC-CH=CH' the maximum principal value of the $\alpha$ proton anisotropic coupling constant is approximately along the C-H bond and the minimum is perpendicular to the radical plane, $A(H^\alpha) = 27, 9.6, 3.9\, \text{G}$.

An ab initio calculation has been reported for a hydrogen orbital exponent of $1.4$, bond lengths of $2.533$ and $2.041$ a.u. for the CC and CH bonds respectively, bond angles of $120^\circ$ for the $\beta$ protons and $137^\circ$ for the $\alpha$ proton, as suggested by the work of Millie and Berthier. The spin density matrix of the calculation was used in the calculation of the anisotropic components of the hyperfine tensor and the results are presented in figure 4.

If a positive value of $13.5\, \text{G}$, for the isotropic coupling constant of $H^\alpha$, is assumed the corresponding anisotropic tensor components are $B(H^\alpha) = 13.5, -3.9, -9.6\, \text{G}$. These agree well with the values, and directions, calculated thus reinforcing the view that the isotropic coupling constant of the $\alpha$ proton is positive.
The principal values and axes of the anisotropic components of the hyperfine coupling tensors for the vinyl radical. (See also the caption to figure 1.)
The Ammonia Radical Cation.

The isotropic hyperfine coupling constants of \( \text{NH}_3^+ \) have been calculated using the ab initio UHF method, with optimisation of the geometry and hydrogen orbital exponent for the planar radical. Allowing for the out of plane zero point energy vibration the calculated coupling constants are \( a_N = 16.92 \text{G} \), \( a_H = -20.02 \text{G} \). These calculations are reported in Chapter 2.

Rao and Symons\(^6\) on \( \gamma \)-irradiation of ammonium perchlorate, at room temperature and 77K, obtained the \( \text{NH}_3^+ \) radical, with isotropic coupling constants and anisotropic components

\[ a_N = 19.3 \text{G} \quad ; \quad A_{\parallel}(N) = 37 \text{G} \quad , \quad A_{\perp}(N) = 10.5 \text{G} \]

\[ a_H = 25.8 \text{G} \quad ; \quad A_{\parallel}(H) = 28 \text{G} \quad , \quad A_{\perp}(H) = 24.7 \text{G} \]

The theoretical anisotropic components of the hyperfine interaction tensor are given in figure 5. These are very similar to those for \( \text{NH}_2 \) (also figure 5) where \( A_{\parallel}(N) = 41.7 \text{G} \), \( A_{\perp}(N) = 0 \pm 3 \text{G} \) experimental compare favourable with the calculated values of \( A_{\parallel}(N) = 41.66 \text{G} \), \( A_{\perp}(N) = -8.05 \text{G} \). The calculation of the anisotropic coupling constants should be at least as reliable as the calculated isotropic coupling constants and therefore equally good estimates for the \( A \) tensor, as obtained for the \( a \) values, are anticipated. Since the calculated \( a_N \) was low by only 2.3G, compared with experiment, the discrepancies between the calculated and experimental \( A \) values should be equally small. The large differences between the calculated values, \( A_{\parallel}(N) = 50 \text{G} \) and \( A_{\perp}(N) = 0.5 \text{G} \), and the experimental values may be associated with the fact that the true \( A_{\parallel} \) and \( A_{\perp} \) are
The principal values and axes of the anisotropic components of the hyperfine coupling tensors for the radicals (i) NH$_3^+$ and (ii) NH$_2$. (See also the caption to figure 1.)
not measured but have been partially averaged by a librational motion about the threefold axis.\textsuperscript{68}

The calculated anisotropy of the proton coupling constants is never completely observed owing to a rapid rotation about the threefold axis. Using $B_\perp = 0.5(B_x + B_y) = 2.575$ G the calculated values may be given as $A_\parallel(H) = -25.17$ G, $A_\perp(H) = 17.46$ G, a difference between $A_\parallel$ and $A_\perp$ of 7.725 G compared to the observed difference of 3.3 G. This discrepancy can also be associated with the librational motion.

\textbf{The Methyl Radical.}

The results obtained from calculations of the isotropic hyperfine coupling constants for CH\textsubscript{3} have been discussed already (Chapter 2). The isotropic values, $a_C = 54.64$ G, $a_H = -19.43$ G, are in reasonable agreement with the generally accepted experimental values of $a_C = 38$ G, $a_H = -23$ G, reported for solution and matrix environment. On Vycor glass below 150 K values less than 38 G for $a_C$ have been measured,\textsuperscript{116} which on extrapolation to 0 K give $a_C = 10.6$ G. Rao and Symons\textsuperscript{69} have suggested that Garbutt et al\textsuperscript{116} have misinterpreted the spectrum and are in fact measuring $A_\perp(C)$ rather than $a_C$. The calculated value of $B_\perp(C)$, after taking into account the out of plane zero point energy vibration, was estimated to be $-30$ G. If Rao and Symons are correct, and the minimum value of $a_C$ is 38 G, then an $A_\perp(C)$ value of about 8 G is obtained. This compares favourably with the extrapolated value of Garbutt et al and therefore their unusual results are rejected by accepting the interpretation of Rao and
Conclusions.

The calculations which have been carried out within the ab initio UHF framework with single spin annihilation after minimisation have demonstrated that consistently good agreement may be obtained between experimental and theoretical anisotropic components of the hyperfine coupling tensor. The results give confidence in the use of the method to explain the observed hyperfine coupling constants of radicals and thus verify the identity and structure of species reported using the electron spin resonance technique. Any improvements in the results would be associated with more adequate basis orbitals, as indicated in the case of the CN radical, rather than abandoning the simple extension to the independent particle model.
CHAPTER 4
Introduction.

The advantage of using Gaussian type orbitals over Slater type orbitals lies particularly in the evaluation of the multicentre two electron integrals which arise in molecular calculations. Since the introduction of Gaussians a considerable amount of effort has been directed towards determining suitable Gaussian expansions for Slater type or atomic SCF orbitals. Methods for obtaining Gaussian exponents and expansion coefficients have been developed by Huzinaga and others, using the criterion of minimisation of the energy or least squares fit to a Slater type orbital.

If the number of Gaussian functions in a calculation is \( N \) then the number of two electron integrals is of the order \( N^4 \). These integrals therefore represent both the most numerous and the most difficult to evaluate. Cook and Palmieri have noted that although large Gaussian expansions are required to reproduce the values of the one electron integrals much smaller expansions are adequate for the two electron integrals. The application of their "mixed" basis method to a molecular system represents a time reduction, in the integral evaluation, of an order of magnitude. The mixed basis method is STO orientated and it is convenient to distinguish that method which is SCF orbital orientated by reference to the double basis method. The philosophy of both methods is identical; in the double basis method large Gaussian expansions are used to represent all one electron and
one centre integrals and small expansions for the multicentre two electron integrals. The approach is to be distinguished from the "combined" basis method of Silver which augments STO basis sets with Gaussian type orbital basis sets.

In the double basis method the "best" Gaussian representation of an atom, using the energy criterion, is chosen to calculate the one electron and one centre integrals. This is invariably the largest expansion available. However, as the multicentre two electron integrals are of solely molecular origin, the small expansions are chosen on the least squares criterion. This is because the energy is very dependent upon the wavefunction close to the nucleus, whereas most multicentre two electron integrals depend on the electron density distribution remote from the nucleus.

A number of Gaussian expansions of SCF atomic orbitals for the first, second and third row atoms are available in the literature and these may be used for the one electron and one centre integral calculations. However small expansions, useful in the double basis method, are few. Stewart has reported small expansions for some of the first row atoms and further work, representing STO's by small Gaussian expansions, has been done.

Small Gaussian basis sets (6s,4p), which are suitable for use in the double basis method, are calculated for the second row atoms by least square fitting to the 12s,9p basis of Veillard. The differences between the available second row basis sets are also analysed. The double basis method is
then applied to the calculation of the isotropic hyperfine coupling constants of the radicals XH₃ and XH₂Me (X=Al⁻, Si, P⁺ and Me is the methyl group, CH₃).

**Determination of Least Squares Basis Sets.**

**Method.**

The 12s type and 9p type fully contracted Gaussian expansions for the atomic SCF orbitals of the second row atoms, due to Veillard, were used as the standard functions to which small Gaussian expansions were to be fitted. The Gaussian expansion of the radial part of an orbital can be represented as

\[ \chi_i = \sum_j c_{ij} r^n \exp(-\alpha_j r^2) \]

(1)

where \( r \) is the distance to the nucleus on which the orbital is centred and \( n=0 \) for an s type and \( n=1 \) for a p type orbital. For all orbitals with the same spherical harmonic, on an atom, the exponent, \( \alpha \), is the same for all \( \chi_i \). This restriction represents a considerable reduction in the time required to evaluate the two electron integrals, and limits the usefulness of the orbitals of Stewart and Hehre. Two Gaussian functions per orbital were considered the minimum necessary for the small basis, leading to six terms in equation (1) for the s orbitals and four terms for the p orbitals. For sodium and magnesium, where there is only one p orbital to fit, three Gaussian functions were considered necessary to give a comparable fit.

The least squares problem which must be solved
is the minimisation of the error function

\[ \epsilon = \sum_i \int (\psi_i - \chi_i)^2 \, d\tau \]  \hspace{1cm} \ldots \ldots \ldots \ldots (2) \]

where \( i \) extends over all functions with the same spherical harmonic; \( \psi_i \) represents one of the standard functions due to Veillard. The minimisation of (2) is subject to the conditions

\[ \int \chi_i \chi_j \, d\tau = \delta_{ij} \]

A regression method, programmed in ALGOL\textsuperscript{119}, was used in an attempt to reduce the chance minimisation on to a local minima. Crudely the function is evaluated many times over varying limits of the variables \( c_{ij} \) and \( a_j \) such that \( \epsilon \) is always reduced. Despite the considerable effort expended, in an attempt to find the true minimum, no guarantee can be given, in common with other methods available.

Results and Discussion.

The orbital exponents are given in Table 1 and the corresponding expansion coefficients are listed in Table 2. Orbital energies were not calculated since these basis sets are not intended for use in single basis calculations.

The 3s orbitals (figure 1) from the 6s, 4p Gaussian set deviate from the 12s, 9p set in the manner expected for a least squares fit. However the deviation of the 3p orbitals (figure 2) is not characteristic of a least squares fit, showing a small positive fluctuation near the nucleus (the 2p orbitals
<table>
<thead>
<tr>
<th>0.1</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
<th>3.5</th>
<th>4.0</th>
<th>4.5</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.7749</td>
<td>1.494197</td>
<td>0.825787</td>
<td>0.539952</td>
<td>0.574387</td>
<td>0.684952</td>
<td>0.704387</td>
<td>0.774387</td>
<td>0.814387</td>
<td>0.874387</td>
<td>0.914387</td>
</tr>
<tr>
<td>4.374197</td>
<td>0.694197</td>
<td>0.425787</td>
<td>0.239952</td>
<td>0.259952</td>
<td>0.364952</td>
<td>0.384387</td>
<td>0.444387</td>
<td>0.474387</td>
<td>0.534387</td>
<td>0.574387</td>
</tr>
<tr>
<td>2.974197</td>
<td>0.294197</td>
<td>0.125787</td>
<td>0.039952</td>
<td>0.059952</td>
<td>0.164952</td>
<td>0.184387</td>
<td>0.244387</td>
<td>0.274387</td>
<td>0.334387</td>
<td>0.374387</td>
</tr>
<tr>
<td>1.974197</td>
<td>0.194197</td>
<td>0.025787</td>
<td>0.009952</td>
<td>0.019952</td>
<td>0.024952</td>
<td>0.028387</td>
<td>0.034387</td>
<td>0.0374387</td>
<td>0.0434387</td>
<td>0.0474387</td>
</tr>
<tr>
<td>1.174197</td>
<td>0.094197</td>
<td>0.005787</td>
<td>0.000952</td>
<td>0.001952</td>
<td>0.002492</td>
<td>0.0028387</td>
<td>0.0034387</td>
<td>0.00374387</td>
<td>0.00434387</td>
<td>0.00474387</td>
</tr>
</tbody>
</table>

**Table 1.**

Orbital exponents for the atom Na-Ga.
<table>
<thead>
<tr>
<th>Na</th>
<th>Ca</th>
<th>Fe</th>
<th>Ti</th>
<th>Zr</th>
<th>Hf</th>
<th>Si</th>
<th>Al</th>
<th>Mg</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>017149</td>
<td>016749</td>
<td>016571</td>
<td>016499</td>
<td>017499</td>
<td>014794</td>
<td>013571</td>
<td>013278</td>
<td>022494</td>
</tr>
<tr>
<td>0.97</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
</tr>
</tbody>
</table>

**Explanation of contents for the atoms Na-Ca:**

**Table 2.**
FIGURE 1. Variation of the difference $g$ as a function of the distance $x$, from the nucleus for the atom $\chi^-$.

Roses and Stewart (c) 1995.
Variation of the difference, $\delta = \chi_{3p} - \chi'_{3p}$, as a function of the distance, $r$, from the nucleus for the atoms indicated. $\chi$ corresponds to the expansion of a) Huzinaga et al.; b) Roos and Siegbahn; c) this work.
show negative deviations in this region). The similarity in the plots for the 3p orbitals of each atom suggests that the orbitals are consistent amongst themselves. The fit of the 6s, 4p set to the 12s, 9p set is very good for all the atoms, the maximum deviation being about 0.01.

The error function

$$\epsilon_i = \int (\varphi_i - \xi_i)^2 \, d\tau$$

......(3)

was evaluated for various functions (Table 3) where \(\varphi_i\) and \(\xi_i\) are any pair of Gaussian expansion representations of SCF atomic orbitals calculated by Veillard (12s,9p)\(^{18}\), Roos and Seigbahn (10s,6p)\(^{23}\), Huzinaga, McWilliams and Domsky (9s,5p)\(^{24}\), all using a minimum energy criterion, and this work (6s,4p).

The error function, \(\epsilon_{3p}\), between the 12s,9p and the 9s,5p set for the 3p orbital is particularly large compared to the error function of the other orbitals and the basis set to the 12s,9p set. Assuming that the 12s,9p set is the best available, consideration of the results in Table 3 suggest that, for molecular calculations using a single basis, the 10s,6p set might be a good compromise. The reasons are twofold;

1) The maximum deviation of the 10s,6p is less than half that of the 9s,5p set in all cases, except aluminium.

2) A considerable reduction in the number of integrals to be evaluated is achieved by using the 10s,6p set rather than the 12s,9p set.
<table>
<thead>
<tr>
<th>This Work</th>
<th>Hüttenberg</th>
<th>Room</th>
<th>Validated</th>
<th>This Work</th>
<th>Hüttenberg</th>
<th>Room</th>
<th>Validated</th>
<th>This Work</th>
<th>Hüttenberg</th>
<th>Room</th>
<th>Validated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0063990</td>
<td>0030050</td>
<td>0063993</td>
<td>000000</td>
<td>0063990</td>
<td>0030050</td>
<td>0063993</td>
<td>000000</td>
<td>0063990</td>
<td>0030050</td>
<td>0063993</td>
<td>000000</td>
</tr>
<tr>
<td>0063991</td>
<td>0030757</td>
<td>0063993</td>
<td>000000</td>
<td>0063991</td>
<td>0030757</td>
<td>0063993</td>
<td>000000</td>
<td>0063991</td>
<td>0030757</td>
<td>0063993</td>
<td>000000</td>
</tr>
<tr>
<td>0063992</td>
<td>0030537</td>
<td>0063993</td>
<td>000000</td>
<td>0063992</td>
<td>0030537</td>
<td>0063993</td>
<td>000000</td>
<td>0063992</td>
<td>0030537</td>
<td>0063993</td>
<td>000000</td>
</tr>
<tr>
<td>0063993</td>
<td>0030757</td>
<td>0063993</td>
<td>000000</td>
<td>0063993</td>
<td>0030757</td>
<td>0063993</td>
<td>000000</td>
<td>0063993</td>
<td>0030757</td>
<td>0063993</td>
<td>000000</td>
</tr>
<tr>
<td>0063994</td>
<td>0030537</td>
<td>0063993</td>
<td>000000</td>
<td>0063994</td>
<td>0030537</td>
<td>0063993</td>
<td>000000</td>
<td>0063994</td>
<td>0030537</td>
<td>0063993</td>
<td>000000</td>
</tr>
<tr>
<td>0063995</td>
<td>0030757</td>
<td>0063993</td>
<td>000000</td>
<td>0063995</td>
<td>0030757</td>
<td>0063993</td>
<td>000000</td>
<td>0063995</td>
<td>0030757</td>
<td>0063993</td>
<td>000000</td>
</tr>
</tbody>
</table>

TABLE 3 (cont.)
<table>
<thead>
<tr>
<th>0.041243</th>
<th>0.004925</th>
<th>0.001031</th>
<th>0.061256</th>
<th>0.001031</th>
<th>0.004925</th>
<th>0.041243</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003739</td>
<td>0.041243</td>
<td>0.001279</td>
<td>0.001279</td>
<td>0.041243</td>
<td>0.003739</td>
<td>0.001279</td>
</tr>
<tr>
<td>0.001031</td>
<td>0.001279</td>
<td>0.061256</td>
<td>0.001279</td>
<td>0.001031</td>
<td>0.001279</td>
<td>0.061256</td>
</tr>
<tr>
<td>0.061256</td>
<td>0.001279</td>
<td>0.001031</td>
<td>0.001031</td>
<td>0.061256</td>
<td>0.001279</td>
<td>0.001031</td>
</tr>
<tr>
<td>0.001279</td>
<td>0.001031</td>
<td>0.061256</td>
<td>0.001031</td>
<td>0.001279</td>
<td>0.001031</td>
<td>0.061256</td>
</tr>
<tr>
<td>0.001031</td>
<td>0.061256</td>
<td>0.001279</td>
<td>0.001279</td>
<td>0.001031</td>
<td>0.061256</td>
<td>0.001279</td>
</tr>
<tr>
<td>0.061256</td>
<td>0.001279</td>
<td>0.001031</td>
<td>0.001031</td>
<td>0.061256</td>
<td>0.001279</td>
<td>0.001031</td>
</tr>
</tbody>
</table>

**Table 3 (cont.)**
Applications of the Double Basis Method.

The magnitude of the proton hyperfine coupling constant is considerably reduced on going from the first row hydride series, $\text{BH}_3$, $\text{CH}_3$, and $\text{NH}_3^+$, to the second row series, $\text{AlH}_3^-$, $\text{SiH}_3$, and $\text{PH}_3^+$. This may be understood if the former are planar and the latter slightly pyramidal $^{120}$, as it is expected that as the deviation from planarity increases the negative proton coupling constant will go through zero and then increase rapidly, accounting for the large positive proton coupling constants observed for such radicals as $\text{HCO}$. As the radicals $\text{AlH}_3^-$, $\text{SiH}_3$, and $\text{PH}_3^+$, from the e.s.r. data available, $^{121-128}$ are thought to have quite large deviations from planarity ($18^\circ40'$, $15^\circ51'$ and $14^\circ30'$ for $\text{AlH}_3^-$, $\text{SiH}_3$ and $\text{PH}_3^+$ respectively) the small magnitudes of the observed proton hyperfine coupling constants are surprising.

Theoretical calculations, using the ab initio UHF double basis method, were done on the isoelectronic series $\text{AlH}_3^-$, $\text{SiH}_3$ and $\text{PH}_3^+$ in order to verify the assignment given to the species observed by the electron spin resonance technique. Calculations were also performed on the related series $\text{AlH}_2\text{Me}^-$, $\text{SiH}_2\text{Me}$ and $\text{PH}_2\text{Me}^+$.  

Method.

The ab initio UHF method using the l.c.a.o.-m.o.-ap-approximation with spin annihilation was used (see Sections I and II). The minimal basis set of orbitals was represented by expansions of Gaussian functions.
in their completely contracted form. The 12s type and 9p type of Veillard\textsuperscript{18} for the aluminium, silicon and phosphorus and the 9s type and 5p type for the carbon and the 6s type for the hydrogen as given by Huzinaga\textsuperscript{21} were used to calculate the one electron and one centre integrals. The 6s type and 4p type for aluminium, silicon and phosphorus as given and the 4s type and 3p type for carbon and the 3s type for hydrogen reported by Stewart\textsuperscript{28} were used to evaluate the multicentre two electron integrals. The hydrogen atomic orbital exponent and the bond length, $r(X-H)$, were optimised to within 0.1 at an angle of 19.5° from planarity for AlH$_3$ and SiH$_3$ and an angle of 14° for PH$_3$. With these optimum hydrogen orbital exponents and bond lengths the angle of the radicals were optimised to within one degree.

The bond lengths and hydrogen orbital exponents of the hydrogens attached directly to the second row atom and the pyramidal angle in XH$_2$Me (X=Al$^-$, Si, P$^+$) were assumed to be the optimum values for the XH$_3$ radicals. The bond lengths $r(C-X)$ were taken to be 3.8, 3.5 and 3.5 a.u. for $X=\text{Al}$, Si and P respectively, $r(C-H)$ for the hydrogens of the methyl group was taken as 2.05 a.u. and the carbon was tetrahedrally placed with respect to the three hydrogens and the central atom, $X$. From the calculations on the methyl radical, a hydrogen orbital exponent of 1.4 was considered suitable for the hydrogens of the methyl group.

All results were calculated from the UHF wavefunction after annihilation of the contaminating
quartet state and are expressed in atomic units, except the hyperfine coupling constants which are expressed in Gauss.

The Radical Anion AlH\textsuperscript{−}.

Catton and Symons\textsuperscript{126} on \(\gamma\)-irradiation of lithium and sodium aluminium hydride at 77K produced a paramagnetic species which, by analogy with the \(\gamma\)-irradiation product of KBH\textsubscript{4} (BH\textsuperscript{−}) was expected to be AlH\textsuperscript{−}. The isotropic coupling constant of aluminium, \(a_{\text{Al}}=223\text{G}\), was reported but no proton coupling constant could be detected, limiting its value to less than 20G. The deviation from planarity was estimated to be 18°40'.

The results of UHF calculations on AlH\textsuperscript{−} are given in Table 4. The total energy was \(-243.57247\text{a.u.}\) at an optimum bond length of 3.2a.u., hydrogen orbital exponent of 1.0 (figure 3) and angle from planarity of 21°. The calculated isotropic hyperfine coupling constants are \(a_{\text{Al}}=213.8\text{G}\) and \(a_{\text{H}}=3.48\text{G}\). The agreement with experiment, of the aluminium coupling constant and the angle, is excellent. The smallness of the calculated coupling constant of the proton is reassuring since the observed small magnitude was unexpected.

The Silyl Radical SiH\textsuperscript{−}.

Two values of the silicon isotropic coupling constant have been reported by Gordy and his co-workers\textsuperscript{121,122}. For the radical trapped in a xenon matrix, \(a_{\text{Si}}=190\text{G}\textsuperscript{122}\), and for the same species in a krypton matrix at 4K, \(a_{\text{Si}}=266\text{G}\textsuperscript{121}\). As the radical is
### TABLE 4.

<table>
<thead>
<tr>
<th>bond length (a.u.)</th>
<th>hydrogen orbital exponent</th>
<th>bending angle $\theta^\circ$</th>
<th>total energy (a.u.)</th>
<th>coupling constants (G)</th>
<th>$&lt;S^2&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>0.9</td>
<td>19.5</td>
<td>-243.56571</td>
<td>225.6</td>
<td>6.14</td>
</tr>
<tr>
<td>3.3</td>
<td>0.9</td>
<td>19.5</td>
<td>-243.56633</td>
<td>242.4</td>
<td>8.03</td>
</tr>
<tr>
<td>3.4</td>
<td>0.9</td>
<td>19.5</td>
<td>-243.56450</td>
<td>260.6</td>
<td>10.36</td>
</tr>
<tr>
<td>3.1</td>
<td>1.0</td>
<td>19.5</td>
<td>-243.56999</td>
<td>190.4</td>
<td>1.10</td>
</tr>
<tr>
<td>3.2</td>
<td>1.0</td>
<td>19.5</td>
<td>-243.57240</td>
<td>203.8</td>
<td>2.45</td>
</tr>
<tr>
<td>3.3</td>
<td>1.0</td>
<td>19.5</td>
<td>-243.57221</td>
<td>217.6</td>
<td>4.02</td>
</tr>
<tr>
<td>3.1</td>
<td>1.1</td>
<td>19.5</td>
<td>-243.56125</td>
<td>170.7</td>
<td>-4.82</td>
</tr>
<tr>
<td>3.2</td>
<td>1.1</td>
<td>19.5</td>
<td>-243.56373</td>
<td>181.6</td>
<td>-3.92</td>
</tr>
<tr>
<td>3.3</td>
<td>1.1</td>
<td>19.5</td>
<td>-243.56315</td>
<td>192.7</td>
<td>-3.00</td>
</tr>
<tr>
<td>3.2</td>
<td>1.0</td>
<td>19.0</td>
<td>-243.57232</td>
<td>200.5</td>
<td>2.10</td>
</tr>
<tr>
<td>3.2</td>
<td>1.0</td>
<td>20.0</td>
<td>-243.57247</td>
<td>207.3</td>
<td>2.83</td>
</tr>
<tr>
<td>3.2</td>
<td>1.0</td>
<td>21.0</td>
<td>-243.57248</td>
<td>213.8</td>
<td>3.48</td>
</tr>
<tr>
<td>3.2</td>
<td>1.0</td>
<td>22.0</td>
<td>-243.57232</td>
<td>220.0</td>
<td>4.06</td>
</tr>
</tbody>
</table>

*marks minimum

Theoretical Results for $\text{AlH}_3^-$
Summary of the calculations of the AlH$_3^-$ radical; variation of the total energy after annihilation with bond length for those values of the hydrogen orbital exponent $\alpha$ as indicated.
uncharged, and hence environmental effects on the conformation are expected to be small, the large difference is surprising (especially as the environments are so similar). Sharp and Symons\textsuperscript{123} have demonstrated that for the radicals SiH\textsubscript{n}Me\textsubscript{3-n} (n=0,1,2) the silicon coupling constants are about the same (180G), that is, addition of a methyl group has little effect on $a_{Si}$. This led to the suggestion that the value of 190G for the coupling constant of silicon should be accepted, being more consistent with the known data, and the value of 226G rejected. Also reported for the silyl radical were $a_{H}=7.84G$ and an estimated angle out of plane of 15°51'.

The results of the calculations on SiH\textsubscript{3} are collected in Table 5 and figure 4. The optimum bond length of 2.9 a.u., hydrogen orbital exponent of 1.2 and angle out of plane of 17° for the SiH\textsubscript{3} give isotropic coupling constants of $a_{Si}=-170.8G$ and $a_{H}=-0.42G$. The agreement with experiment is still very good for the heavy atom coupling constant. The theoretical proton coupling constant does not permit the sign of the experimental value to be unequivocally assigned.

The Radical Cation PH\textsuperscript{+}.

The species formed when phosphonium sulphate is $\gamma$-irradiated at 77K has been assigned to the radical cation PH\textsubscript{3}\textsuperscript{+}.\textsuperscript{128} A phosphorus coupling constant of $a_{P}=517G$ was estimated but the proton hyperfine coupling constant was not detected, limiting its value to less than 10G. The angle out of the plane was
TABLE 5.

<table>
<thead>
<tr>
<th>bond length (a.u.)</th>
<th>hydrogen orbital exponent</th>
<th>bending angle $\theta$</th>
<th>total energy (a.u.)</th>
<th>coupling constants((G)) (^a_{\text{Si}}) (^a_{\text{H}})</th>
<th>(&lt;S^2&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9</td>
<td>1.1</td>
<td>19.5</td>
<td>-290.54541</td>
<td>-207.1</td>
<td>7.12</td>
</tr>
<tr>
<td>3.0</td>
<td>1.1</td>
<td>19.5</td>
<td>-290.54595</td>
<td>-215.5</td>
<td>9.22</td>
</tr>
<tr>
<td>3.1</td>
<td>1.1</td>
<td>19.5</td>
<td>-290.54146</td>
<td>-223.1</td>
<td>11.67</td>
</tr>
<tr>
<td>2.8</td>
<td>1.2</td>
<td>19.5</td>
<td>-290.54207</td>
<td>-184.0</td>
<td>1.54</td>
</tr>
<tr>
<td>2.9</td>
<td>1.2</td>
<td>19.5</td>
<td>-290.54688</td>
<td>-191.4</td>
<td>2.94</td>
</tr>
<tr>
<td>3.0</td>
<td>1.2</td>
<td>19.5</td>
<td>-290.54557</td>
<td>-198.3</td>
<td>4.27</td>
</tr>
<tr>
<td>2.8</td>
<td>1.3</td>
<td>19.5</td>
<td>-290.53512</td>
<td>-169.6</td>
<td>-3.73</td>
</tr>
<tr>
<td>2.9</td>
<td>1.3</td>
<td>19.5</td>
<td>-290.53865</td>
<td>-175.6</td>
<td>-2.26</td>
</tr>
<tr>
<td>3.0</td>
<td>1.3</td>
<td>19.5</td>
<td>-290.53555</td>
<td>-181.0</td>
<td>-1.25</td>
</tr>
<tr>
<td>2.9</td>
<td>1.2</td>
<td>19.0</td>
<td>-290.54702</td>
<td>-187.6</td>
<td>2.33</td>
</tr>
<tr>
<td>2.9</td>
<td>1.2</td>
<td>18.0</td>
<td>-290.54720</td>
<td>-179.4</td>
<td>0.86</td>
</tr>
<tr>
<td>2.9</td>
<td>1.2</td>
<td>17.0</td>
<td>-290.54724</td>
<td>-170.8</td>
<td>-0.42</td>
</tr>
<tr>
<td>2.9</td>
<td>1.2</td>
<td>16.0</td>
<td>-290.54718</td>
<td>-162.1</td>
<td>-2.01</td>
</tr>
</tbody>
</table>

*marks minimum

Theoretical Results for SiH₃
Summary of the calculations on the SiH₃ radical;
- variation of the total energy after annihilation with bond length for those values in α indicated.
- estimated minimum total energy after annihilation as a function of bond length.
estimated, from the e.s.r. data, to be 11°30'.

The theoretical results (Table 6 and figure 5) give hyperfine coupling constants $a_p=196.5\text{G}$, $a_H=-15.91\text{G}$ for a bond length of 2.8 a.u., hydrogen orbital exponent of 1.3 and angle from planarity of 8°. The phosphorus coupling constant is very low and the angle of bending is also unsatisfactory.

The method which has given good agreement with experiment for the radicals AlH$_3$ and SiH$_3$ would be expected to give an adequate result for the isoelectronic radical PH$_3^+$. That this is not the case, and the assignment of the e.s.r. species reported as PH$_3^+$ seems reasonable, suggests that effects not important for AlH$_3$ or SiH$_3$ are influential for PH$_3^+$. A similar situation was found for the isoelectronic series BH$_3$, CH$_3$, NH$_3^+$ (see Chapter 2), although the interpretation was obscured by the large vibronic contribution to the isotropic coupling constants. A qualitative argument based on the effects of the environment was suggested to explain the discrepancies found for the first row hydride series and a similar stance can be taken when considering the radical PH$_3^+$.

Begum, Lyons and Symons $^{128}$ have suggested that the result for PH$_3^+$ could be exaggerated by hydrogen bonding to the oxygens of the medium. If all the hydrogens of PH$_3^+$ were bonded in this way, loss of a hydrogen to give PH$_3^+$ would leave the radical constrained somewhat to a tetrahedral configuration. Constraint of the radical, in this manner, would result in an increase in the phosphorus hyperfine coupling
<table>
<thead>
<tr>
<th>bond length (a.u.)</th>
<th>hydrogen orbital exponent</th>
<th>bending angle $\Theta^\circ$</th>
<th>total energy (a.u.)</th>
<th>coupling constants ($G$)</th>
<th>$&lt;S^2&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7</td>
<td>1.2</td>
<td>14.0</td>
<td>-342.03723</td>
<td>330.7</td>
<td>-2.18</td>
</tr>
<tr>
<td>2.8</td>
<td>1.2</td>
<td>14.0</td>
<td>-342.04385</td>
<td>335.0</td>
<td>-1.63</td>
</tr>
<tr>
<td>2.9</td>
<td>1.2</td>
<td>14.0</td>
<td>-342.04258</td>
<td>337.3</td>
<td>-1.26</td>
</tr>
<tr>
<td>2.7</td>
<td>1.3</td>
<td>14.0</td>
<td>-342.04740</td>
<td>310.4</td>
<td>-4.93</td>
</tr>
<tr>
<td>2.8</td>
<td>1.3</td>
<td>14.0</td>
<td>-342.05096</td>
<td>312.6</td>
<td>-4.87</td>
</tr>
<tr>
<td>2.9</td>
<td>1.3</td>
<td>14.0</td>
<td>-342.04639</td>
<td>312.7</td>
<td>-4.94</td>
</tr>
<tr>
<td>2.7</td>
<td>1.4</td>
<td>14.0</td>
<td>-342.04918</td>
<td>286.1</td>
<td>-7.99</td>
</tr>
<tr>
<td>2.8</td>
<td>1.4</td>
<td>14.0</td>
<td>-342.05007</td>
<td>286.4</td>
<td>-8.04</td>
</tr>
<tr>
<td>2.9</td>
<td>1.4</td>
<td>14.0</td>
<td>-342.04258</td>
<td>287.1</td>
<td>-8.46</td>
</tr>
<tr>
<td>2.8</td>
<td>1.3</td>
<td>15.0</td>
<td>-342.05056</td>
<td>333.5</td>
<td>-3.01</td>
</tr>
<tr>
<td>2.8</td>
<td>1.3</td>
<td>13.0</td>
<td>-342.05127</td>
<td>291.8</td>
<td>-6.68</td>
</tr>
<tr>
<td>2.8</td>
<td>1.3</td>
<td>12.0</td>
<td>-342.05150</td>
<td>271.4</td>
<td>-8.55</td>
</tr>
<tr>
<td>2.8</td>
<td>1.3</td>
<td>11.0</td>
<td>-342.05166</td>
<td>251.5</td>
<td>-10.46</td>
</tr>
<tr>
<td>2.8</td>
<td>1.3</td>
<td>10.0</td>
<td>-342.05177</td>
<td>232.2</td>
<td>-12.31</td>
</tr>
<tr>
<td>2.8</td>
<td>1.3</td>
<td>9.0</td>
<td>-342.05183</td>
<td>213.8</td>
<td>-14.15</td>
</tr>
<tr>
<td>2.8</td>
<td>1.3</td>
<td>8.0</td>
<td>-342.05185</td>
<td>196.5</td>
<td>-15.91</td>
</tr>
<tr>
<td>2.8</td>
<td>1.3</td>
<td>7.0</td>
<td>-342.05184</td>
<td>180.4</td>
<td>-17.52</td>
</tr>
</tbody>
</table>

*marks minimum

Theoretical Results for PH$_3^+$
Summary of the calculations on the PH$_3^+$ radical.
(See also caption to figure 4).
constant, \( a_p \), through the increased deviation from planarity (see figure 7), and also the increase in the bond length, \( r(P-H) \), by hydrogen bonding. A further enhancement of \( a_p \) may be conjectured if it is considered that the bonding of the hydrogens to the medium results in a more diffuse hydrogen orbital. An increased diffuseness of the hydrogen orbital implies a decrease in the hydrogen atomic orbital exponent, leading to an increased value of \( a_p \) (see figure 6). The net result would be a considerable increase in the hyperfine coupling constant of the phosphorus. In fact, with only a slight change in the parameters much better agreement with experiment can be obtained, for example, with a bond length of 2.9 a.u., hydrogen orbital exponent of 1.2 and angle out of plane of 14° the coupling constants are \( a_p = 337.3 \text{G} \) and \( a_H = -1.26 \text{G} \).

Theoretical trends in the variation of the angle out of plane, for the isoelectronic radicals \( \text{AlH}_3^- \), \( \text{SiH}_3 \) and \( \text{PH}_3^+ \), follow the experimental trends and are in the order expected in terms of Pauling's electronegativity theory,\(^{79-81}\) that is, the radicals are predicted to flatten on going from aluminium to phosphorus. The trend in the hydrogen atomic orbital exponents is also in the order expected from the excess charge effect \(^{83} \) (1.0, 1.2, 1.3 for \( \text{AlH}_3^- \), \( \text{SiH}_3 \), \( \text{PH}_3^+ \) respectively). Generally the agreement with experiment is satisfactory, if environmental effects are assumed to be important for \( \text{PH}_3^+ \).
Variation of $a_P$ with $\alpha$ for $r(P-H)=2.8\text{ a.u.}$ and $\Theta=14^\circ$. 
Variation of $a_p$ with $\Theta$ for $r(P-H)=2\cdot8\text{a.u.}$ and $\alpha=1.5$. 
The Radicals AlH\text{Me}_2, SiH\text{Me}_2 and PH\text{Me}_3$^+$

Of the radicals XH\text{Me}_2 (X=Al, Si, P) only the silicon species has been observed, as the product of $\gamma$-irradiation of SiH\text{Me}_2$^{124-128}$. However, radicals AlR$_3$, SiR$_3$ and PR$_3$$^{125,128}$, where R is an alkyl group or hydrogen, have been reported experimentally and some of these are compiled in Table 7, with the calculated results for XH\text{Me}_2 and XH$_3$. The theoretical results are not compatible with experiment.

The experimental trends in the coupling constants of the heavy atoms generally show an increase on going from AlH$_3$ to AlR$_3$, no significant change between SiH$_3$ and SiR$_3$, and a decrease for PH$_3$ to PR$_3$. The trends suggest that alkylation has little effect upon the shape of silyl radicals but opposite effects on the AlR$_3$ and PR$_3$ radicals, the former being induced to bend further and the latter to flatten. The argument, using electronegativity differences, requires that the radicals should bend further on alkylation, and this can be used to account for the trend in the aluminium coupling constants but not for the trend in the phosphorus, which is in opposition to this view. The results for the silicon suggest that, to within the accuracy of the experiment, there is no significant increase in the bending.

This trend may be rationalised with the concept of hyperconjugation$^{128}$ but, as pointed out previously, hydrogen bonding of PH$_3$ to the environment, an effect which is not possible for PR$_3$ radicals, may considerably increase the hyperfine coupling constant of the
TABLE 7. Experimental hyperfine coupling constants for the radicals XR$_3$ (X=Al$^-$, Si, P$^+$; R=H or alkyl).

<table>
<thead>
<tr>
<th>Radical</th>
<th>Hyperfine coupling constant</th>
<th>angle out of plane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a_M$</td>
<td>$a_H(\alpha)$</td>
</tr>
<tr>
<td>AlH$_3^-$</td>
<td>233</td>
<td>3.13</td>
</tr>
<tr>
<td>AlMe$_3$</td>
<td>324</td>
<td>21.00</td>
</tr>
<tr>
<td>AlEt$_3^-$</td>
<td>325</td>
<td>21.42</td>
</tr>
<tr>
<td>Al(isoBu)$_3^-$</td>
<td>322</td>
<td>21.80</td>
</tr>
<tr>
<td>AlH(OCH$_2$CH$_2$OCH$_3$)$_3^-</td>
<td>179</td>
<td>18.05</td>
</tr>
<tr>
<td>AlH$_3^-$</td>
<td>213.8</td>
<td>3.48</td>
</tr>
<tr>
<td>AlH$_2$Me$^-</td>
<td>103.3</td>
<td>-10.88</td>
</tr>
<tr>
<td>SiH$_3$</td>
<td>190</td>
<td>7.84</td>
</tr>
<tr>
<td>SiH$_2$Me</td>
<td>181</td>
<td>11.8</td>
</tr>
<tr>
<td>SiHMes</td>
<td>183</td>
<td>17</td>
</tr>
<tr>
<td>SiMe$_3$</td>
<td>181</td>
<td>6.3</td>
</tr>
<tr>
<td>SiH$_3$</td>
<td>-170.8</td>
<td>-0.42</td>
</tr>
<tr>
<td>SiH$_2$Me</td>
<td>-114.7</td>
<td>-11.56</td>
</tr>
<tr>
<td>PH$_3^+$</td>
<td>517</td>
<td>14.50</td>
</tr>
<tr>
<td>PEt$_3^+$</td>
<td>384</td>
<td>12.43</td>
</tr>
<tr>
<td>P(n-Bu)$_3^+$</td>
<td>360</td>
<td>12.25</td>
</tr>
<tr>
<td>PH$_2$Me$^+$</td>
<td>195.5</td>
<td>-15.91</td>
</tr>
<tr>
<td>PH$_2$Me$^+$</td>
<td>192.2</td>
<td>-19.98</td>
</tr>
</tbody>
</table>

*marks calculated values
phosphorus. If the view is taken that the interaction with the environment is important for \( \text{PH}_3^+ \) then it may be conjectured that the trend is only apparent, as the unrestricted radical, \( \text{PH}_3^+ \), may have a smaller phosphorus coupling constant, and hence smaller angle of bending, than the alkyl derivatives. The calculated coupling constant of \( a_p = 192.2 \) for \( \text{PH}_2\text{Me}^+ \) is very similar to the value calculated for \( \text{PH}_3^+ \), although optimisation of the bond lengths and hydrogen orbital exponents may increase its magnitude. If it is assumed that the deviation from planarity is greater in the radical \( \text{PH}_2\text{Me}^+ \) than in \( \text{PH}_3^+ \), that is, if the electronegativity differences have a dominant effect, then the isotropic coupling constant of the phosphorus would be increased, to bring the theoretical result more into line with the experimental values.

The calculated hyperfine coupling constant of the silicon, \( a_{\text{Si}} = -114.7 \), may also be increased by optimisation of bond lengths and hydrogen orbital exponents. Combining this optimisation with any increase arising from further bending, which may occur, would be expected to give a value of \( a_{\text{Si}} \) closer to the experimental value. The experimental \( \beta \) proton coupling constant (8G)\(^{125}\) compares unfavourably with the calculated value (53.56G), however, the agreement may be improved when the conformation of the radical is optimised.

The calculated value of the hyperfine coupling constant of the aluminium in \( \text{AlH}_2\text{Me}^- \), \( a_{\text{Al}} = 103.5 \), is surprisingly low. Experimental values for \( \text{AlR}_3^- \) show
an increased coupling constant compared to AlH$_3^-$, implying an increased bending, in accord with the electronegativity theory. The position may be improved with optimisation, leading to an increased $a_{Al}^-$, but there is little reason to believe that a value comparable with AlH$_3^-$ could be attained.

An examination of the theoretical results reveals that the unpaired electron occupies similar orbitals in AlH$_2$Me$^-$ and AlH$_3^-$ but the orbital in the methyl derivative has less 3s character and more 3p character. The unpaired electron is delocalised over the methyl group, to some extent, in AlH$_2$Me$^-$. The reduction in 3s character and partial delocalisation on to the methyl group appears to account for the fall in the hyperfine coupling constant of the central atom. It may be that the radicals XH$_2$Me show an exaggerated delocalisation of the unpaired electron, which might be equated with hyperconjugation, resulting from the lack of d orbitals in the calculation.

Although the general trend for the AlR$_3^-$ radicals is to an increase in the aluminium coupling constant, the radical identified as AlH(OCH$_2$CH$_2$OCH$_3$)$_2^-$, produced by gamma irradiation of NaAlH$_2$(OCH$_2$CH$_2$OCH$_3$)$_2$, has a reduced value of $a_{Al}^-$=179G. If the assignment is correct the result would be compatible with that calculated for AlH$_2$Me$^-$. 

Conclusions.

The calculations on the radicals XH$_3$ and XH$_2$Me (X=Al$^-$, Si, P$^+$) indicate that the double basis method can give hyperfine coupling constants in good agreement
with experiment. The results reinforce the conclusions drawn from the calculations on BH\textsuperscript{3}, CH\textsubscript{3} and NH\textsubscript{3}\textsuperscript{+} (Chapter 2) that in order to obtain consistent agreement with experiment the hydrogen orbital exponent and the geometry must be optimised as far as it is possible. Also the problem of a strong interaction with the environment is possibly encountered again. The use of the double basis method makes optimisation feasible for AlH\textsubscript{3}, SiH\textsubscript{3} and PH\textsubscript{3}\textsuperscript{+} but not for AlH\textsubscript{2}Me\textsuperscript{−}, SiH\textsubscript{2}Me and PH\textsubscript{2}Me\textsuperscript{+}, this deficiency in the calculations on the latter series may account for the inconclusive nature of the results obtained.
Introduction.

In the preceding sections ab initio calculations of radicals systems have been discussed and the applicability of the full basis and double basis Unrestricted Hartree Fock method with single annihilation evaluated. The spin density distributions predicted have, generally, proven to be in good agreement with the experimental data, offering some confidence in the use of this formulation. A factor of considerable importance which emerges from the calculations of hyperfine coupling constants is the need for optimisation, of the geometry and hydrogen atomic orbital exponent, if a coherent analysis is envisaged. In many cases optimisation cannot be complete and any experience gained from other studies must be used.

The species which have been studied contain no more than two atoms, other than hydrogen atoms, since the number of integrals computed rises as the fourth power of the number of basis orbitals. The time consuming nature of ab initio calculations therefore prohibits the study of large molecular systems in most laboratories, although Clementi has demonstrated that such systems may be examined and reasonable results obtained. This barrier, imposed by computational considerations, precludes the extensive analysis of many radicals, such as aryl ions and transition metal complexes, using the non-empirical methods developed in this thesis. However an attempt to evaluate the applicability of
the ab initio UHF method in a test case was considered necessary and this Chapter is concerned with calculations on the pyrazine anion and the monoprotonated pyrazine radical, using the double basis approach. The closed shell pyrazine molecule is also presented for comparison with the results obtained by Clementi.\textsuperscript{132}

Method.

The ab initio Closed Shell and Unrestricted Hartree Fock methods were used in the l.c.a.o.-m.o. approximation, with spin annihilation in the UHF method. The minimal basis set of orbitals was represented by expansions of Gaussian functions in their completely contracted form; for the one electron and one centre integral calculation the 9s type and 5p type for carbon and nitrogen and the 10s type for hydrogen as given by Huzinaga\textsuperscript{21} and for the multicentre two electron integrals the 4s type and 3p type for the carbon and nitrogen and the 3s type for hydrogen, from the work of Stewart\textsuperscript{28}, were used. The coordinate system of pyrazine is given in Table 1. (The additional hydrogen in the monoprotonated pyrazine is H(5) in Table 1.) Hydrogen atomic orbital exponents of 1.2 and 1.4 were used for the calculations on the pyrazine molecule and 1.4 for the pyrazine anion and monoprotonated pyrazine, as suggested from the work on CH\textsubscript{3} (Chapter 2).

The function 
\[
\alpha E_{\text{UHF}} + (1 - \alpha) < S^2 >_{\text{UHF}}
\]
was minimised in the
Coordinate System used in the Calculations on the Pyrazine molecule, the Pyrazine anion and the Monoprotonated Pyrazine. (Distances are expressed in atomic units.)
case of the pyrazine anion in an attempt to remove spin contamination (see Section VI). The values of the scalar, $a$, used were $0.85$, $0.90$, $0.95$, $0.98$ and $1.00$ (the last being a normal unconstrained UHF minimisation). The results for the pyrazine anion and the monoprotonated pyrazine radical were calculated from the UHF wavefunction after annihilation of the contaminating quartet spin state and all quantities given are expressed in atomic units, except for the hyperfine coupling constants which are expressed in Gauss.

Results and Discussion.

The Pyrazine Molecule.

Bene and Jaffe\textsuperscript{133} have performed calculations on diazine molecules, using the CNDO method, in an attempt to study the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions which occur in the ultraviolet spectra of these compounds. Also an ab initio calculation on pyrazine, using a 180 Gaussian basis, has been reported by Clementi\textsuperscript{132}, giving as the first electronic transition the nonbonding to $\pi$ antibonding, $n \rightarrow \pi^*$, consistent with experiment.

The results of the calculations for a hydrogen orbital exponent 1.2 and 1.4 are summarised in Tables 2 and 3 and figure 1. The corresponding results for the Clementi calculation are also given for comparison. As the coordinate system for the calculations reported is slightly different from that used by Clementi the results are not directly comparable. The orbital energies computed (Table 2 and
### TABLE 2.

Total Energy and Orbital Energies (in a.u.'s) for the Pyrazine Molecule.

<table>
<thead>
<tr>
<th>type</th>
<th>Clementi $^{132}$</th>
<th>$\alpha=1.2$</th>
<th>$\alpha=1.4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1(\sigma)$</td>
<td>$-15.69544$</td>
<td>$-15.68278$</td>
<td>$-15.63389$</td>
</tr>
<tr>
<td></td>
<td>$-11.47642$</td>
<td>$-11.48648$</td>
<td>$-11.43777$</td>
</tr>
<tr>
<td></td>
<td>$-11.47541$</td>
<td>$-11.46762$</td>
<td>$-11.41879$</td>
</tr>
<tr>
<td></td>
<td>$-1.37619$</td>
<td>$-1.45422$</td>
<td>$-1.41834$</td>
</tr>
<tr>
<td>$B_2(\sigma)$</td>
<td>$-1.27295$</td>
<td>$-1.33609$</td>
<td>$-1.30466$</td>
</tr>
<tr>
<td></td>
<td>$-0.95711$</td>
<td>$-0.88175$</td>
<td>$-0.84282$</td>
</tr>
<tr>
<td></td>
<td>$-0.77967$</td>
<td>$-0.76214$</td>
<td>$-0.71687$</td>
</tr>
<tr>
<td></td>
<td>$-0.72282$</td>
<td>$-0.64203$</td>
<td>$-0.62133$</td>
</tr>
<tr>
<td></td>
<td>$-0.53275$</td>
<td>$-0.49157$</td>
<td>$-0.43807$</td>
</tr>
<tr>
<td></td>
<td>$-0.44125$</td>
<td>$-0.43424$</td>
<td>$-0.38488$</td>
</tr>
<tr>
<td></td>
<td>$-11.47649$</td>
<td>$-11.47025$</td>
<td>$-11.42109$</td>
</tr>
<tr>
<td></td>
<td>$-11.47540$</td>
<td>$-11.46149$</td>
<td>$-11.41265$</td>
</tr>
<tr>
<td></td>
<td>$-1.13257$</td>
<td>$-1.42624$</td>
<td>$-1.39338$</td>
</tr>
<tr>
<td>$B_1(\pi)$</td>
<td>$-0.93097$</td>
<td>$-0.89910$</td>
<td>$-0.85614$</td>
</tr>
<tr>
<td></td>
<td>$-0.75519$</td>
<td>$-0.77060$</td>
<td>$-0.75037$</td>
</tr>
<tr>
<td></td>
<td>$-0.68371$</td>
<td>$-0.69657$</td>
<td>$-0.66113$</td>
</tr>
<tr>
<td></td>
<td>$-0.61071$</td>
<td>$-0.63165$</td>
<td>$-0.59500$</td>
</tr>
<tr>
<td>$A_2(\pi)$</td>
<td>$-0.64940$</td>
<td>$-0.87123$</td>
<td>$-0.83834$</td>
</tr>
<tr>
<td></td>
<td>$-0.49355$</td>
<td>$-0.32672$</td>
<td>$-0.29194$</td>
</tr>
<tr>
<td>Total Energy</td>
<td>$-261.55432$</td>
<td>$-262.23830$</td>
<td>$-262.11569$</td>
</tr>
<tr>
<td>$-V/T$</td>
<td>2.0001</td>
<td>1.999</td>
<td></td>
</tr>
</tbody>
</table>
Orbital Energies in Pyrazine.

Figure 1.

Clementi*3

a = 1.2

Orbital energy (eV)

0

1.0

1.5

2.0

3.0

4.0

5.0

6.0

7.0

8.0

9.0

10.0

11

12

13

14

15

all represent doublet states
TABLE 3.

Electronic Configuration of Pyrazine.

<table>
<thead>
<tr>
<th>separate atoms</th>
<th>In the pyrazine molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clementi\textsuperscript{132}</td>
</tr>
<tr>
<td>C</td>
<td></td>
</tr>
<tr>
<td>1s</td>
<td>2</td>
</tr>
<tr>
<td>2s</td>
<td>2</td>
</tr>
<tr>
<td>2p_{\sigma_1}</td>
<td>1</td>
</tr>
<tr>
<td>2p_{\sigma_2}</td>
<td>1</td>
</tr>
<tr>
<td>2p_{\pi}</td>
<td>1</td>
</tr>
<tr>
<td>N</td>
<td></td>
</tr>
<tr>
<td>1s</td>
<td>2</td>
</tr>
<tr>
<td>2s</td>
<td>2</td>
</tr>
<tr>
<td>2p_{\sigma_1}</td>
<td>1</td>
</tr>
<tr>
<td>2p_{\sigma_2}</td>
<td>1</td>
</tr>
<tr>
<td>2p_{\pi}</td>
<td>1</td>
</tr>
<tr>
<td>H</td>
<td></td>
</tr>
<tr>
<td>1s</td>
<td>1</td>
</tr>
</tbody>
</table>
13k  

Figure 1) show that the highest occupied orbital is the \( \pi \) orbital of \( A_2 \) symmetry, in disagreement with experiment and Clementi, although a lower energy was obtained in these calculations. The gross population charges have not been evaluated but the electronic configuration of the separate atoms in pyrazine is given in Table 3.

The lack of agreement, between the results of Clementi and those using the double basis technique, is not wholly discouraging. The optimisation of the geometry and hydrogen orbital exponents could easily correct the situation since the difference in energy of the higher occupied orbitals is not very great.

The Pyrazine Anion.

On reduction of pyrazine with potassium metal Carrington and Santos-Veiga\(^{134}\) produced a species which they identified as the mononegative ion of pyrazine, with isotropic hyperfine coupling constants \( a_N = 7.22 \text{G}, a_H = 2.66 \text{G} \). The theoretical results are summarised in Table 4, with the \( \pi \) orbital of \( A_2 \) symmetry occupied by the unpaired electron. In fact during the minimisation of the energy it was noted that the anion was converging on to the wrong symmetry —that is the orbital the unpaired electron was occupying was not that found practically. This observation led to the conclusion that it would be necessary to intervene and force the correct symmetry if meaningful results were to be obtained, so that the summarised results are those for the forced, rather
TABLE 4.

Theoretical Results for the Pyrazine anion.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>EUHFAA</th>
<th>hyperfine coupling constants</th>
<th>$a_C$</th>
<th>$a_N$</th>
<th>$a_H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.85</td>
<td>-261.9857</td>
<td>-1.28</td>
<td>5.55</td>
<td>-1.97</td>
<td></td>
</tr>
<tr>
<td>-0.90</td>
<td>-261.9901</td>
<td>-2.20</td>
<td>7.05</td>
<td>-1.83</td>
<td></td>
</tr>
<tr>
<td>-0.95</td>
<td>-261.9955</td>
<td>-3.71</td>
<td>9.19</td>
<td>-1.43</td>
<td></td>
</tr>
<tr>
<td>-0.98</td>
<td>-261.9984</td>
<td>-5.36</td>
<td>11.11</td>
<td>-0.74</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>-261.9991</td>
<td>-6.46</td>
<td>12.48</td>
<td>-0.31</td>
<td></td>
</tr>
<tr>
<td>Expt.</td>
<td></td>
<td></td>
<td>7.2</td>
<td>±2.7</td>
<td></td>
</tr>
</tbody>
</table>

Unpaired electron in $\pi$ orbital ($A_2$)
FIGURE 2.
Variation of (i) $E_{\text{UHF}}$, (ii) $E_{\text{UHF AA}}$, (iii) $<S^2>$ and (iv) $<S^2>_{\text{UHF AA}}$ with $\alpha$. 
Variation of (i) $a_N$ and (ii) $a_H$ with $\alpha$. 
than the natural but incorrect, minimisation.

The unsatisfactory $S^2$ value (1.0458 before annihilation) suggests serious contamination of the doublet spin state, and for this reason the function

$$\alpha E_{\text{UHF}} + (1-\alpha) <S^2>_{\text{UHF}}$$

was minimised. The variation of the energy, $S^2$ value, nitrogen and proton hyperfine coupling constants with $\alpha$ are given in figures 2 and 3.

The theoretical coupling constants, $a_N = 12.48G$ and $a_H = -0.31G$, are in reasonable agreement with experiment. The removal of the contaminating spin states would produce a reduction in $a_N$ and an increase in $a_H$ (see figures 2 and 3) resulting in values closer to those found experimentally. Although the small value of the calculated proton coupling constant does not permit an unequivocal statement on the sign of the experimental coupling constant it might tentatively be concluded that the sign is negative.

The unfortunate difficulties during the minimisation of the energy naturally reduce the potency of any conclusions drawn. The reason for the wrong orbital occupancy is not clear, although such results are not unknown with the UHF method. The fault may also lie with the application of the double basis approach to large systems, where small errors in individual integrals accumulate due to the size of the problem.
The Monoprotonated Pyrazine Radical.

While the neutral monoprotonated pyrazine radical has not yet been reported the lithium salt of the pyrazine anion is well characterised by its e.s.r. spectrum. The experimental data indicates that the two nitrogens are not equivalent, suggesting that an ion pair is formed with the lithium cation in the molecular plane in the region of the nitrogen lone pair electrons. Extended Hückel and CNDO/2 calculations have failed to predict the non-equivalence of the nitrogens, locating the most probable position of the lithium cation as above the centre of the pyrazine ring.

By calculating the electron distribution of the monoprotonated system, with the extra proton 1.9 a.u. from one of the nitrogens, values of the isotropic coupling constants will be obtained which should resemble the coupling constants in the lithium-pyrazine ion pair. In this way some verification of the experimental assignment may be achieved.

The results of the ab initio calculations are given in figure 4, with the corresponding coupling constants calculated for the pyrazine anion. In Table 5 the electronic configurations of the atoms in the pyrazine molecule, the pyrazine anion and the monoprotonated pyrazine radical are collected, showing the considerable inequality in the charge distribution resulting from protonation. Experimentally, for lithium pyrazine, Atherton and Goggins deduced two proton values of 1.98G and 3.33G and two
a) Hyperfine coupling constants for the monoprotonated Pyrazine.

b) Hyperfine coupling constants for the Pyrazine anion.
<table>
<thead>
<tr>
<th>( t )</th>
<th>( H )</th>
<th>( H )</th>
<th>( H )</th>
<th>( H )</th>
<th>( H )</th>
</tr>
</thead>
<tbody>
<tr>
<td>96.2x10^{-6}</td>
<td>798.3</td>
<td>798.3</td>
<td>798.3</td>
<td>798.3</td>
<td>798.3</td>
</tr>
<tr>
<td>9.694</td>
<td>1.050</td>
<td>1.050</td>
<td>1.050</td>
<td>1.050</td>
<td>1.050</td>
</tr>
<tr>
<td>6.749</td>
<td>1.274</td>
<td>1.274</td>
<td>1.274</td>
<td>1.274</td>
<td>1.274</td>
</tr>
<tr>
<td>8.710</td>
<td>8.968</td>
<td>8.968</td>
<td>8.968</td>
<td>8.968</td>
<td>8.968</td>
</tr>
<tr>
<td>9.796</td>
<td>8.530</td>
<td>8.530</td>
<td>8.530</td>
<td>8.530</td>
<td>8.530</td>
</tr>
<tr>
<td>8.000</td>
<td>2.001</td>
<td>2.001</td>
<td>2.001</td>
<td>2.001</td>
<td>2.001</td>
</tr>
<tr>
<td>8.518</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
</tr>
<tr>
<td>1.047</td>
<td>8.328</td>
<td>8.328</td>
<td>8.328</td>
<td>8.328</td>
<td>8.328</td>
</tr>
<tr>
<td>1.026</td>
<td>1.020</td>
<td>1.020</td>
<td>1.020</td>
<td>1.020</td>
<td>1.020</td>
</tr>
<tr>
<td>6.695</td>
<td>1.126</td>
<td>1.126</td>
<td>1.126</td>
<td>1.126</td>
<td>1.126</td>
</tr>
<tr>
<td>2.002</td>
<td>2.003</td>
<td>2.003</td>
<td>2.003</td>
<td>2.003</td>
<td>2.003</td>
</tr>
</tbody>
</table>

*For all systems.*
nitrogen values of 5.36G and 8.68G. A comparison of the theoretical and experimental hyperfine coupling constants is not very fruitful and no definite conclusions can be drawn.

The orbital occupied by the unpaired electron in the monoprotonated species is different from that occupied by the unpaired electron in the pyrazine anion since in the latter case a specific orbital was forcibly occupied. (Cf pyrazine anion; for the protonated species the unpaired electron occupies a π orbital with a node through the nitrogens.) Since the monoprotonated species has not been observed there is no rationale for forcing the unpaired electron into a different orbital, although, intuitively, it would be felt that the orbital scheme of the two species should be very similar.

Conclusions.

By using the double basis method calculations on benzene type systems just enter the area of feasibility of computation but no optimisation is possible. This lack of optimisation of geometry and hydrogen orbital exponents, forced by the size of the problems considered, may account for the discrepancies in the theoretical results. A further source of error, for large molecular systems, may result from the use of the double basis method. Although the absolute error in the individual multicentre integrals, incurred by use of small Gaussian expansions, may be small the percentage error for the molecule may
be large. This accumulation of errors may account for the unsatisfactory observation made for the anion, where the unpaired electron was occupying the wrong orbital (the lack of consideration of environmental effects may also play a part in this anomaly). However the results given for the pyrazine anion do permit some optimism on the value of the double basis ab initio UHF method for the prediction of isotropic hyperfine coupling constants in large molecular systems. Moreover, for the smaller systems of Chapter 4 the double basis method represents a very useful tool for spin density calculations as it permits a comprehensive study by reducing the computational times to a reasonable level while still retaining the accuracy expected in full ab initio calculations.
REFERENCES


12 See, for example, the comments following reference 10.


29 B. Roos, C. Salez, A. Veillard and E. Clementi, 
"A General Program for Calculation of Atomic 
SCF Orbitals by the Expansion Method" 
Special IBM Technical Report, IBM Research 
Laboratory, San Jose, California, 1968.
30 B. Ford, G.G. Hall and J.C. Packer, Int. J. 
31 E. Clementi, J. Mehl and W. von Niessen, 
32 I.H. Hillier and V.R. Saunders, Int. J. Quantum 
13, 553, (1967).
34 D.B. Cook and P. Palmieri, Mol. Phys., 17, 271, 
36 S.Y. Chang, E.R. Davidson and G. Vincow, 
(1954).
496, (1956).
42 R.Fletcher and C.M.Reeves, Computer J., 7, 149, (1964).


47 E.Fermi and E.Segre, Z. Physik, 82, 729, (1933)
A discussion of relativistic additions to the Schrodinger Hamiltonian is given in reference 1.


87 M. Yamazaki, M. Sakamoto, K. Hijikata and C. C. Lin,


89 M. B. D. Bloom, R. S. Eachus and M. C. R. Symons,

90 T. A. Claxton and D. McWilliams, Trans. Farad.

91 D. W. Wylie, A. J. Shuskus, C. G. Young and

92 R. B. Horst, J. H. Anderson and D. F. Mulligan,


97 J. R. Brailsford, J. R. Morton and L. E. Vanetti,

98 R. Beringer and J. R. Castle, Phys. Rev., 78,


100 H. Ohigashi and Y. Kurita, J. Phys. Soc. Japan,
24, 654, (1968).

101 J. J. Gallagher, W. C. King and G. M. Johnson,
113 M.C.R.Symons, private communication.
119  A. Weinmann, unpublished.
129  A.R. Lyons, private communication.
This thesis is concerned with the calculation of spin density distributions in molecular species with an unpaired electron. The ab initio Unrestricted Hartree Fock method with single spin annihilation is used for this purpose and the construction of the wavefunction and methods by which the energy may be minimised and the hyperfine coupling constants evaluated are discussed. The atomic basis sets used are represented by combinations of Gaussian type orbitals; sufficiently large expansions are used to ensure that the wavefunction is of the accuracy required. A mixed basis approach, where smaller Gaussian expansions are used for the two electron multicentre integrals than for the other integrals, is also put forward as a reasonable approximation which results in a considerable reduction in computational times.

The merits of the Roothaan, steepest descents and conjugate gradient methods, in minimising the energy, are analysed for the CN radical, leading to the conclusion that a combination of the Roothaan and conjugate gradient methods should be employed.

In Chapter 2 the UHF method is used to calculate the isotropic hyperfine coupling constants of NH$_3^+$, CH$_3$, BH$_3$ and the importance of optimisation and the out-of-plane zero point energy vibration is emphasised.

The third chapter deals with the calculation of anisotropic coupling constants, demonstrating the value of the anisotropic coupling constants, and their directions, in supporting experimental assignments.
A mixed basis approach is then applied to AlH$_3^-$, SiH$_3$, PH$_3^+$ and associated radicals, using small expansions fitted by a least squares technique. The retention of accuracy in the calculated coupling constants combined with the considerable time saving suggests that the technique may prove very useful.

The final chapter is concerned with large scale calculations on pyrazine systems using the mixed basis method.