AB INITIO CALCULATIONS OF HYPERFINE COUPLING CONSTANTS.

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STATEMENT.

The work described in this thesis, unless otherwise
acknowledged in the text, has been carried out by the
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The work has not been presented, and is not being
concurrently presented, for any other degree.

Signed

Nigel A. Smith.

November, 1971

CONTENTS

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 α and β
electrons to occupy different spatial orbitals
correlation is implicitly incorporated into the
wavefunction.

For an N electron system of p α electrons and q
β electrons (p>q) the UHF wavefunction Ψ_{UHF} takes the
single determinantal form,

$$\Psi_{UHF}=(N!)^{-\frac{1}{2}}\det\|\psi_1(1)\alpha(1)\ldots\psi_p(p)\alpha(p)\varphi_1(p+1)\beta(p+1)\ldots$$
$$\ldots\varphi_q(N)\beta(N)\| \qquad \ldots\ldots\ldots(1)$$

Without loss of generality the one electron

functions of the α electrons ψ_i and of the β electrons φ_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[1,2]. These have the property,

$$\int \psi_i^* \varphi_j \, d\tau = T_i \delta_{ij}; \qquad 0 \leqslant T_i \leqslant 1 \quad \dots\dots\dots(2)$$

In the linear combinations of atomic orbitals (l.c.a.o.) approximation the functions ψ_i and φ_i, written as column vectors ψ and φ ($\psi^+ = [\psi_i : i=1 \rightarrow p]$; $\varphi^+ = [\varphi_i : i=1 \rightarrow q]$), are chosen in the form,

$$\psi = A^+ \omega \qquad\qquad \dots\dots\dots\dots(3)$$
$$\varphi = B^+ \omega$$

where ω is the column vector, with elements $\omega_i : i=1 \rightarrow m$, of the atomic orbital basis functions; A is an m×p and B an m×q matrix of coefficients which must be determined to define ψ and φ and hence Ψ_{UHF}.

Defining the unrestricted bond order matrices P and Q, for the α and β electrons respectively, as

$$P = AA^+ \qquad\qquad \dots\dots\dots\dots(4)$$
$$Q = BB^+$$

and the overlap matrix S as

$$S_{ij} = \int \omega_i^* \omega_j \, d\tau \qquad \dots\dots\dots\dots(4a)$$

The matrices PS and QS are idempotent with traces corresponding to the number of α and β electrons respectively,

$$(PS)^2 = PS; \qquad (QS)^2 = QS \qquad \dots\dots\dots(5)$$
$$\text{Tr}(PS) = p; \qquad \text{Tr}(QS) = q$$

The UHF energy E_{UHF} may now be written as,

$$E_{UHF}=Tr(PF^{\alpha})+Tr(QF^{\beta})-\tfrac{1}{2}Tr(PG^{\alpha})-\tfrac{1}{2}Tr(QG^{\beta}) \quad\ldots\ldots\ldots(6)$$

where

$$F^{\alpha}=h+G^{\alpha}$$
$$F^{\beta}=h+G^{\beta} \quad\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

h is the one electron matrix with elements,

$$h_{ij}=\int \omega_i^{*}(-\tfrac{1}{2}\nabla^2-\sum_{\alpha}Z_{\alpha}/r_{\alpha})\omega_j d\tau \quad\ldots\ldots\ldots\ldots\ldots(8)$$

and G^{α} and G^{β} are the two electron matrices defined by,

$$G_{ij}^{\alpha}=\sum_{k,l}^{m}[(P_{kl}+Q_{kl})<ik|jl>-P_{kl}<ik|lj>]$$
$$G_{ij}^{\beta}=\sum_{k,l}^{m}[(P_{kl}+Q_{kl})<ik|jl>-Q_{kl}<ik|lj>] \quad\ldots\ldots(9)$$

$$<ij|kl>=\int \omega_i^{*}(1)\omega_j^{*}(2)[1/r_{12}]\omega_k(1)\omega_l(2)d\tau_1 d\tau_2 \quad\ldots\ldots(10)$$

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,

$$\underline{q}(r)=\sum_i^{N}\delta(r-r_i)$$

and the spin density operator,

$$\underline{\rho}(r)=\sum_i^{N}2S_{zi}\delta(r-r_i)$$

over the atomic basis functions ω_i are given by,[3]

$$q(r)=\sum_{u,v}^{m}(P_{uv}+Q_{uv})\omega_u^{*}(r)\omega_v(r) \quad\ldots\ldots\ldots\ldots(11)$$

$$\rho(r)=\sum_{u,v}^{m}(P_{uv}-Q_{uv})\omega_u^{*}(r)\omega_v(r)$$

II. The Use of Annihilation and Projection Operators

Fundamental theoretical objections may be raised against the UHF method on the grounds that, although the wavefunction is an eigenfunction of the $\underset{\sim}{S}_z$ operator it is not, in general, an eigenfunction of the $\underset{\sim}{S}^2$ 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,

$$\psi_{UHF}= \sum_{k=0}^{q} c_{s+k}\Phi_{s+k}$$

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

$$\underset{\sim}{S}^2 \Phi_{s+k}=(s+k)(s+k+1)\Phi_{s+k}$$

The projection operator,

$$A_k=\underset{\sim}{S}^2-k(k+1) \qquad \dots\dots\dots\dots\dots\dots(12)$$

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

$$\underset{\sim}{O}_s=\prod_{k=s+1} [(\underset{\sim}{S}^2-k(k+1))/(s(s+1)-k(k+1))]$$

$$\dots\dots\dots\dots\dots(13)$$

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 $\underset{\sim}{O}_s\psi_{UHF}$. This is an extremely difficult procedure, but Harriman et al[6-10] have developed a successful approach.

The difficulties inherent in the practical application of $\underset{\sim}{O}_S$ led Amos and Hall[2] to suggest the use of the single annihilator A_{s+1} rather than $\underset{\sim}{O}_S$. The justification for this approximation results from the demonstration that the major unwanted component in Ψ_{UHF} is that with spin (s+1), the states of higher multiplicity decreasing rapidly in importance[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,

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

where the second result, equation (15), is given as $\underset{\sim}{S}^2$ 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[11],

$$E_{UHFAA} = E_{UHF} - x^{-1} [Tr((PSQSP+QSPSQ-PSQ-QSP)h)$$

$$+ \sum_{stuv} (PSQSP+QSPSQ-PSQ-QSP)_{st} (P+Q)_{uv} <su \mid tv>$$

$$- \sum_{stuv} ((PSQSP)_{st} P_{uv} + (QSPSQ)_{st} Q_{uv}$$

$$- (PSQ+QSP)_{st} (P+Q)_{uv} + P_{st} Q_{uv}$$

$$+ (PSQ)_{st} (QSP)_{uv}) <su \mid vt>] \quad \ldots\ldots\ldots\ldots (17)$$

where,

$$x = \tfrac{1}{4}(p-q)^2 + \tfrac{1}{2}(p+q) - (s+1)(s+2) - Tr(PSQS)$$

and E_{UHF} is the UHF energy.

The charge and spin density functions are given by,[3]

$$q(r) = \sum_{u,v}^{m} (J_{uv}+K_{uv}) \omega_u^*(r) \omega_v(r)$$

$$\ldots\ldots\ldots\ldots\ldots (18)$$

$$\rho(r) = \sum_{u,v}^{m} (J_{uv}-K_{uv}) \omega_u^*(r) \omega_v(r)$$

where

$$M\underset{\sim}{J} = [A^2 + pq - q + (3-2A-N+2Tr(PSQS))Tr(PSQS)$$

$$-2Tr(PSQSPSQS)]P + [p-Tr(PSQS)]Q$$

$$+QSPSQ + [N-3+2A-4Tr(PSQS)]PSQSP$$

$$+[1-p-A+2T(PSQS)][PSQ+QSP]$$

$$-2[PSQSPSQ+QSPSQSP]+4PSQSPSQSP$$

and

$$A = q-2(s+1)$$

$$M = A^2 + pq + [2-2A-N+2Tr(PSQS)]Tr(PSQS)$$

$$-2Tr(PSQSPSQS)$$

$\underset{\sim}{K}$ is given by a similar expression to that for $\underset{\sim}{J}$ with the P and p interchanged with the Q and q. As the $\underset{\sim}{S}^2$ and the $\rho(r)$ operators do not commute the expectation value is from

$$\rho(r) = \frac{<A_{s+1} \Psi_{UHF} \mid \rho(r) \mid A_{s+1} \Psi_{UHF}>}{<A_{s+1} \Psi_{UHF} \mid A_{s+1} \Psi_{UHF}>}$$

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[12], 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. <u>Application of Gaussians to Molecular Calculations</u>

In practical applications of the Unrestricted
Hartree Fock method on a radical with m basis
functions, ω_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,

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

Infact 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[13] have suggested the use
of the Gaussian Expansion method,

$$e^{-Sr} = \frac{S}{2\pi^{1/2}} \int_0^\infty \alpha^{-3/2} e^{-S^2/4\alpha} e^{-\alpha r^2} d\alpha$$

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[14]. 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[15,16], 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 χ_j is a Gaussian of
the form

$$\chi_j = N_n r^{n-1} \exp(-\alpha_j r^2) Y_{lm}(\theta, \varphi)$$

Y_{lm} are normalised spherical harmonics and N_n the normalisation factor,

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

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 φ_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[31]. 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 SO_4^{2-}, using a reasonable basis,[32] 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[33,34].

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

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

where as n increases the truncation error $\delta\omega_i$ decreases. It has been

demonstrated by Cook and Palmieri[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

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

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[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[28].

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[35,36]. 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

$$\varphi_i(\zeta_i) = \sum_j c_j S_j(\alpha_j') \; ; \qquad \alpha_j' = \zeta_i \alpha_j$$

where ζ_i 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 approachs 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,

$$F^{\alpha}A = SA\epsilon^{\alpha}$$
$$F^{\beta}B = SB\epsilon^{\beta} \qquad \dots\dots\dots\dots\dots(20)$$

which the orbitals must satisfy. The Fock matrices F^{α} and F^{β} for the α and β 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 ϵ^{α} and ϵ^{β} matrices are diagonal. The energy is then given by,[37,38]

$$E_{UHF} = \sum_{i}^{p} \epsilon^{\alpha}_{ii} + \sum_{i}^{q} \epsilon^{\beta}_{ii} - \tfrac{1}{2}Tr(PG^{\alpha}) - \tfrac{1}{2}Tr(QG^{\beta}) \quad \dots(21)$$

As the Fock matrices are functions of the matrices A and B the manner of solution must be by successive approximation. Thus F^α and F^β 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[39,40] for closed shell systems and later extended to the UHF method[41].

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 $|x\rangle$ using Dirac notation, if there is a first approximation $|x_0\rangle$ to $|x\rangle$ and the gradient of $f(x_0)$, $|g_0\rangle$ $(=|g(x_0)\rangle)$, can be found, then a better approximation, $|x_1\rangle$, to $|x\rangle$ is given by

$$|x_1\rangle = |x_0\rangle - \lambda_0|g_0\rangle$$

or generally,

$$|x_{i+1}\rangle = |x_i\rangle - \lambda_i|g_i\rangle \qquad \ldots\ldots(22)$$

Thus an iterative cycle is formed. The positive scalar λ_i is chosen at each iteration so that $|x_{i+1}\rangle$ is approximately the minimum in the direction $|g_i\rangle$ from $|x_i\rangle$.

As the first order density matrix and consequently the density matrices of all other orders may be expressed in terms of P and 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[41] for the changes

$$P \rightarrow P + \delta P$$
$$Q \rightarrow Q + \delta Q$$

............(23)

subject to the conditions

$$(PS)^2 = PS; \qquad (QS)^2 = QS$$
$$Tr(PS) = p; \qquad Tr(QS) = q$$

............(24)

Defining the matrices,

$$P' = S^{-1} - P$$
$$s = P'F^{\alpha}P$$
$$I = s + s^{+}$$
$$J = s - s^{+}$$

and similar expression for Q', t, K and L respectively, by replacing P by Q and F^{α} by F^{β}. Then the directions of descent are, to second order,

$$\delta P = -\lambda^{\alpha}(1 + \lambda^{\alpha^2} ISI)^{-1}(I + \lambda^{\alpha} ISJ)$$
$$\delta Q = -\lambda^{\beta}(1 + \lambda^{\beta^2} KSK)^{-1}(I + \lambda^{\beta} KSL)$$

.......(25)

The inverse in equation (25) may be neglected to first order in λ^{α} and λ^{β} to give the more approximate result,

$$\delta P = -\lambda^{\alpha}(I + \lambda^{\alpha} ISJ)$$
$$\delta Q = -\lambda^{\beta}(I + \lambda^{\beta} KSL)$$

..........(26)

The step lengths λ^{α} and λ^{β} are given by the expressions,

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

$$a = Tr(ISJF^{\alpha})$$
$$b = Tr(IF^{\alpha})$$
$$c = \sum_{ijkl} I_{ij} I_{kl} [<ik|jl> - <ik|lj>]$$

with similar expressions

for a', b' and c' by replacing I, J and F^{α} by K, L and F^{β} respectively.

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

Generally the modified bond order matrices obtained are neither idempotent nor have the correct traces necessitated by the conditions (24). 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[44] for closed shell systems and extended by Sutcliffe[45] 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 mxp matrix A must satisfy the orthonormality condition

$$A^+SA=I$$

where I is the identity matrix

To unconstrain the minimisation problem an m×p matrix Y^α is defined such that

$$A = Y^\alpha U^\alpha \qquad \ldots\ldots\ldots\ldots\ldots\ldots(27)$$

where U^α is constructed in a manner to ensure that A satisfies the condition of orthonormality

By defining Y^β and U^β in a similar fashion for B, then the P and Q matrices may be calculated and hence the energy. A and B may be obtained by any orthonormalisation procedure to give the same energy, so that the energy, in Y^α and Y^β, 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 Y^α and Y^β obtained is irrelevant and the problem of constraints may be ignored.

Following the work of Fletcher[44] for the closed shell problem the matrices U^α and U^β are defined as

$$U^\alpha = (Y^{\alpha^+} S Y^\alpha)^{-\frac{1}{2}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(28)$$
$$U^\beta = (Y^{\beta^+} S Y^\beta)^{-\frac{1}{2}}$$

The bond order matrices may be written as

$$P = Y^\alpha M^\alpha Y^{\alpha^+} \qquad \ldots\ldots\ldots\ldots\ldots(29)$$
$$Q = Y^\beta M^\beta Y^{\beta^+}$$

with

$$M^\alpha = U^\alpha U^{\alpha^+} = (Y^{\alpha^+} S Y^\alpha)^{-1} \qquad \ldots\ldots\ldots\ldots\ldots(30)$$

and similarly for M^β.

If a change in Y^α to $Y^\alpha + \delta Y^\alpha$ is made then M^α is changed by δM^α. Neglecting terms higher than first order in δY^α

$$M^\alpha + \delta M^\alpha = (Y^{\alpha^+} S Y^\alpha + \delta Y^{\alpha^+} S Y^\alpha + Y^{\alpha^+} S \delta Y^\alpha)^{-1}$$

$$= (I + M^\alpha \epsilon^\alpha)^{-1} M^\alpha$$

$$= (I - M^\alpha \epsilon^\alpha) M^\alpha \qquad . \qquad \dots \dots \dots (31)$$

$$\epsilon^\alpha = \delta Y^{\alpha^+} S Y^\alpha + Y^{\alpha^+} S \delta Y^\alpha .$$

Thus from (31),

$$\delta M^\alpha = -M^\alpha \epsilon^\alpha M^\alpha$$

The change δP in P can be obtained as

$$\delta P = Y^\alpha M^\alpha \delta Y^{\alpha^+} + \delta Y^\alpha M^\alpha Y^{\alpha^+} + Y^\alpha \delta M^\alpha Y^{\alpha^+}$$

$$= Y^\alpha M^\alpha \delta Y^{\alpha^+} (I - SP) + (I - SP)^+ \delta Y^\alpha M^\alpha Y^{\alpha^+} \qquad .. .(32)$$

and similar expressions may be derived for δM^β and δQ.

The change in the energy is then,

$$\delta E = \mathrm{Tr}(F^\alpha \delta P) + \mathrm{Tr}(F^\beta \delta Q),$$

$$= 2\mathrm{Tr}(F^\alpha Y^\alpha M^\alpha \delta Y^{\alpha^+}(I-SP)) + 2\mathrm{Tr}(F^\beta Y^\beta M^\beta \delta Y^{\beta^+}(I-SQ))$$

$$= 2[(I-SP)F^\alpha Y^\alpha M^\alpha] : \delta Y^\alpha + 2[(I-SQ)F^\beta Y^\beta M^\beta] : \delta Y^\beta .. (33)$$

where the colon : represents summation over two suffices. By virtue of the relation-ship between the gradient ∇E^α (or ∇E^β) and the increments in Y^α (or Y^β) from equation (33),

$$\nabla E^\alpha = 2(I-SP)F^\alpha Y^\alpha M^\alpha$$

$$\dots \dots \dots \dots (34)$$

$$\nabla E^\beta = 2(I-SQ)F^\beta Y^\beta M^\beta$$

and the complete gradient of the energy is given by the $m \times (p+q)$ 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 ∇E the method of conjugate gradients

proposed by Fletcher and Reeves[42] may be used. The Fletcher and Powell method[43] 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,

$$f = f_0 + \langle a | x \rangle + \tfrac{1}{2} \langle x | G | x \rangle \qquad \ldots \ldots \ldots (35)$$

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 $|g_i\rangle$ is

$$|g_i\rangle = |a\rangle + G | x_i \rangle \qquad \ldots \ldots \ldots (36)$$

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

$$\langle g_{i+1} | p_i \rangle = 0 \qquad \ldots \ldots \ldots (37)$$

$$|x_{i+1}\rangle = |x_i\rangle + \lambda_i | p_i \rangle \qquad \ldots \ldots \ldots (38)$$

where λ_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

$$|x_n\rangle = |x_{j+1}\rangle + \sum_{i=j+1}^{n-1} \lambda_i | p_i \rangle \; ; \quad 0 \leqslant j \leqslant n-1$$

and hence

$$|g_n\rangle = |g_{j+1}\rangle + \sum_{i=j+1}^{n-1} \lambda_i G | p_i \rangle \qquad \ldots \ldots \ldots (39)$$

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

$$\langle g_n | p_j \rangle = \sum_{i=j+1}^{n-1} \lambda_i \langle p_i | G | p_j \rangle \qquad \ldots \ldots \ldots (40)$$

From (40) if

$$\langle p_i | G | p_j \rangle = 0 \; ; \quad i \neq j \qquad \ldots \ldots (41)$$

then

$$<g_n| p_j>=0$$

and since $|p_0>,|p_1>\ldots|p_{n-1}>$ form

a basis

$$|g_n>=0$$

so that

$$|x_n>=|x>$$

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[43] procedure $|p_i>$ is defined as

$$|p_i>=-H_i|g_i> \qquad \ldots\ldots\ldots\ldots(42)$$

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 $|p_{i+1}>$ is a linear combination of $|g_{i+1}>$ and $|p_0>,|p_1>,\ldots\ldots|p_i>$ which satisfy the orthonormality condition (41)

The equations are found to reduce to

$$|p_{i+1}>=-|g_{i+1}>+\beta_i|p_i> \qquad \ldots\ldots\ldots(43)$$

where the scalar β_i is

$$\beta_i = \langle g_{i+1} | g_{i+1} \rangle / \langle g_i | g_i \rangle$$

$(|p_0\rangle$ is defined as $-|g_0\rangle$ so that initially a steepest descent is taken).

In summary $|x_{i+1}\rangle$ is given by equation (38); $|g_{i+1}\rangle$ and hence $|p_{i+1}\rangle$ are calculated and the cycle repeated. λ_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 Ψ_{UHF}

The energy after annihilation

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

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

as $\underset{\sim}{S}^2$ 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

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

As the annihilation is achieved after functional minimisation, and infact 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 $i \geqslant 2$ in the equation

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

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[46]

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

where α is a scalar in the range $0 \leqslant \alpha \leqslant 1$, rather than minimising E_{UHF}.

Experience has shown that cases do arise when the expectation value of $\underset{\sim}{S}^2$, even after annihilation, is unusually high. These cases are due to severe contamination from spin states of multiplicity $(2(s+i)+1)$, for $i \geqslant 2$, and for this reason the function (47) has been used. The improvement obtained in the expectation value of $\underset{\sim}{S}^2$, however, is achieved at the expense of a higher energy.

VII. The Calculation of Hyperfine Coupling Constants

In the electron spin resonance technique the spin Hamiltonian[47] considered is generally that involving coupling of the electrons and the nuclei and may be expressed as

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

where i and N refer to the electrons and nuclei respectively and S_i is the spin of the ith electron and I_N the spin of the Nth nucleus. g_e and g_N are the electronic and nuclear g values, β_e and β_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

$$T_N = \frac{8\pi}{3} \delta(r_N) I + T_N' \qquad \ldots \ldots \ldots (49)$$

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,

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

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

$$\mathcal{H}_2 = g_e \beta_e \sum_i \sum_N g_N \beta_N S_i \cdot T_N' \cdot I_N \qquad \ldots (51)$$

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

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

$$= \frac{8}{3}\pi g_e \beta_e \gamma_N \hbar \rho(r_N) \qquad \ldots\ldots\ldots(52)$$

where γ_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

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

$\mathcal{H}_2$, 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_N' may be written

$$T_N'(kl) = (r_N^2 \delta_{kl} - 3kl)/r_N^5$$

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

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

$$[a_{kl}(N)]_{rs} = \int \omega_r^* T_N'(kl) \omega_s d\tau$$

where ω_r are the basis functions. Then the anisotropic coupling constant,

$B_{kl}(N)$, for nucleus N, is

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

$$k,l=x,y,z$$

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.[48,49]

Silverstone and Todd[50] 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[51]

have reported an expression for the integral over s type Gaussian functions by using the Gaussian transform method

$$\frac{3q^2-r^2}{r^5} = \frac{\partial^2}{\partial q^2}(1/r)+\frac{4}{3}\pi\delta(r); \qquad q=x,y,z$$

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

$$<a_{pq}(C)>=<g_A|a_{pq}(C)|g_B> \qquad \ldots\ldots\ldots\ldots(54)$$

are required where g_A is a Gaussian centred at A (with coordinates A_x, A_y, A_z)

$$g_A=N_A x_A^{l_A} y_A^{m_A} z_A^{n_A} e^{-\alpha_A r_A^2} =(A,\alpha_A,l_A,m_A,n_A)$$

$$x_A=x-A_x$$

$$r_A^2=x_A^2+y_A^2+z_A^2$$

N_A is the normalisation constant; l_A,m_A,n_A are non-negative integers. Similarly

$$g_B=(B,\alpha_B,l_B,m_B,n_B)$$

for a Gaussian centred on B (with coordinates B_x,B_y,B_z) and

$$a_{pq}(C)=\frac{3pq-r_C^2\delta_{pq}}{r_C^5}$$

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,[52]

$$\frac{1}{r^5}=8(3\pi^{1/2})^{-1}\int_0^{\infty} u^4 e^{-r^2u^2}du=8(3\pi^{1/2})^{-1}\int_0^1 \frac{v^4}{(1-v^2)^2}\frac{e^{-r^2v^2/(1-v^2)}}{(1-v^2)^{3/2}}dv$$

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

$$<a_{pq}(C)> = \triangle[3W_{pq}-W\delta_{pq}] \qquad \ldots\ldots\ldots(55)$$

where $p,q=x,y,z$ and

$$W=W_{xx}+W_{yy}+W_{zz}$$

$$\triangle=\frac{8\pi}{3}(\alpha_A+\alpha_B)\exp(-\overline{AB}^2\alpha_A\alpha_B/(\alpha_A+\alpha_B))N_A N_B$$

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

The W's in (55) are defined as

$$W_{xx}=2V_{100}^{000}-4\overline{CP}_x V_{100}^{100}+\overline{CP}_x^2 V_{000}^{000}$$

$$W_{yy}=2V_{010}^{000}-4\overline{CP}_y V_{010}^{010}+\overline{CP}_y^2 V_{000}^{000}$$

$$W_{zz}=2V_{001}^{000}-4\overline{CP}_z V_{001}^{001}+\overline{CP}_z^2 V_{000}^{000}$$

$$W_{xy}=4V_{110}^{110}-2\overline{CP}_x V_{010}^{010}-2\overline{CP}_y V_{100}^{100}+\overline{CP}_x\overline{CP}_y V_{000}^{000}$$

$$W_{xz}=4V_{101}^{101}-2\overline{CP}_x V_{001}^{001}-2\overline{CP}_z V_{100}^{100}+\overline{CP}_x\overline{CP}_z V_{000}^{000}$$

$$W_{yz}=4V_{011}^{011}-2\overline{CP}_y V_{001}^{001}-2\overline{CP}_z V_{010}^{010}+\overline{CP}_y\overline{CP}_z V_{000}^{000}$$

$$\left.\begin{array}{c}\end{array}\right\}..(56)$$

where, for example,

$$\overline{CP}_x=C_x-P_x$$

$$P_x=\frac{\alpha_A A_x+\alpha_B B_x}{\alpha_A+\alpha_B}$$

In equation (56) the V's are defined by the general expression

$$V_{t_1 t_2 t_3}^{s_1 s_2 s_3} = \sum_{i_1 r_1} R_{i_1 r_1}^{s_1 t_1} (1_A, 1_B, A_x, B_x, C_x, \gamma)$$

$$\times \sum_{i_2 r_2} R_{i_2 r_2}^{s_2 t_2} (m_A, m_B, A_y, B_y, C_y, \gamma)$$

$$\times \sum_{i_3 r_3} R_{i_3 r_3}^{s_3 t_3} (n_A, n_B, A_z, B_z, C_z, \gamma)$$

$$\times \sum_{u=0}^{r-t+s} \binom{r-t+s}{u} (-1)^u F_\nu (\gamma \cdot \overline{CP}^2) \qquad \dots (57)$$

where

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

$$t = t_1 + t_2 + t_3 \quad , \quad \nu = i - 2r + u + 2 - s$$

and the gamma function

$$F_\nu (g) = \int_0^1 u^{2\nu} e^{-gu^2} du$$

The general form of the R's as given in equation (57) is

$$R_{ir}^{st} (k_A, k_B, A_q, B_q, C_q, \gamma) = f_i (k_A, k_B, \overline{PA}_q, \overline{PB}_q)$$

$$\times \frac{i! \, \overline{CP}_q^{i-2r-s} \, \epsilon^{r+t} (2r+1)^{t-s}}{r! \, (i-2r-s)!} \qquad \dots (58)$$

where

$$\gamma = \alpha_A + \alpha_B$$

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

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

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_{100}^{ooo}, V_{010}^{ooo} and V_{001}^{ooo} 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[15]

$$W_{ij}^{oo}=\Gamma S^{oo}I^{oo}$$

$$W_{ij}^{ko}=\Gamma[S^{ko}I^{oo}+S^{oo}I^{ko}]$$

$$W_{ij}^{ok}=\Gamma[S^{ok}I^{oo}+S^{oo}I^{ok}]$$

$$W_{ij}^{kl}=\Gamma[S^{kl}I^{oo}+S^{ko}I^{ol}+S^{ol}I^{ko}+S^{oo}I^{kl}]$$

where

$$I^{oo}=\overline{CP}_i\overline{CP}_jF_2(t)$$

$$I^{ko}=I^{ok}=\overline{CP}_i\overline{CP}_j\overline{CP}_kF_3(t)-\frac{1}{2S_1}(\overline{CP}_i\delta_{jk}+\overline{CP}_j\delta_{ik})F_2(t)$$

$$I^{kl}=\overline{CP}_i\overline{CP}_j\overline{CP}_k\overline{CP}_lF_4(t)$$
$$-\frac{1}{2S_1}[(\overline{CP}_i\overline{CP}_j\delta_{kl}+\overline{CP}_i\overline{CP}_k\delta_{jl}+\overline{CP}_i\overline{CP}_l\delta_{jk}+\overline{CP}_j\overline{CP}_k\delta_{il}$$
$$+\overline{CP}_j\overline{CP}_l\delta_{ik})F_3(t)-\frac{1}{2S_1}(\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{jk}\delta_{il})F_2(t)]$$

$$S^{oo}=N_AN_B(\pi/(\alpha_A+\alpha_B))^{3/2}\exp(-\alpha_A\alpha_B\overline{AB}^2/(\alpha_A+\alpha_B))$$

$$S^{ko}=-S^{oo}(A_k-B_k)\alpha_B/(\alpha_A+\alpha_B)$$
$$=-S^{ok}\alpha_B/\alpha_A$$

$$S^{kl}=[\delta_{kl}/2(\alpha_A+\alpha_B)-(A_k-B_k)(A_l-B_l)\alpha_A\alpha_B/(\alpha_A+\alpha_B)^2]S^{oo}$$

$$\overline{CP}_i = C_i - P_i$$

$$\overline{CP}^2 = (C_x - P_x)^2 + (C_y - P_y)^2 + (C_z - P_z)^2$$

$$P_i = (\alpha_A A_i + \alpha_B B_i)/(\alpha_A + \alpha_B) \; ; \quad (i,j,k,l = x, y \text{ or } z)$$

$$\Gamma = \frac{8}{3} \frac{S_1^5}{\pi}$$

$$t = S_1 \overline{PC}^2$$

$$S_1 = \alpha_A + \alpha_B$$

we have the following special formulae with

$$W^{kl} = W^{kl}_{xx} + W^{kl}_{yy} + W^{kl}_{zz}$$

$$<s_A| a_{ij}(C)| s_B> = 3W^{oo}_{ij} - W^{oo}\delta_{ij}$$

$$<p_{kA}| a_{ij}(C)| s_B> = 3W^{ko}_{ij} - W^{ko}\delta_{ij}$$

$$<s_A| a_{ij}(C)| p_{kB}> = 3W^{ok}_{ij} - W^{ok}\delta_{ij}$$

$$<p_{kA}| a_{ij}(C)| p_{lB}> = 3W^{kl}_{ij} - W^{kl}\delta_{ij}$$

The matrix $\underset{\sim}{a}_{pq}(c)$ 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_C 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

$$A_i(C) = a_C + B_i(C) \; ; \qquad i = x, y, \text{ or } z$$

VIIb. <u>Vibronic Contributions to the Hyperfine Constants</u>

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[53]. 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

$$\psi = (\alpha/\pi)^{\frac{1}{2}} e^{-\alpha x^2/2} \qquad \dots \dots \dots \dots (59)$$

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

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

μ is the reduced mass and E_{vib} is the zero point energy for the vibration

$$E_{vib} = (\nu + \tfrac{1}{2})(k/\mu)^{1/2} \quad ; \quad \nu = 0,1,2\dots$$

k is the force constant of the vibration defined by

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

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

The general variation of the hyperfine coupling constant a with x is

$$a=\sum_{n=0}^{\infty}c_n x^n \qquad \ldots\ldots\ldots\ldots\ldots(60a)$$

If it is assumed that terms with $n>2$ can be neglected

$$a=c_0+c_1 x+c_2 x^2 \qquad \ldots\ldots\ldots\ldots(60)$$

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

$$<a>=c_0+c_2/(2\alpha) \qquad \ldots\ldots\ldots\ldots(61)$$

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 $\underline{S}^2$ is not obtained and correlation is not correctly reproduced[12,54] 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[55] 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[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, λ, 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 λ 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, λ, 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[42] finds the minimum of the energy on a line though 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,

$$A = YU \qquad \ldots\ldots\ldots\ldots\ldots(1)$$

and U is defined as

$$U = (Y^+ SY)^{-1/2} \qquad \ldots\ldots\ldots\ldots\ldots(2)$$

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[44]. 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 CN radical have been done[57]
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[21] 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 2·0a.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 2·2a.u. the Roothaan
method minimises on to two values, oscillating
infinitely between them (curve (iii)) and never

FIGURE 1.
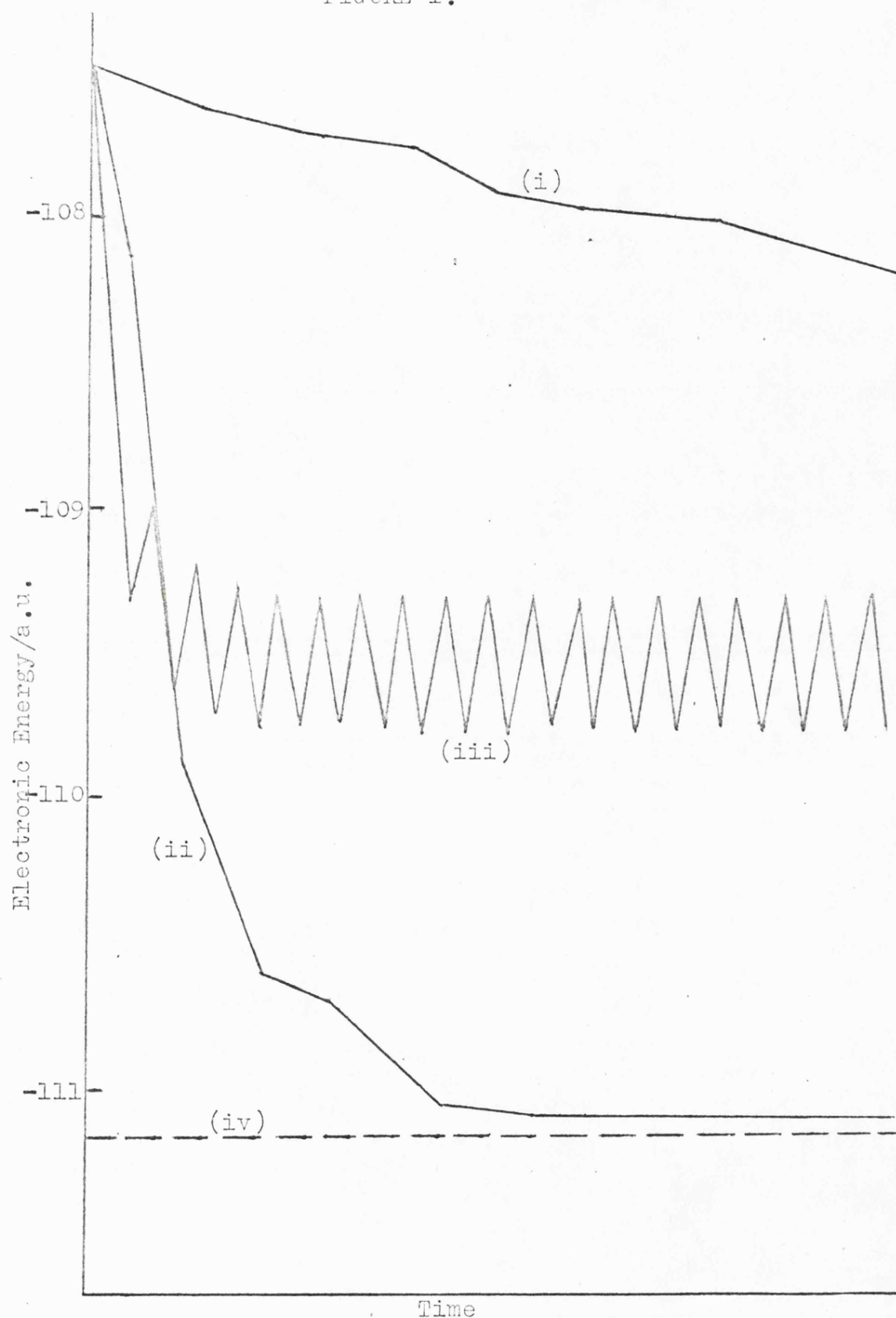
Minimisation of the CN radical (bond distance 2·2 a.u.)

(i) McWeeny   (ii) Fletcher   (iii) Roothaan

(iv) Minimum energy obtained by using Roothaan's method

after McWeeny's or Fletcher's method.

FIGURE 2.
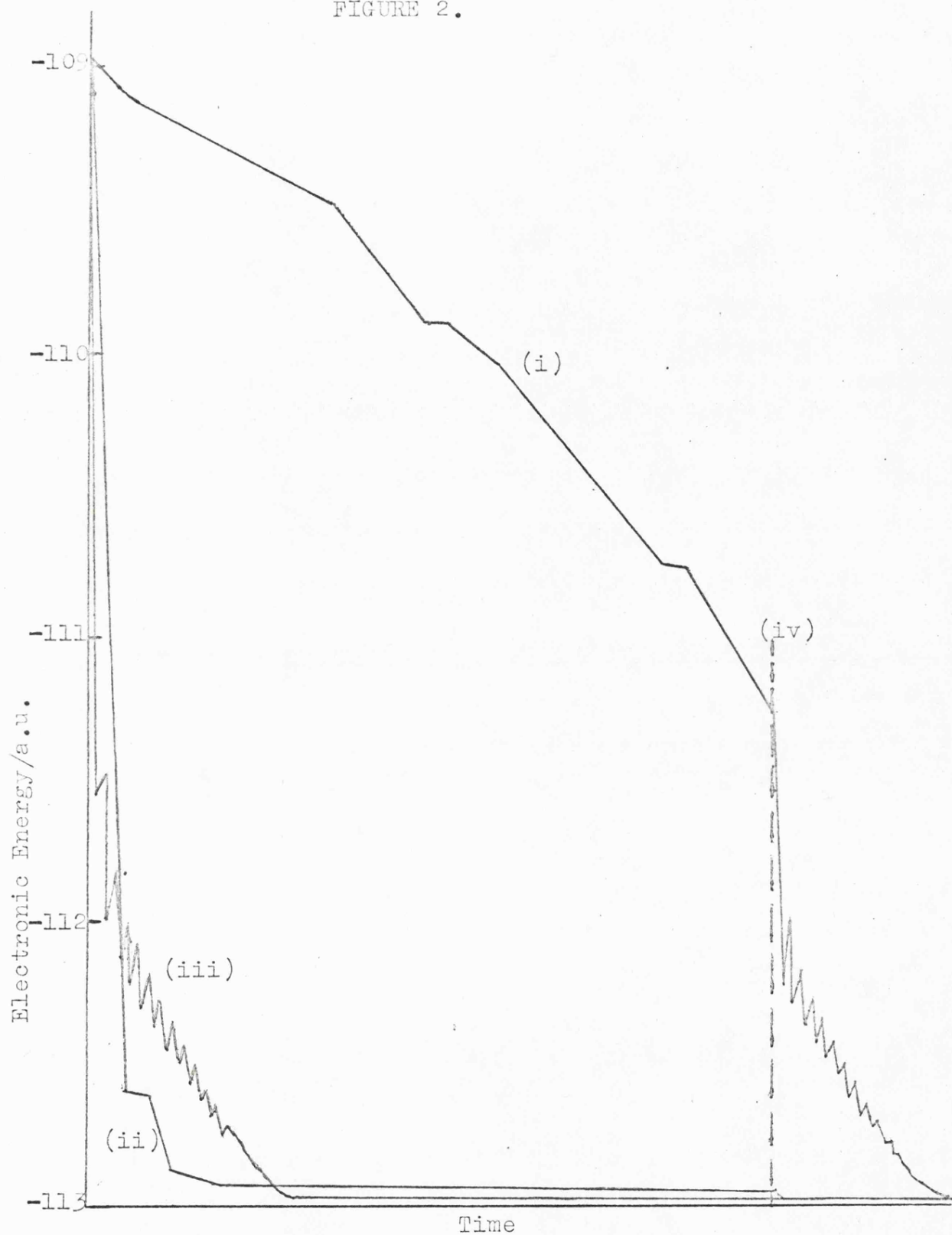
Minimisation of the CN radical (bond distance 2.0 a.u.)

(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[58] 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^-, $CH_3^{\bullet}$ and NH_3^+, has been the subject of many investigations.[59-66] 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.[60] The out-of-plane vibration is also generally considered to augment the heavy atom coupling constants,[53,67,68] although other explanations have been suggested.[69]

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.[70] 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^+ radical.[71] 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.[69,72,73]

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.[21] The orbital exponent,
α, 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 1a.u.=0·529167Å, 1a.u.=27·06eV.) 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

$$\langle a \rangle = c_0 + c_2/(2\alpha) \qquad \ldots\ldots\ldots(1)$$

c_0 is the calculated
hyperfine coupling constant at equilibrium, $\langle a \rangle$ the
observed coupling constant,

$$\alpha = 2\mu E$$

μ 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 a_1' stretching mode and a_2'' 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 α and c_2, calculations were made at various values of the angle of bending θ and extrapolated back to $\theta = 0°$. 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.[68]

The Ammonium Radical Cation.

Hyde and Freeman[66] and Cole[65] 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 NH_3^+, with isotropic hyperfine coupling constants

a_N=18·1G, a_H= ·25G and a_N=19·3G, a_H=25·8G respectively.
Rao and Symons[69] on γ-irradiation of ammonium

perchlorate found the same radical with a_N=19·3G,

a_H=25·8G at 77 and 293K. Evidence that the radical was

undergoing restricted rotation limited mainly to an

in-plane motion[66], 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 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 1·95a.u. was

calculated to be −55·85625a.u. The hyperfine coupling

constants were a_N=10·57G and a_H=−22·65G. 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 representa-

tion 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=0·1136a.u. (a.u.=1·544x10⁶gs^{-2})

TABLE 1.

bond length (a.u.)	hydrogen orbital exponent	bending angle $\Theta°$	total energy (a.u.)	coupling constants(G) a_N	a_H	$<S^2>$
1·80	1·40	0	−55·79987	11·67	−17·76	·750018
2·00	1·40	0	−55·84325	13·10	−20·40	·750046
2·20	1·40	0	−55·82179	14·43	−24·22	·750125
1·80	1·60	0	−55·83262	9·737	−20·86	·750010
2·00	1·60	0	−55·85422	10·82	−23·36	·750023
2·20	1·60	0	−55·81273	11·69	−26·92	·750056
1·80	1·80	0	−55·83769	7·929	−22·56	·750005
2·00	1·80	0	−55·83908	8·662	−24·58	·750011
2·20	1·80	0	−55·77890	9·095	−27·32	·750022
1·90	1·55	0	−55·85126	10·83	−21·39	*750018
1·95	1·55	0	−55·85500	11·12	−22·06	·750023
2·00	1·55	0	−55·85426	11·39	−22·79	·750028
1·90	1·60	0	−55·85383	10·31	−22·00	·750015
1·95	1·60	0	−55·85625	10·57	−22·65	·750019 *
1·90	1·65	0	−55·85472	9·794	−22·51	·750013
1·95	1·65	0	−55·85584	10·03	−23·13	·750016
2·00	1·65	0	−55·85254	10·26	−23·82	·750019
1·95	1·60	2·5	−55·85584	11·26	−22·37	·750019
1·95	1·60	5	−55·85455	13·30	−21·56	·750018
1·95	1·60	10	−55·84869	20·98	−18·50	·750017

*marks minimum

Theoretical Results for NH_3^+

FIGURE 1.
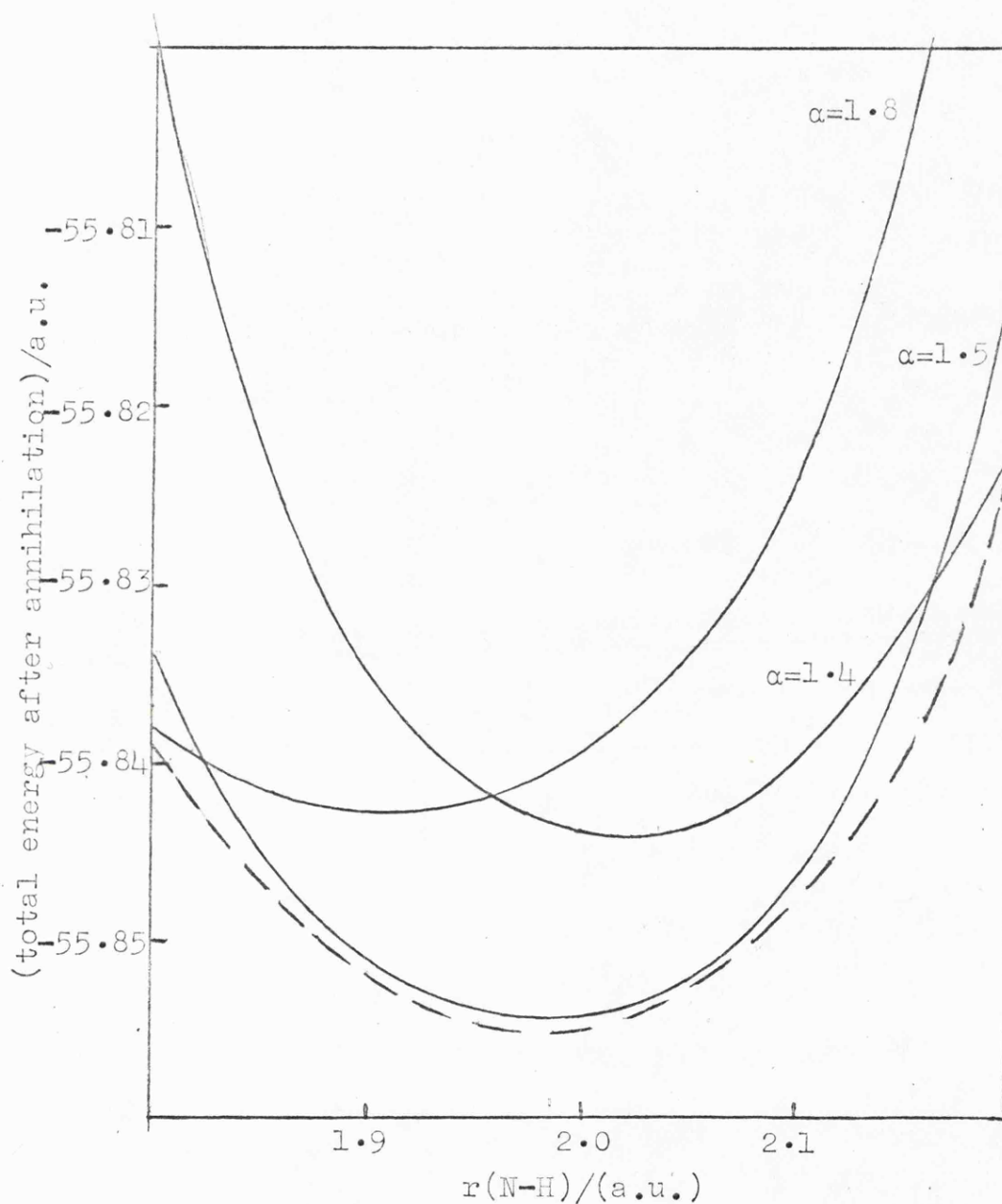
Summary of the calculations on the NH_3^+ radical;
——, variation of the total energy after annihilation
with bond length for those values of the hydrogen
orbital exponent α as indicated.
– – –, estimated minimum total energy after annihilation
as a function of bond length.

FIGURE 2.

degrees of bending/Θ
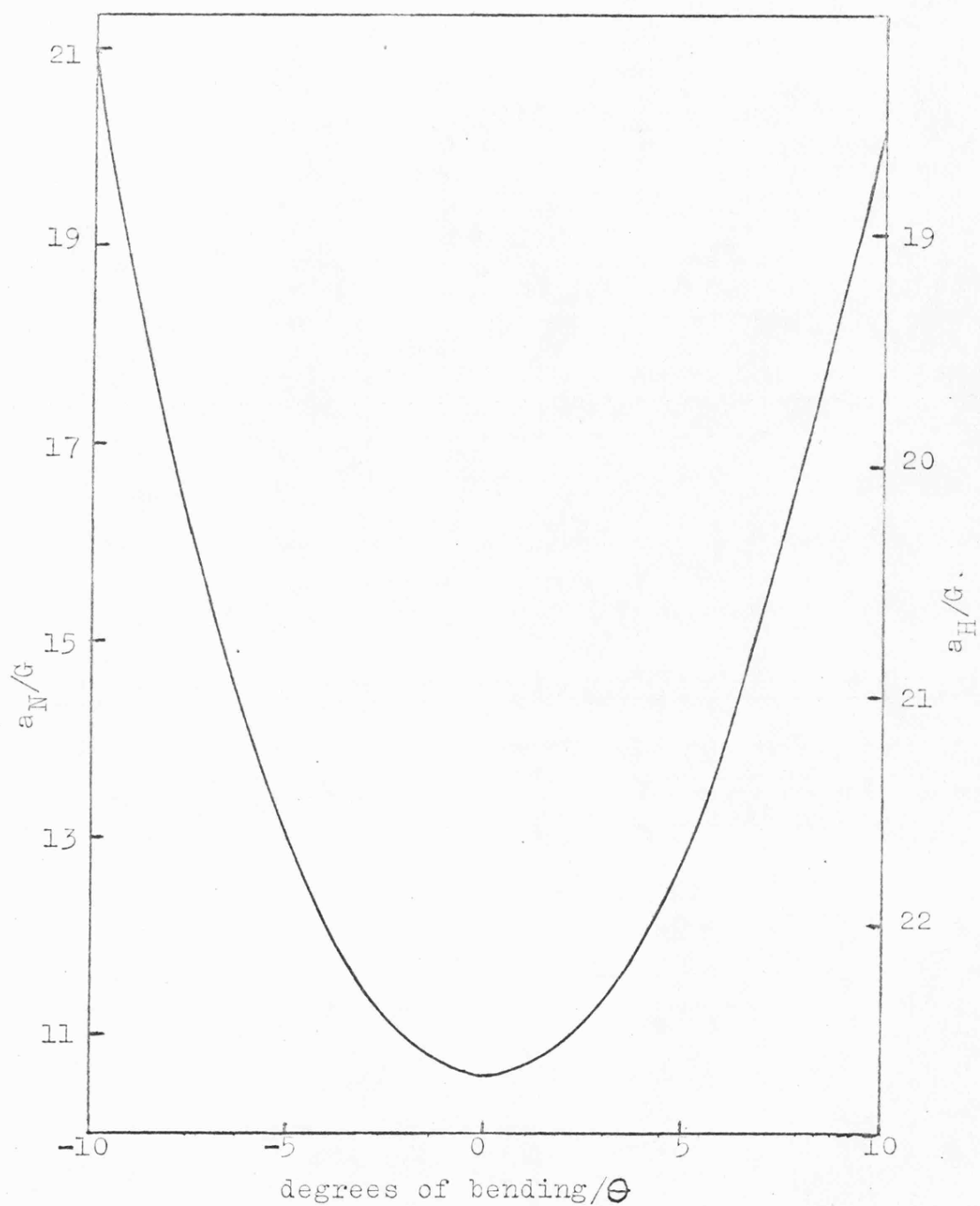
Variation of the nitrogen and hydrogen isotropic
coupling constants with angle of bending Θ.

FIGURE 3.

$\alpha = 1.55$

$\alpha = 1.60$

$\alpha = 1.65$

$\alpha = 1.55$

$\alpha = 1.60$

$\alpha = 1.65$

a_H/G

-21.5

-22.0

-23.0

-24.0

a_N/G

11.5

11

10.5

10.5

9.5

1.90

1.95

2.00

1.90

1.95

2.00

$r(N-H)/a.u.$
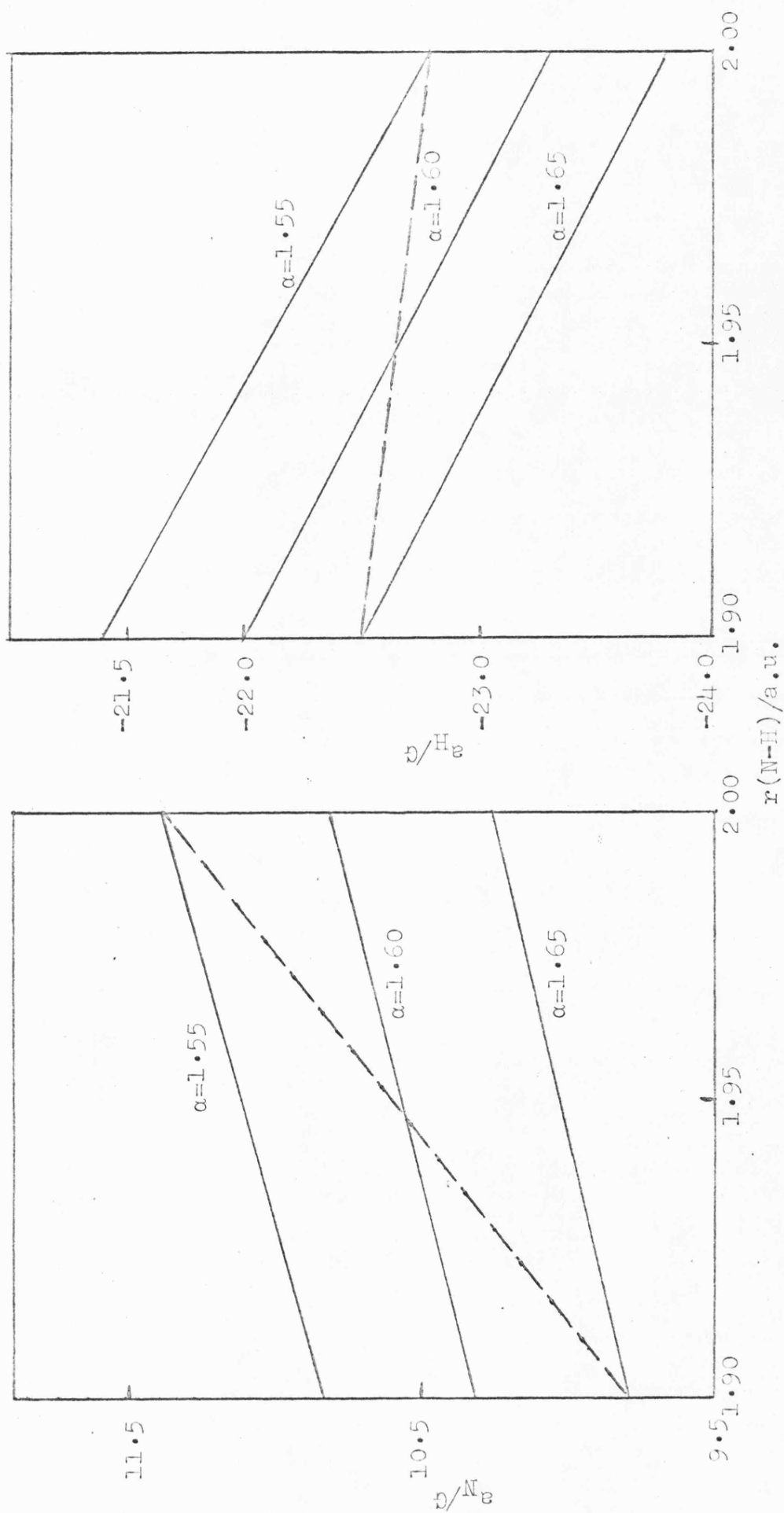
———, variation of the nitrogen and hydrogen hyperfine coupling constants with the bond distance for those values of the hydrogen atomic orbital exponent, α, which have been indicated. — · — · —, estimated variation of the nitrogen and hydrogen hyperfine coupling constants with bond distance at minimum total energy.

was evaluated for the out of plane vibrational mode.

This compares with k=1·372a.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

$$a_N = 10·57 + 6·35 = 16·92G$$

Similarly the inclusion of the vibronic

contribution for hydrogen gives a_H=-20·02G 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 α 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 $CH_3^\bullet$ radical. An early determination

by Cole et al[62] , of the carbon isotropic coupling

constant, a_C=41G, showed, by the relative smallness of

its value, that the radical is planar. Experimental

values of a_C=38G and a_H=-23G[74] seem to be generally

true in solution and matrix' environments; however

these hyperfine coupling constants are temperature

dependent. Although calculations on $CH_3^\bullet$ 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[53]. The temperature dependence is well explained by including the effects of this vibration.[67,68] Fessenden[74] has suggested that a rigid planar model for the methyl radical may have a_C=28G, the other 10G being due to the out of plane vibration.

The results for the calculations on $CH_3^\bullet$ are summarised in Table 2. The optimised planar configuration has an energy of −39·5428a.u. for a bond length of 2·05a.u. and hydrogen orbital exponent of 1·40 (figure 4). The isotropic hyperfine coupling constants are a_C=27·33G and a_H=−23·39G for the rigid planar configuration. The contribution of the out of plane zero point vibration was estimated in the same way as for NH_3^+. The out of plane vibrational force constant was calculated to be k=0·0405a.u.. This is much less than that calculated for NH_3^+ (k=0·1136a.u.) thereby accounting for the marked temperature dependence shown by $CH_3^\bullet$ but not NH_3^+. The symmetrical stretching vibrational force constant, k=1·292a.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 27·31G and 3·96G, 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 2.

bond length (a.u.)	hydrogen orbital exponent	bending angle $\theta°$	total energy (a.u.)	coupling constants (G)		$<S^2>$
				a_C	a_N	
1·80	1·20	0	−39·42928	25·76	−15·55	·750017
2·00	1·20	0	−39·51166	31·72	−18·04	·750047
2·20	1·20	0	−39·52256	38·70	−21·69	·750139
1·80	1·40	0	−39·48438	20·80	−19·58	·750010
2·00	1·40	0	−39·54090	25·96	−22·46	·750026
2·20	1·40	0	−39·52824	31·74	−26·79	·750074
1·80	1·60	0	−39·49501	16·74	−22·15	·750005
1·90	1·60	0	−39·52256	18·87	−23·48	·750008
2·00	1·60	0	−39·52818	20·94	−25·13	·750013
2·10	1·60	0	−39·51700	23·07	−27·15	·750021
2·00	1·35	0	−39·53818	27·35	−21·52	·750030
2·05	1·35	0	−39·54161	28·78	−22·42	·750039
2·10	1·35	0	−39·54131	30·27	−23·41	·750051
2·05	1·40	0	−39·54284	27·33	−23·39	·750033 *
2·10	1·40	0	−39·54107	28·74	−24·42	·750043
2·00	1·45	0	−39·54099	24·63	−23·30	·750022
2·05	1·45	0	−39·54146	25·91	−24·25	·750028
2·10	1·45	0	−39·53824	27·23	−25·28	·750037
2·05	1·40	2	−39·54273	28·68	−23·21	·750033
2·05	1·40	5	−39·54216	35·44	−22·13	·750031
2·05	1·40	10	−39·53978	57·85	−18·84	·750025

*marks minimum

Theoretical Results for $CH_3^{\cdot}$
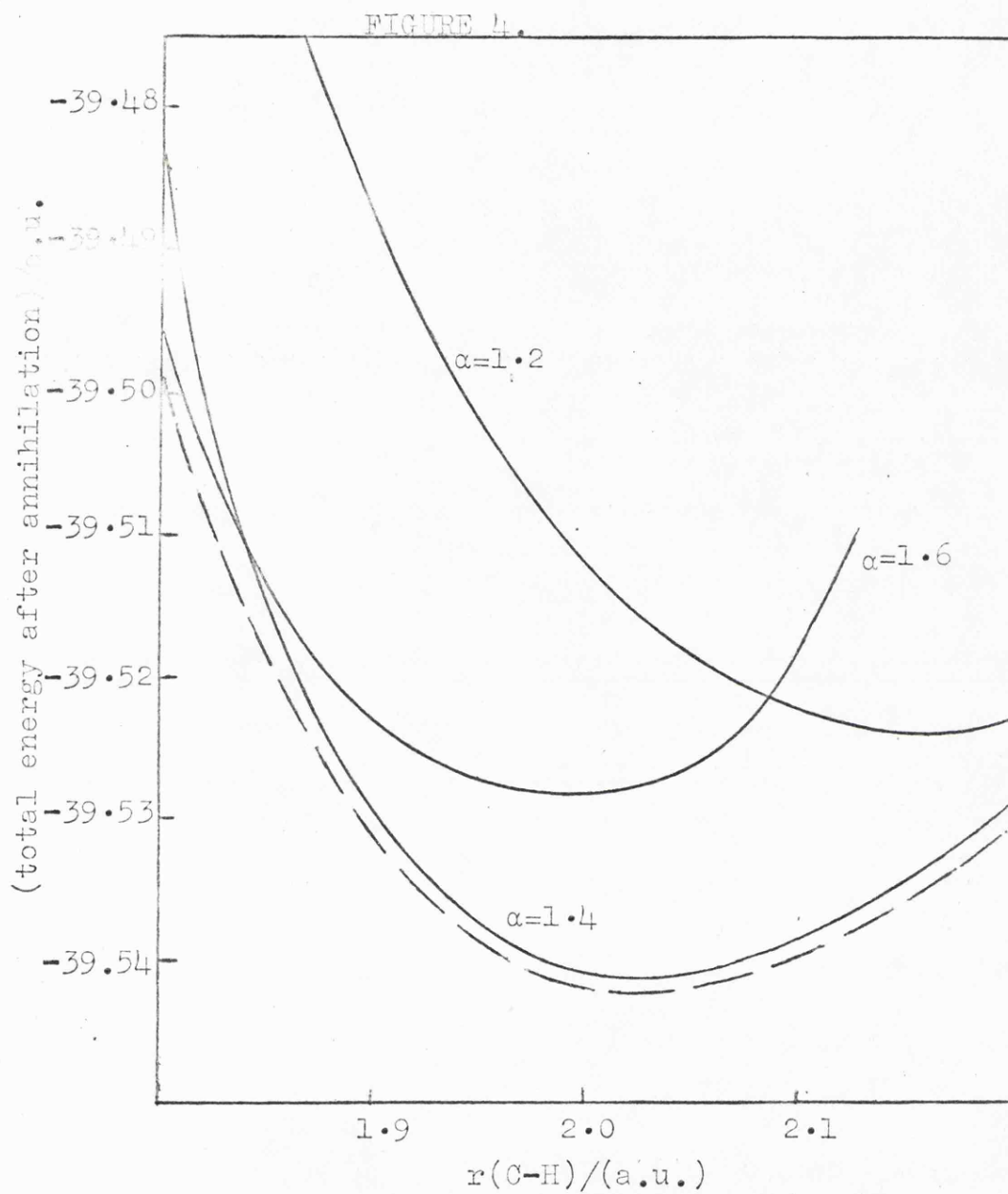
Summary of the calculations on the CH$_3^\bullet$ radical. (See also caption to figure 1.)
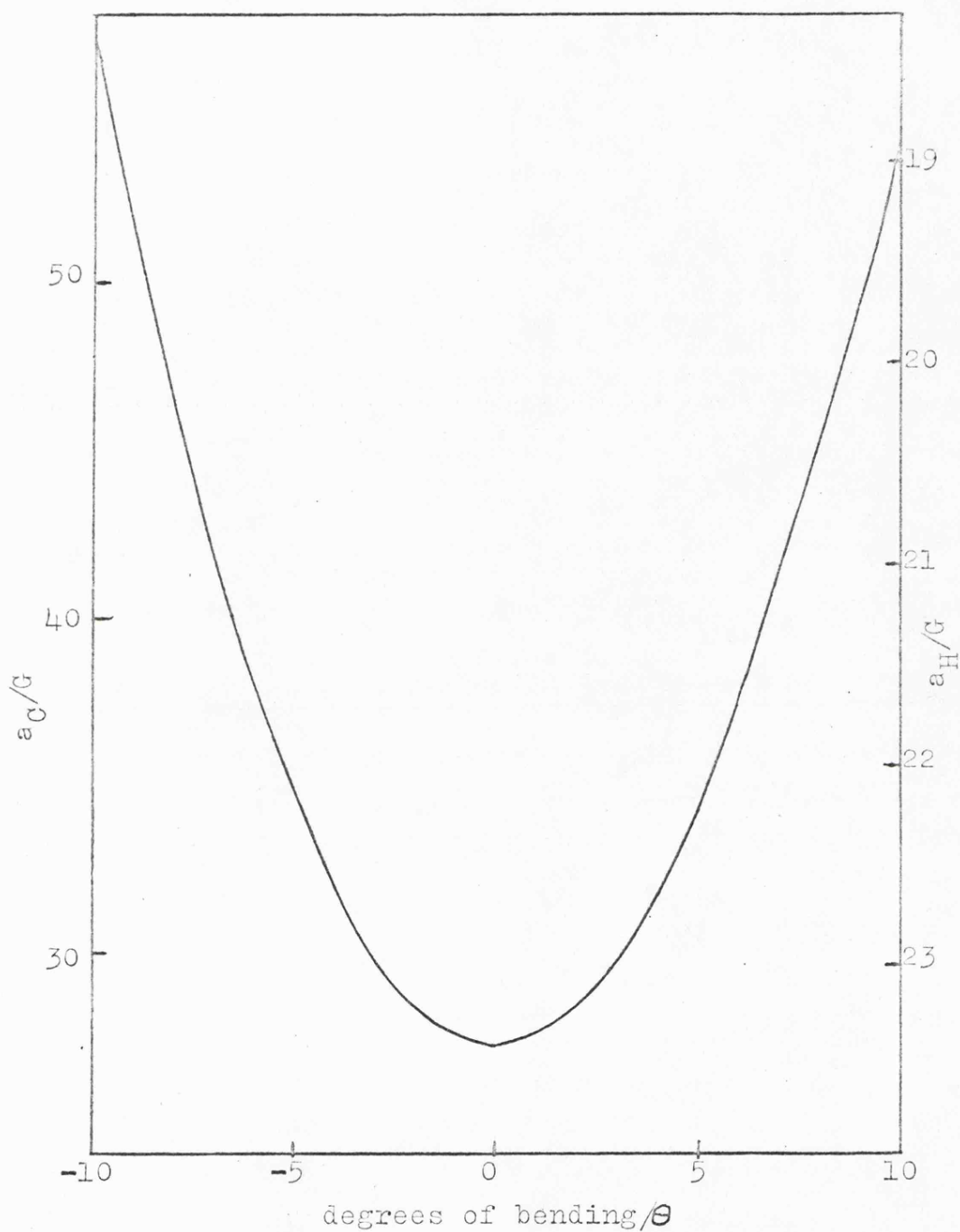
FIGURE 5.

Variation of the carbon and hydrogen isotropic
hyperfine coupling constants with angle of bending
Θ.

FIGURE 6.

Variation of carbon and hydrogen hyperfine coupling constants with bond distance. (see also caption to figure 2.)

r(O—H)/a.u.

a_H/G

a_O/G

α=1·35 α=1·40 α=1·45

2·00 2·05 2·10

·22 ·24 ·26

·25 ·27 ·29
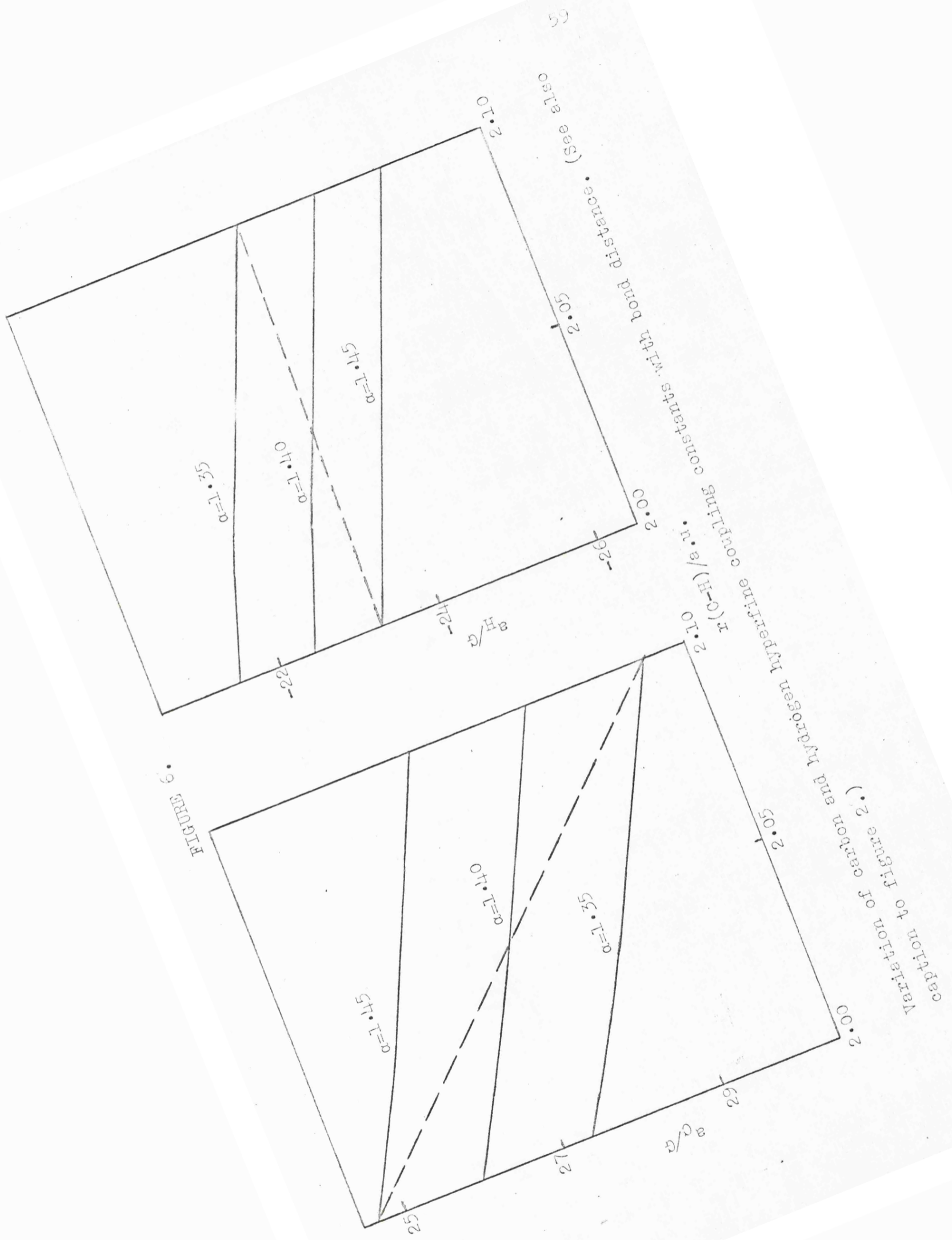
observed isotropic hyperfine coupling constants then become $a_C=54 \cdot 64G$ and $a_H=-19 \cdot 43G$. Although the results are not in as good agreement with experiment as those for NH_3^+ they are still reasonable. The trend of the temperature variation of both a_C and a_H is correctly predicted since 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 γ-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, $a_B=24 \cdot 2G, a_H=16 \cdot 3G$[60] and $a_B=20 \cdot 7G, a_H=15 \cdot 1G$.[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 2·35a.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,[79-81] 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[82] 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 BH_3^-

bond length (a.u.)	hydrogen orbital exponent	bending angle $\Theta°$	total energy (a.u.)	coupling constants(G)		$<S^2>$
				a_B	a_H	
2·20	1·00	0	−26·28152	21·90	−13·93	·750054
2·40	1·00	0	−26·30533	27·14	−15·96	·750133
2·60	1·00	0	−26·30050	33·71	−18·76	·750344
2·00	1·20	0	−26·27049	13·62	−17·21	·750015
2·20	1·20	0	−26·31680	17·95	−19·30	·750035
2·40	1·20	0	−26·31956	22·76	−22·40	·750088
2·60	1·20	0	−26·29524	28·83	−26·91	·750243
2·00	1·40	0	−26·26927	11·15	−20·52	·750044
2·20	1·40	0	−26·29534	14·82	−23·21	·750055
2·40	1·40	0	−26·27808	18·91	−27·24	·750076
2·35	1·10	0	−26·32147	23·48	−18·58	·750086
2·40	1·10	0	−26·32160	24·84	−19·30	·750109
2·45	1·10	0	−26·32004	26·28	−20·10	·750138
2·30	1·15	0	−26·32299	21·15	−19·41	·750061
2·35	1·15	0	−26·32370	22·41	−20·15	·750077 *
2·40	1·15	0	−26·32252	23·73	−20·96	·750098
2·25	1·20	0	−26·32081	19·08	−19·97	·750044
2·30	1·20	0	−26·32243	20·25	−20·70	·750055
2·35	1·20	0	−26·32193	21·47	−21·51	·750070
2·35	1·15	2	−26·32374	23·66	−19·94	·750076
2·35	1·15	5	−26·32392	30·04	−18·87	·750068
2·35	1·15	8	−26·32410	40·98	−17·11	·750057
2·35	1·15	10	−26·32411	50·19	−15·72	·750050
2·35	1·15	15	−26·32309	77·27	−12·11	·750033
2·35	1·15	20	−26·31933	106·8	−9·167	·750024
2·00	1·40	5	−26·26866	16·99	−19·71	·750005
2·00	1·40	10	−26·26691	33·22	−17·66	·750003

*marks minimum

FIGURE 7.
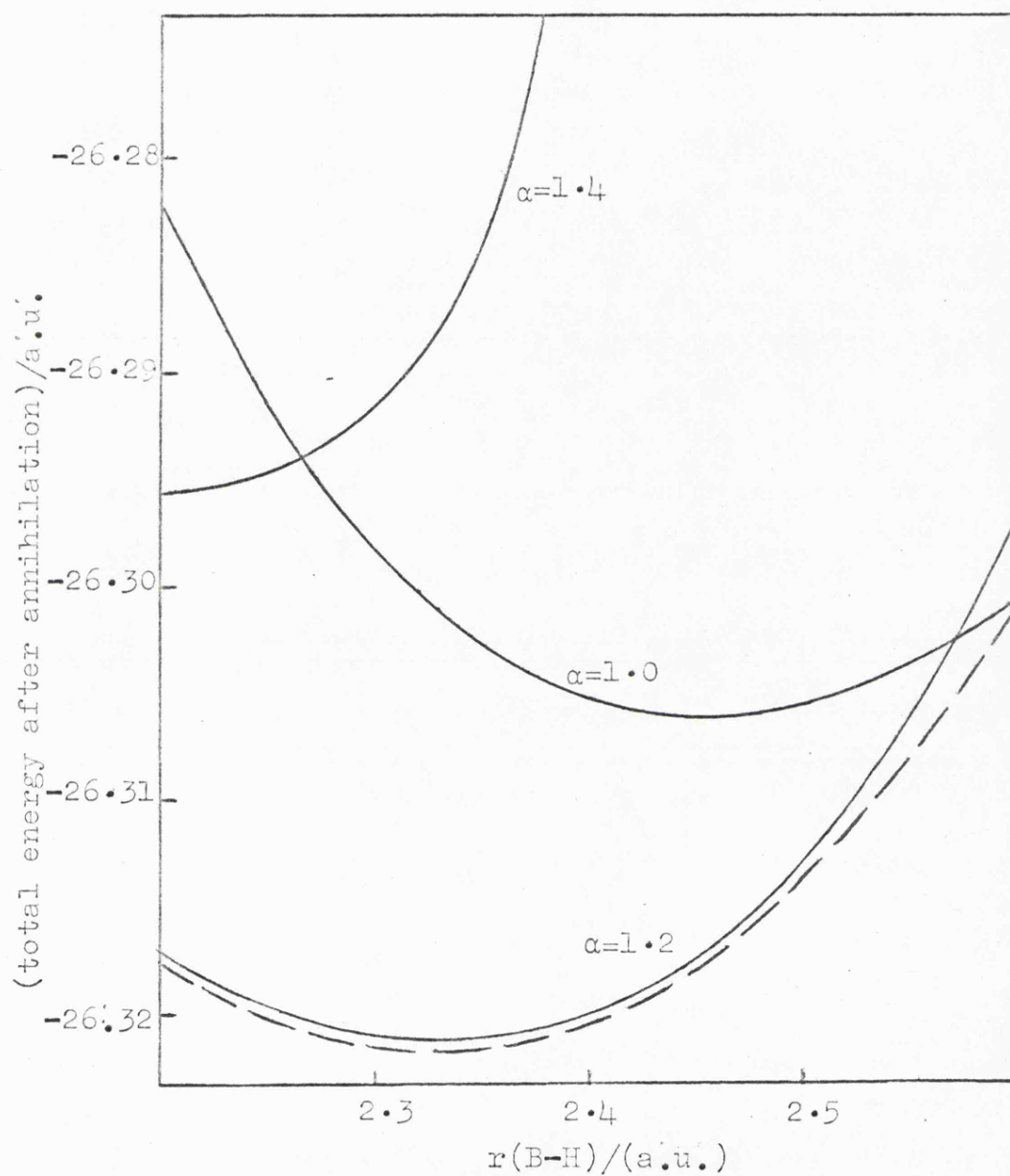
Summary of the calculations on the BH_3^- radical
(See also caption to figure 1.)

04

FIGURE 8.
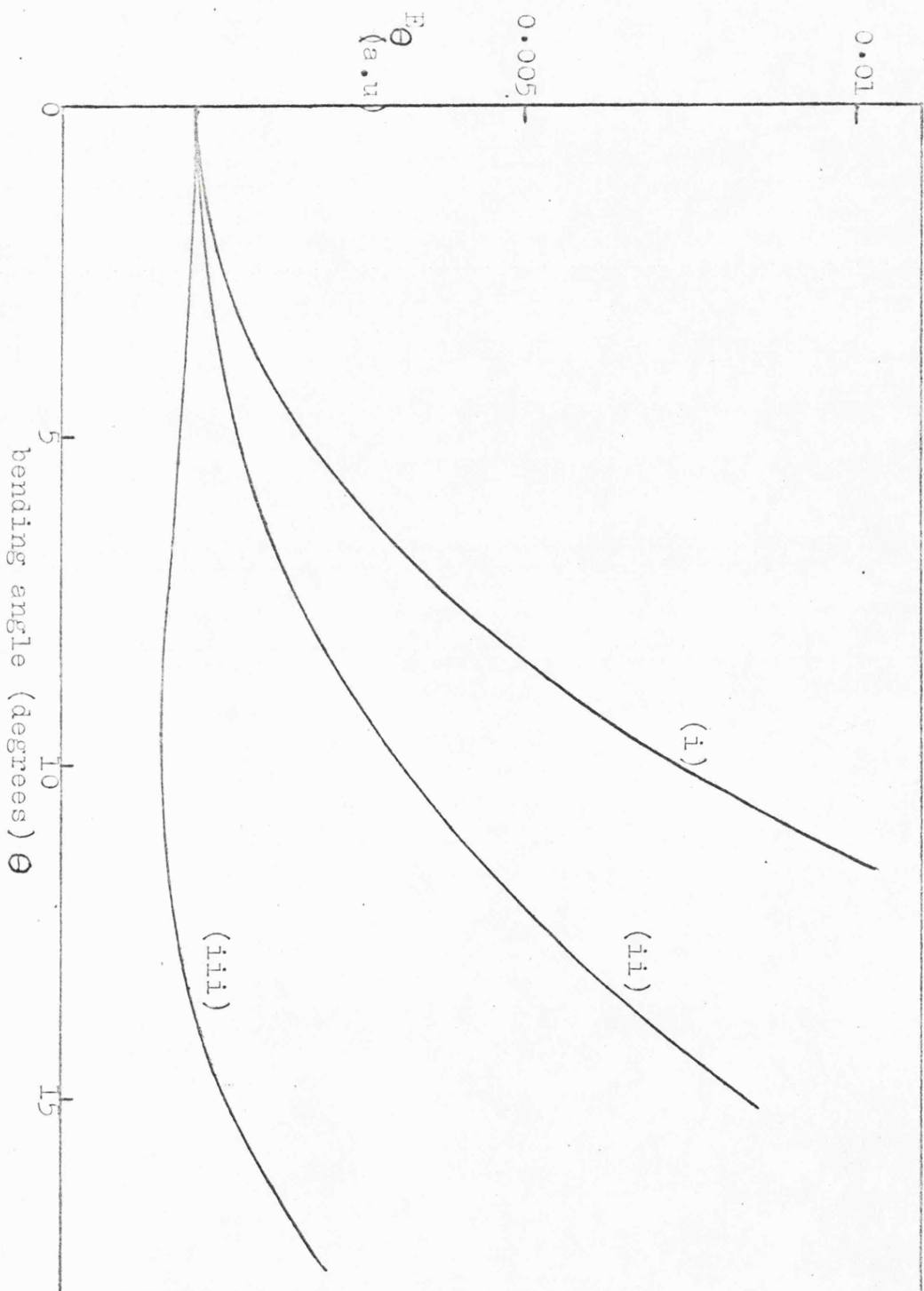
Variation of the total energy after spin annihilation, E_θ, as a function
of the bending angle θ relative to E_0 for the radicals; (i) NH_3^+ ($E_0=-55.85625$)
(ii) $CH_3^{\,\circ}$ ($E_0=-39.54284$) (iii) BH_3^- ($E_0=-26.32370$).

bending angle (degrees) θ

E_θ
(a.u.)

0.01

0.005

0

0   5   10   15

(i)

(ii)

(iii)

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 $CH_3^{\cdot}$ so that a large
temperature variation in a_B would be expected, which
has not been observed.

The calculations which have given reasonable
isotropic hyperfine coupling constants for NH_3^{+} and
$CH_3^{\cdot}$ should give a comparable accuracy for BH_3^{-}. That
this is not the case implies that external effects,
not large for $CH_3^{\cdot}$ and NH_3^{+} but dominant for BH_3^{-},
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_C and the estimation given by Fessenden[74]
(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 $BH_3^{-}, CH_3^{\cdot}, NH_3^{+}$ (−16·5G,−23·0G
and −25·9G) as predicted from the excess charge effect.[83,84]
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 (-20.15G, -23.39G,-22.65G). 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 (-23.21G,-22.46G,-20.04G).

(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 2a.u. the hydrogen orbital exponents are 1.2,1.4,1.6 for $BH_3^-,CH_3^{\cdot},NH_3^+$ respectively and the resulting proton coupling constants (-17.32G, -22.46G,-23.36G) 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]B), 3.4 (^{13}C), 3.5 (^{14}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_3^- increases
still further the out of plane vibrational force
constant qualitative agreement with experiment may be
obtained. The overall effect for BH_3^- would be a
considerable increase in the force constant, accounting
for the temperature dependence, and a smaller increase
for the neutral $CH_3^{\cdot}$, resulting in a smaller vibronic
contribution to the hyperfine coupling constants.
Since NH_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_3^-
as bent is embarrasing. 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_3^- induces a bond length and

hydrogen orbital exponent similar to $CH_3^{\cdot}$ ($\alpha=1\cdot4$, $r(B-H)=2a.u.$) 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 BH_3^{-}, $CH_3^{\cdot}$ and 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 BH_3^{-} are seriously affected by the environment. Although $CH_3^{\cdot}$ and NH_3^{+} may be treated, theoretically, in isolation it appears that the environment of 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[85], 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.[86]

The evaluation of the expectation value of the isotropic, or Fermi contact, term, between an unpaired

electron and a magnetic nucleus

$$(8\pi/3)g_e g_N \beta_e \beta_N S \cdot I \qquad \ldots\ldots\ldots(1)$$

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

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

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[51] have

suggested using the Gaussian Transform of the field

gradient operator, for example

$$\frac{3x^2 - r^2}{r^5} = \frac{\partial^2}{\partial x^2}(1/r) + \frac{4\pi}{3}\delta(r) \qquad \ldots\ldots\ldots(3)$$

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[50] have recently

derived analytical formulae for the three centre one

electron integrals of the operator $r^n Y_l^m(\theta, \varphi)$ with

Slater type orbitals, where Y_l^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.[87,88] 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_2CN, 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[18] for sodium and the 6s type for hydrogen excluding the sodium hydride cation calculation where the hydrogen was represented by a 10s type expansion[21]. 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[89] 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 γ-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, $a_H=511\cdot5G$, $a_{Na}=17\cdot2G$. Ab initio UHF calculations supported the assignment[90] giving calculated isotropic coupling constants, at a bond distance of $3\cdot6$a.u., of $a_{Na}=26\cdot1$, $a_H=508G$ 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 $502\cdot1G$, 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 $514\cdot4G$) 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,

$B_{\parallel}(Na)=4 \cdot 2G$ $\qquad$ $B_{\perp}(Na)=-2 \cdot 1G$

$B_{\parallel}(H)=1 \cdot 7G$ $\qquad$ $B_{\perp}(H)=-0 \cdot 85G$

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
$B_{\parallel}(H)$ and $-B$ to $B_{\perp}(H)$. If B were $1 \cdot 01G$ exact agreement
with experiment would result. For an electron in a
2p atomic orbital of hydrogen the calculated value of
B is $3 \cdot 17G$, 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 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 2·1a.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

TABLE 1.

host crystal	reference	A_x	A_y	A_z
(theory)	this work	25·66	−8·99	−8·38
KN₃	90	6·5	−4	−4
KN₃	91, 92	12·0	−3·8	−4
KCl	93	21	−4·5	−6·6
NaN₃	94	23·5	−3·9	−11
Ba(N₃)₂	95	20·0	−3·6	−4·1
KCl	96	21·3	−5·04	−6·07
KBr	96	21·4	−3·6	−5·4
KI	96	21·6	−5·4	−7·1

Hyperfine Coupling Constants (in G) for N_2^- for various Host Crystals

axis and the unpaired electron occupies a π_x^* antibonding orbital.

A fortunate feature of the UHF method[2] 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 π^* 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,[98] absorbed on magnesium oxide[99] and in single crystals of hydroxylammonium chloride[100], after irradiation with X rays at 77K. The latter study of Ohigashi and Kurita[100] gave the A hyperfine tensor of the nitrogen.

$$A_x(N)=36 \cdot 4G \quad , \quad A_y(N')=5 \cdot 4G \quad , \quad A_z(N)=11 \cdot 5G$$

with the z axis coincident with the molecular axis. The unpaired electron was found to be in a π_x^* antibonding orbital lying $2000 cm^{-1}$ below the π_y^* 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[101] have deduced approximate values of $a_N=14 \cdot 2G$ and $B_z(N)=-20 \cdot 83G$, from the microwave spectrum of the NO ground state, suggesting that $A_z(N)$ is negative.

Using a bond length of 2·175a.u. the unpaired electron was calculated to occupy the π_x^* antibonding orbital.[90] The calculated coupling constants are

$$a_N=5\cdot39G \quad ; \quad B_x(N)=26\cdot97G \quad , \quad B_y(N)=-10\cdot72G \quad , \quad B_z(N)=-16\cdot25G$$

$$a_O=-2\cdot11G \quad ; \quad B_x(O)=-43\cdot39G, \quad B_y(O)=30\cdot08G \quad , \quad B_z(O)=13\cdot31G$$

from which,

$$A_x(N)=32\cdot36G \quad , \quad A_y(N)=-5\cdot33G \quad , \quad A_z(N)=-10\cdot86G$$

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[102] 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

$$a_C=210G \quad ; \quad B_\parallel(C)=32G \quad , \quad B_\perp(C)=-16G$$

$$a_N=-4\cdot5G \quad ; \quad B_\parallel(N)=11G \quad , \quad B_\perp(N)=-5\cdot5G$$

Ab initio UHF calculations on the radical[57] have given isotropic coupling constants of $a_C=339\cdot2G$, $a_N=-6\cdot182G$, 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 CN 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,
$B_{\parallel}(C)=17 \cdot 15G$ whereas the calculated value of $B_{\parallel}(N)$ is
$9 \cdot 55G$, 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° and for HCO a
hydrogen orbital exponent of $1 \cdot 4$ was chosen while a
value of $1 \cdot 2$ was taken for the anions. The BO, CO, CN
bond lengths were chosen as $2 \cdot 4$, $2 \cdot 3$, and $2 \cdot 2$ a.u.
respectively and the CH of HCN⁻ was set at $2 \cdot 0$ a.u.,
the others, HB and HC for HBO⁻ and HCO, being taken
as $2 \cdot 2$ 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

Hyperfine Coupling Constants (in G) for HCO

nucleus	reference	a	B_x	B_y	B_z
H	102	136	-4	-4	8
H	103	137	-4.2	-0.8	5
H	105	126	-2.85	-6.1	8.92
H	*	112.5	-4.8	-6.4	11.1
^{13}C	104	135	-13.8	-4.2	18
^{13}C	105	130	-17.13	-8.56	25.69
^{13}C	*	148.4	-22.2	-10.8	33.0

*this work and reference (106)

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.

HBO$^-$

The γ-irradiation of alkali borohydrides at 20K
gave values of the B tensors for the HBO$^-$ radical[106];
for boron 12, -6, -6G and for hydrogen 8, -4, -4G.
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=91.6G,
a_B=123G[107] (compared with the a_H=94G, a_B=101G found
experimentally[60].)

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

FIGURE 1.
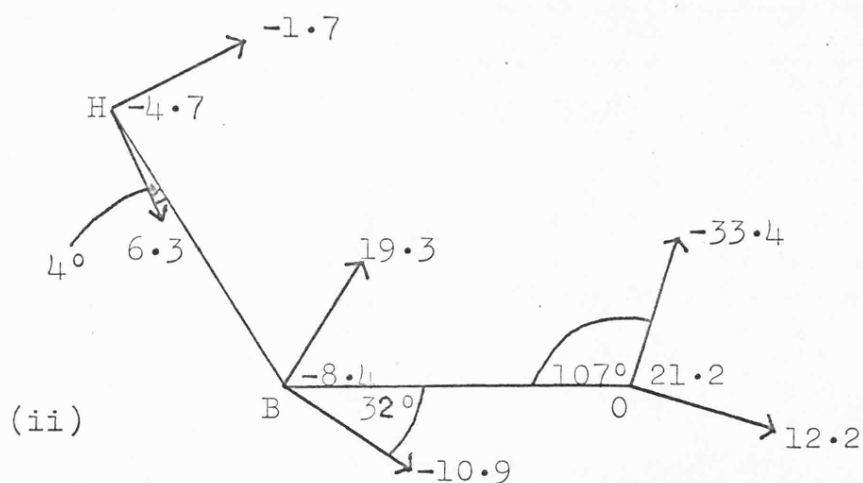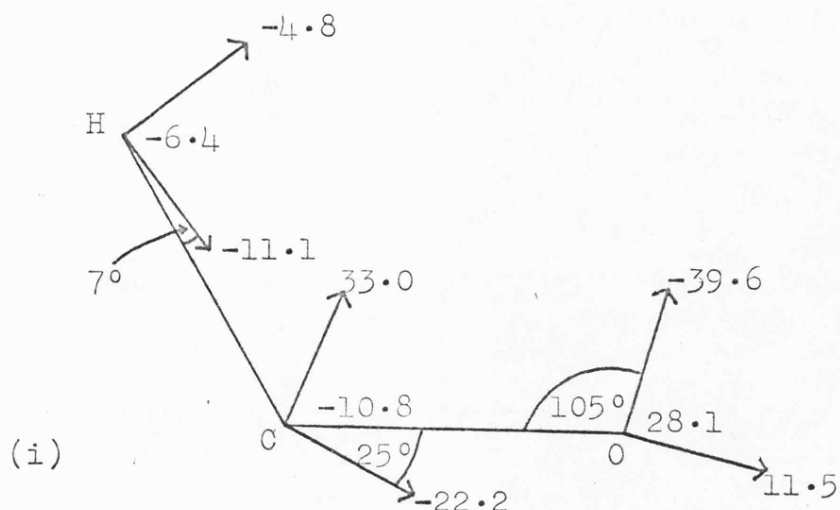
(i)

(ii)

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 $a_H=140 \cdot 3$, $a_C=74 \cdot 4$ and $a_N=4 \cdot 92G$ for the isotropic coupling constants agree excellently with experiment, where an angle of $131°$ was estimated; $a_H=136 \cdot 4G$, $a_C=74 \cdot 7G$ and $a_N=7G$. 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 HCN^- radical ion as a derivative of the linear HCN molecule, formed by bending and addition of an electron, two extreme situations can be envisaged. Assuming homolytic fission of the inplane π bond on bending, an electron will occupy an sp^2 hybrid orbital on the carbon and an inplane 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.

FIGURE 2.
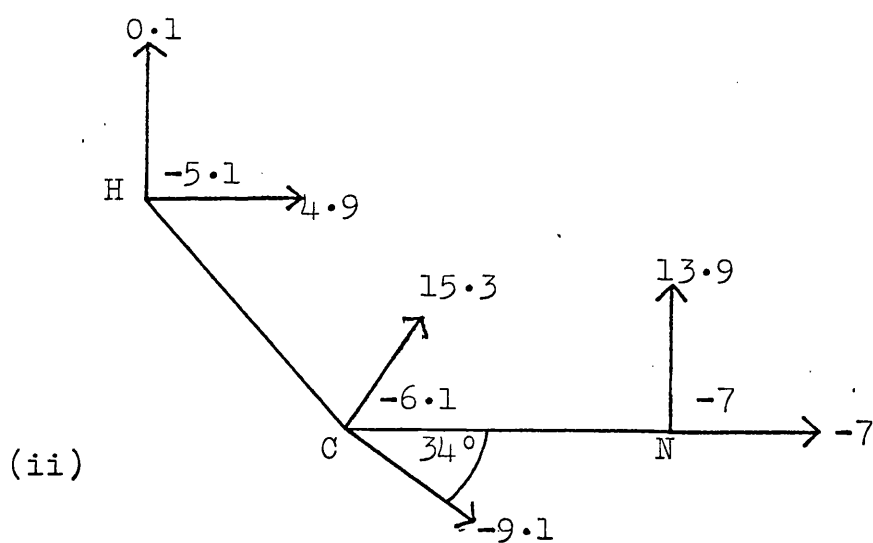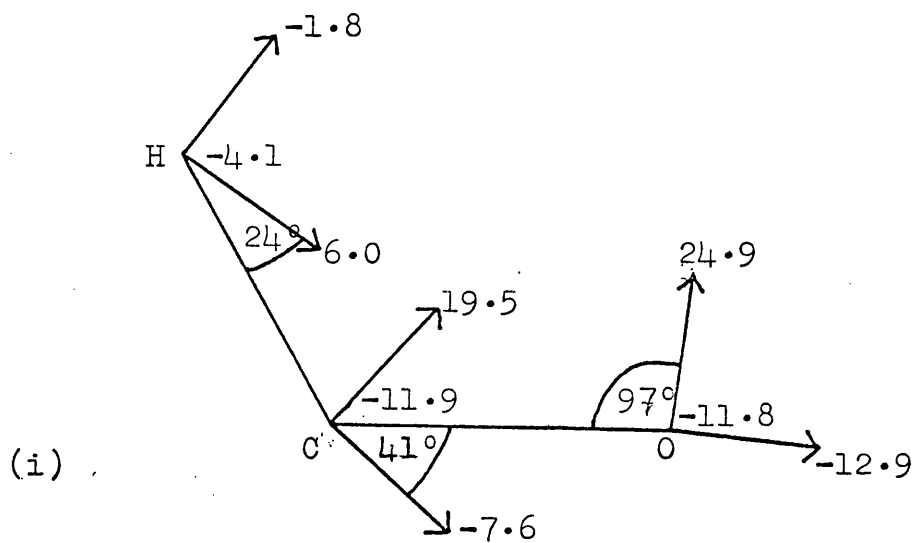
(i)

(ii)

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 H_2CN is associated with the
particularly favourable conditions for hyperconjugation,
arising from the planar structure of the radical,[107,111]
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[111]

$$a_N = 9 \cdot 5G \quad ; \quad A_{\parallel}(N) = 34 \cdot 4G \quad , \quad A_{\perp}(N) = -3G$$

The proton isotropic coupling constant $a_H = 87 \cdot 4G$[112]
or $92 \cdot 1G$[111], 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[107]

$$a_H = 84 \cdot 8G \quad , \quad a_N = 7 \cdot 2G \quad , \quad a_C = -18 \cdot 7G$$

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

$$A_y(N) = 37 \cdot 3G \quad , \quad A_z(N) = -10 \cdot 5G \quad , \quad A_x(N) = -5 \cdot 3G$$

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[113] and if this is the case should
correspond closely to $A_{\parallel}(H)$. Since $a_H = A_{\parallel}(H) - B_{\parallel}(H) = 90 \cdot 2G$
better agreement with experiment, for the 91·2G proton
value from the powder spectrum[111], is obtained.

FIGURE 3.
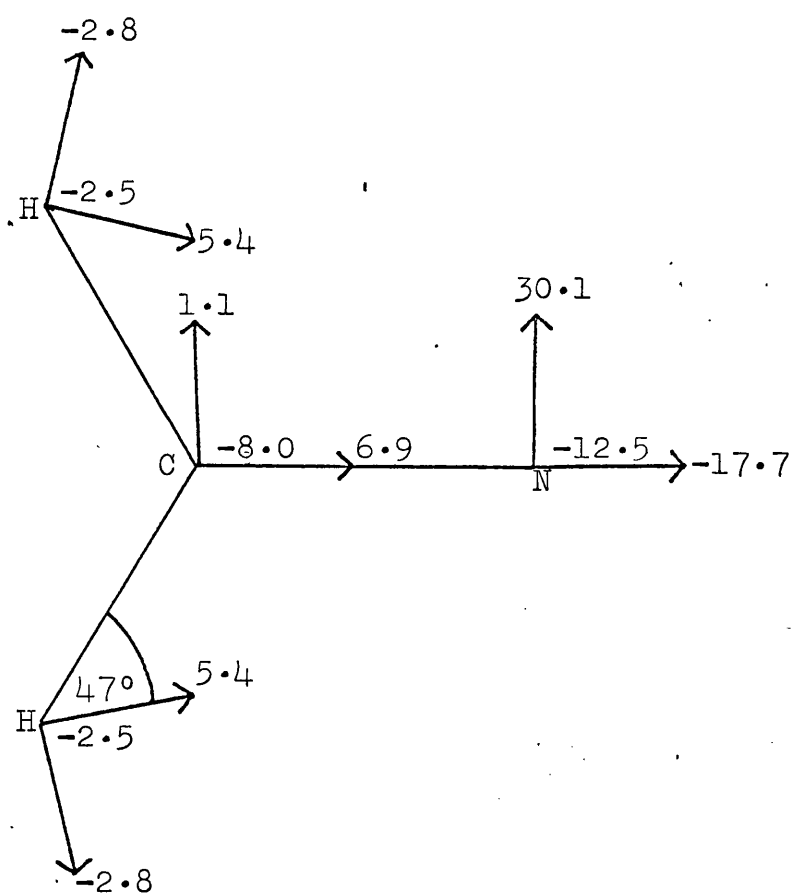
The principal values and axes of the anisotropic
components of the hyperfine coupling tensors of H_2CN.
(See also the caption to figure 1.)

The Vinyl Radical.

The sensitivity of the sign of the α proton coupling constant of the vinyl, ($a_H = \pm 13 \cdot 5G$ experimental) to the bond angle CCH_α 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 $DOOC-CH=CH^\cdot$, produced by irradiation of a single crystal of deuterated maleic acid[114], has been studied. For $DOOC-CH=CH^\cdot$ the maximum principal value of the α proton anisotropic coupling constant is approximately along the $C-H_\alpha$ bond and the minimum is perpendicular to the radical plane, $A(H_\alpha) = 27$, $9 \cdot 6$, $3 \cdot 9G$.

An ab initio calculation[115] has been reported for a hydrogen orbital exponent of $1 \cdot 4$, bond lengths of $2 \cdot 533$ and $2 \cdot 041$ a.u. for the CC and CH bonds respectively, bond angles of $120°$ for the β protons. and $137°$ for the α proton, as suggested by the work of Millie and Berthier[56]. 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 $13 \cdot 5G$, for the isotropic coupling constant of H_α, is assumed the corresponding anisotropic tensor components are $B(H_\alpha) = 13 \cdot 5$, $-3 \cdot 9$, $-9 \cdot 6G$. These agree well with the values, and directions, calculated thus reinforcing the view that the isotropic coupling constant of the α proton is positive.

FIGURE 4.

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 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 $a_N=16\cdot92G$, $a_H=-20\cdot02G$. These calculations are reported in Chapter 2.
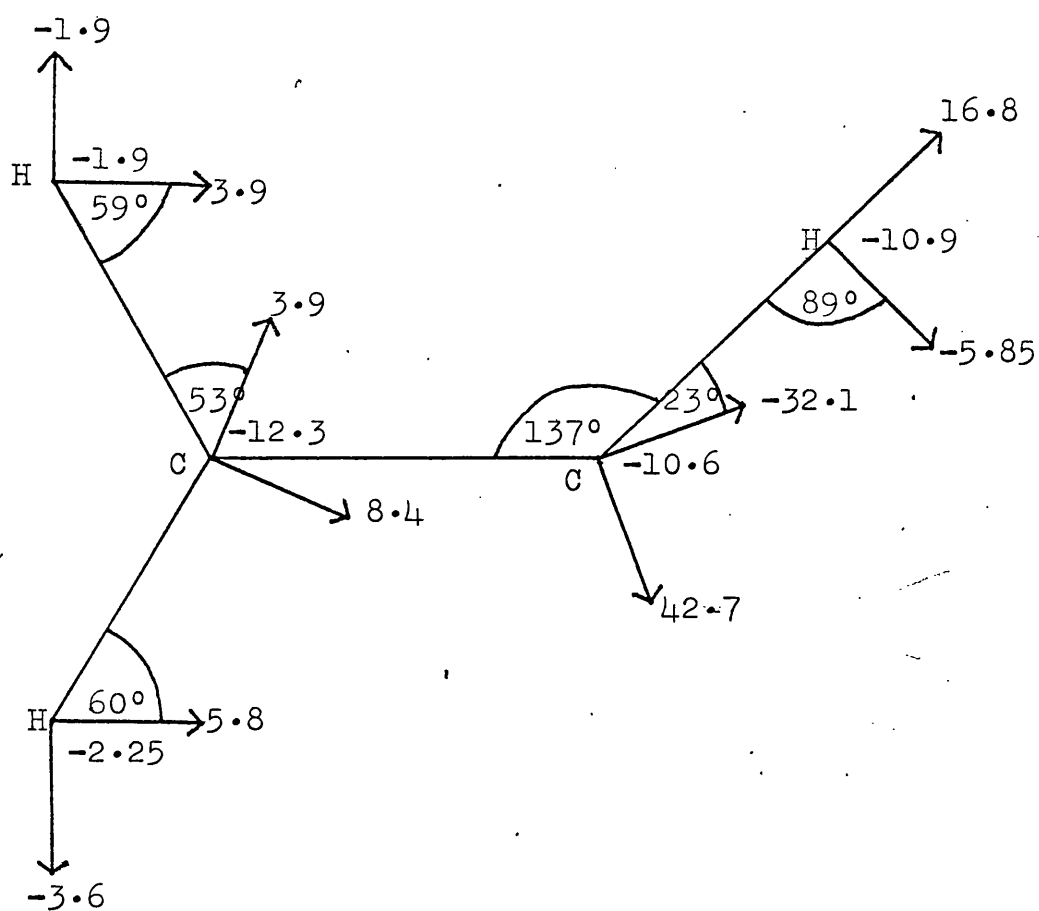
Rao and Symons[69] on γ-irradiation of ammonium perchlorate, at room temperature and 77K, obtained the NH_3^+ radical, with isotropic coupling constants and anisotropic components

$$a_N=19\cdot3G \quad ; \quad A_\parallel(N)=37G \quad , \quad A_\perp(N)=10\cdot5G$$

$$a_H=25\cdot8G \quad ; \quad A_\parallel(H)=28G \quad , \quad A_\perp(H)=24\cdot7G$$

The theoretical anisotropic components of the hyperfine interaction tensor are given in figure 5. These are very similar to those for NH_2 (also figure 5) where $A_\parallel(N)=41\cdot7G$, $A_\perp(N)=0\pm3G$ experimental compare favourable with the calculated values of $A_\parallel(N)=41\cdot66G$, $A_\perp(N)=-8\cdot05G$. The calculation of the anisotropic coupling constants should be atleast 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 $2\cdot3G$, compared with experiment, the discrepancies between the calculated and experimental A values should be equally small. The large differences between the calculated values, $A_\parallel(N)=50G$ and $A_\perp(N)=0\cdot5G$, and the experimental values may be associated with the fact that the true $A_\parallel$ and $A_\perp$ are

FIGURE 5.
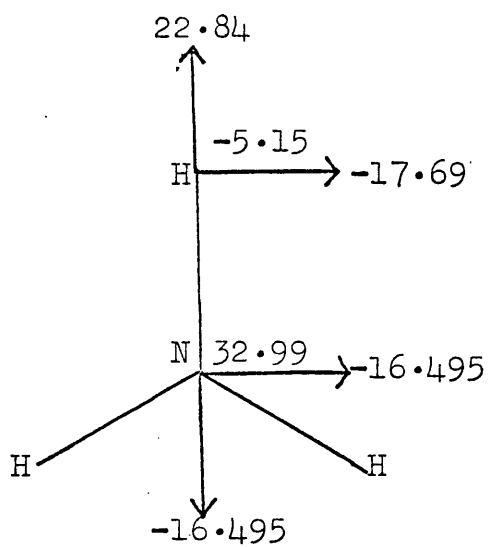
(i)
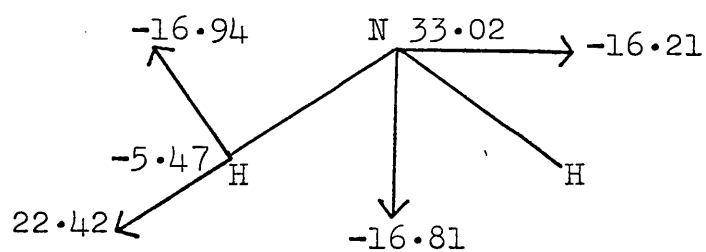
(ii)

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.)

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not measured but have been partially averaged by a librational motion about the threefold axis.[68]

The calculated anisotropy of the proton coupling constants is never completely observed owing to a rapid rotation about the threefold axis. Using $B_\perp=0\cdot5(B_x+B_y)=2\cdot575G$ the calculated values may be given as $A_{\parallel}(H)=-25\cdot17G$, $A_\perp(H)=17\cdot46G$, a difference between $A_{\parallel}$ and $A_\perp$ of $7\cdot725G$ compared to the observed difference of $3\cdot3G$. This discrepancy can also be associated with the librational motion.

The Methyl Radical.

The results obtained from calculations of the isotropic hyperfine coupling constants for CH_3 have been discussed already (Chapter 2). The isotropic values, $a_C=54\cdot64G$, $a_H=-19\cdot43G$, are in reasonable agreement with the generally accepted experimental values of $a_C=38G$, $a_H=-23G$, reported for solution and matrix environment. On Vycor glass below 150K values less than 38G for a_C have been measured,[116] which on extrapolation to OK give $a_C=10\cdot6G$. Rao and Symons[69] have suggested that Garbutt et al[116] have misinterpreted the spectrum and are infact 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 $-30G$. If Rao and Symons are correct, and the minimum value of a_C is 38G, then an $A_\perp(C)$ value of about 8G 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

Symons.

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,[17-29] 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[34] 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[117] 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[20-24] 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[28] has reported small expansions for some of the first row atoms and further work, representing STO's by small Gaussian expansions, has been done[118].

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[18]. 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 XH_3 and

XH_2Me (X=Al$^-$, Si, P$^+$ and Me is the methyl group,CH_3).

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,[18] 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

$$\chi_i = \sum_j c_{ij} r^n \exp(-\alpha_j r^2) \qquad \ldots\ldots(1)$$

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, α, is the same for all χ_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[118]. 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

$$\epsilon = \sum_i \int (\psi_i - \chi_i)^2 \, d\tau \qquad \dots\dots(2)$$

where i extends over all functions with the same spherical harmonic; ψ_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,[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 α_j such that ϵ 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 1.

Orbital exponents for the atoms Na—Cl

type	Na	Mg	Al	Si	P	S	Cl
1s	111·227	134·844	161·147	189·876	220·942	254·622	291·089
and	19·3927	23·5833	28·2602	33·3739	38·9184	44·9307	51·4563
2s	2·03032	2·65013	3·36996	4·17415	5·13708	6·06132	7·21092
and	·673459	·939751	1·25741	1·61353	2·02664	2·44758	2·94131
3s	·0568152	·106827	·174090	·250321	·331263	·419642	·517819
>	·0243412	·0404781	·0654338	·0937598	·124194	·156061	·192321
2p	10·4051	13·8296	9·18018	11·6797	14·3844	17·2573	20·3878
and	2·26735	3·07812	1·82337	2·39028	3·01217	3·67964	4·41311
3p	·574517	·814328	·193724	·291788	·400179	·511454	·637749
			·0536952	·0825787	·114423	·140106	·172008

TABLE 2.

Expansion coefficients for the atoms Na-Cl

type	Na	Mg	Al	Si	P	S	Cl
1s	.378210	.372851	.367474	.362817	.358876	.355074	.351338
	.697320	.697434	.697575	.697624	.697342	.697401	.697074
	.084284	.093982	.103659	.111729	.115935	.124378	.129717
	-.032257	-.037668	-.043273	-.047613	-.046093	-.053328	-.054849
	.008934	.010091	.012263	.013730	.007312	.015265	.015730
	-.005246	-.005141	-.005956	-.006441	.000001	-.006884	-.007110
2s	-.104184	-.105331	-.106082	-.106727	-.107222	-.107728	-.107799
	-.276630	-.289290	-.299778	-.308422	-.316083	-.321839	-.327381
	.543841	.496994	.452238	.415975	.375296	.357385	.326797
	.556180	.596233	.633101	.662821	.697771	.711525	.737404
	.022404	.028578	.037871	.045339	.052796	.056716	.062328
	-.010794	-.011549	-.013521	-.014694	-.016151	-.016245	-.017149

TABLE 2. (cont.)

type	Na	Mg	Al	Si	P	S	Cl
3s	.016503	.020774	.024925	.027731	.029785	.031533	.032815
	.041178	.056729	.071391	.082090	.090767	.098266	.104607
	-.087001	-.112107	-.127774	-.134300	-.132705	-.138088	-.134064
	-.219744	-.270223	-.328948	-.371407	-.407006	-.431636	-.457898
	.611708	.599934	.610159	.606418	.610698	.629231	.633463
	.467648	.510779	.524553	.545350	.551965	.544829	.547990
2p	.249157	.237312	.468740	.451130	.439155	.431414	.424827
	.575825	.576580	.670879	.677276	.681179	.683585	.685526
	.403887	.403673	.072095	.080276	.085020	.086286	.087835
			-.022476	-.023452	-.023960	-.022268	-.021280
3p			-.093948	-.108112	-.117761	-.125725	-.131960
			-.110451	-.134132	-.150631	-.158374	-.166499
			.595584	.578746	.565310	.556031	.548826

FIGURE 1. Variation of the difference, $\delta (=\psi_{3s} - \chi_{3s})$ as a function of the distance, r, from the nucleus for the aluminium atom. χ corresponds to the expansion of a) Huzinaga et al[24]; b) Roos and Siegbahn[23]; c) this work.
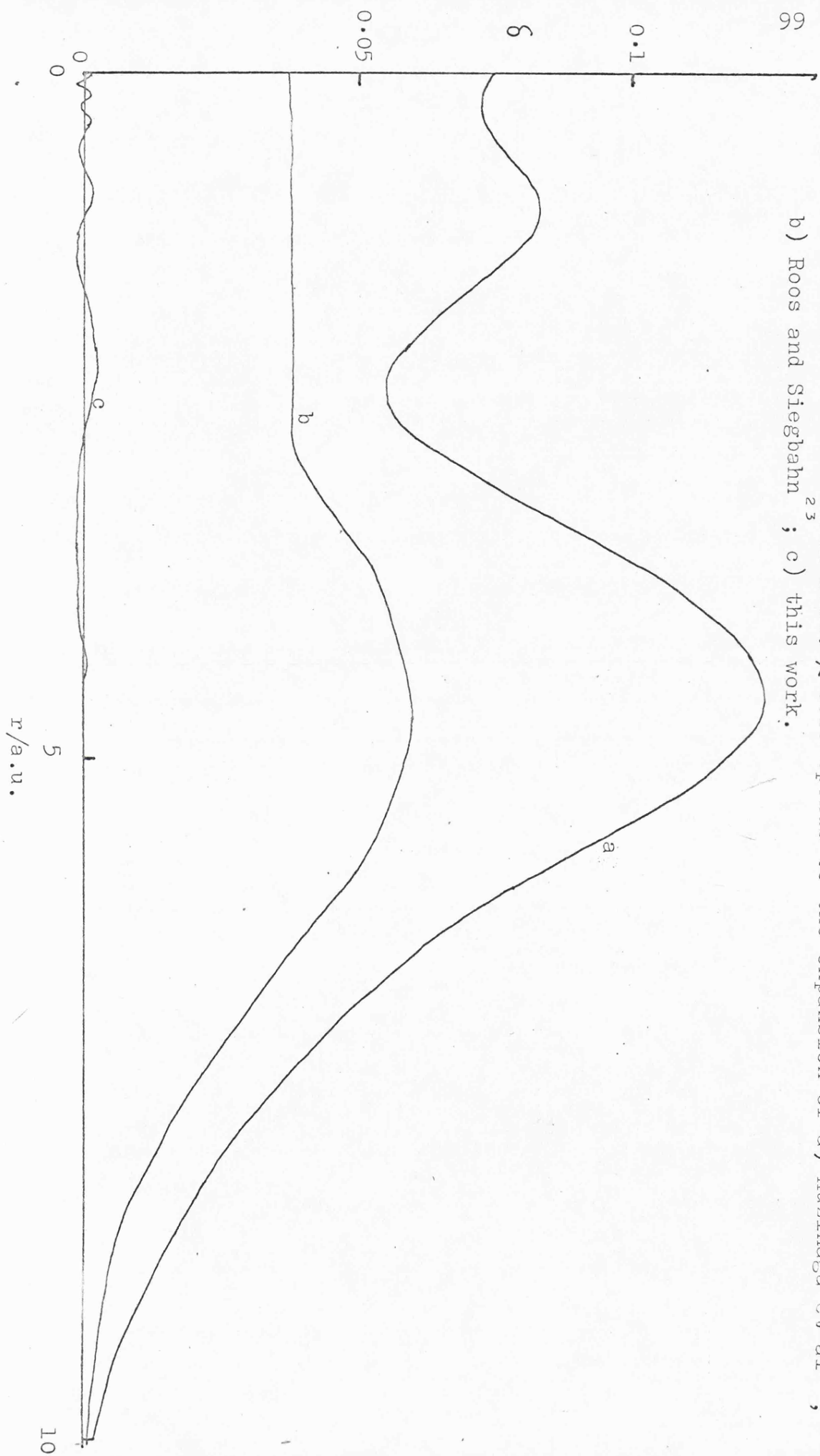
FIGURE 2.

Variation of the difference, δ (=$\psi_{3p}-\chi_{3p}$) as a
function of the distance, r, from the nucleus for
the atoms indicated. χ corresponds to the expansion
of a) Huzinaga et al[24]; b) Roos and Siegbahn[23];
c) this work.
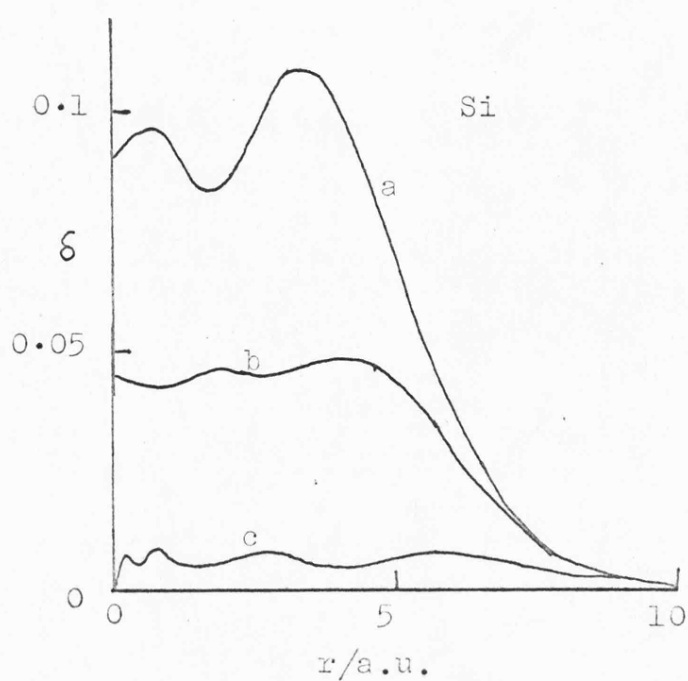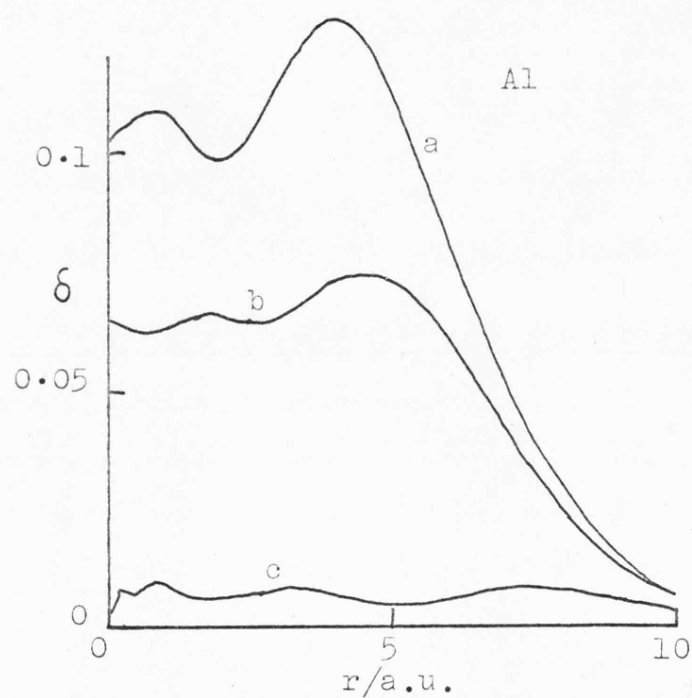
FIGURE 2 (cont.)
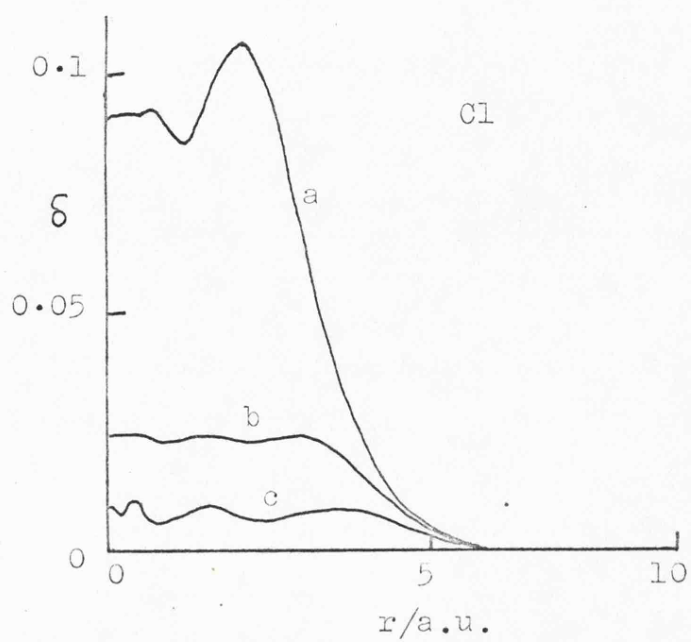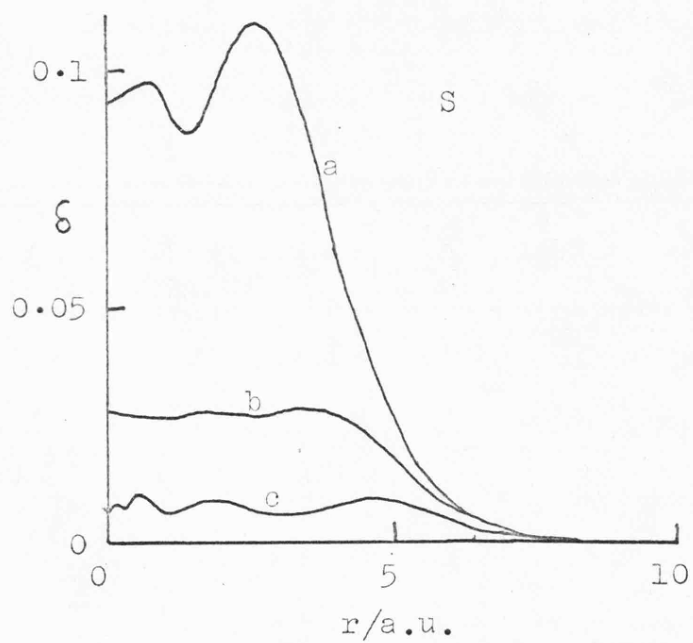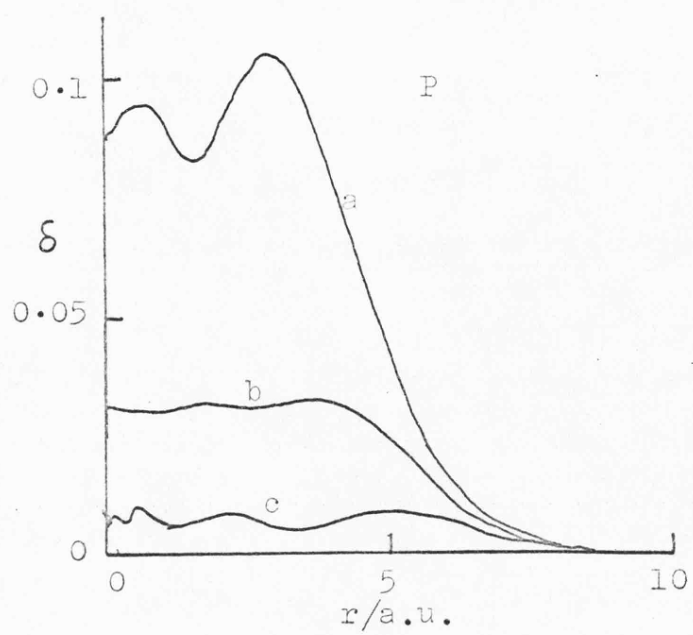
show negative deviations in this region). The similarity in the plots for the 3p orbitals of each atom suggests that the orbitals are consistent amongst themselves. The fit of the 6s, 4p set to the 12s, 9p set is very good for all the atoms, the maximum deviation being about .0·01.

The error function

$$\epsilon_i=\int(\varphi_i-\zeta_i)^2d\tau \qquad \dots\dots(3)$$

was evaluated for various functions (Table 3) where φ_i and ζ_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, ϵ_{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 3.

Values of the error function defined by equation (3) for all the orbitals of the second row elements.

1s orbitals

Element	Veillard[18]	Roos[23]	Huzinaga[24]	This work
Na	.0000115	.0000366	.0000453	.0024293
Mg	.0000047	.0000534	.0000490	.0023263
Al	.0000604	.0000019	.0000015	.0020655
Si	.0000557	.0000369	.0000423	.0021710
P	.0000459	.0000490	.0000441	.0019132
S	.0000412	.0000033	.0000456	.0018702
Cl	.0002253	.0002315	.0000032	.0019007

TABLE 3 (cont.)

2s orbitals

Na (upper triangle) ⟍ Mg (lower triangle)

Na ⟍ Mg	Veillard	Roos	Huzinaga	This work
Veillard		·0001043	·0002211	·0001985
Roos	·0000322		·0001313	·0001881
Huzinaga	·0000997	·0002807		·0002774
This work	·0002263	·0001974	·0001901	

Al (upper triangle) ⟍ Si (lower triangle)

Al ⟍ Si	Veillard	Roos	Huzinaga	This work
Veillard		·0000515	·0001499	·0002354
Roos	·0000588		·0001755	·0001976
Huzinaga	·0001810	·0006951		·0003074
This work	·0002802	·0002261	·0003342	

S (upper triangle) ⟍ P (lower triangle)

S ⟍ P	Veillard	Roos	Huzinaga	This work
Veillard		·0000448	·0001748	·0002892
Roos	·0000468		·0001409	·0002318
Huzinaga	·0001491	·0001339		·0003634
This work	·0002864	·0002087	·0003655	

Cl

Cl	Veillard	Roos	Huzinaga	This work
Veillard		·0001018	·0001532	·0003853
Roos			·0002418	·0002782
Huzinaga				·0003138
This work				

TABLE 3. (cont.)

3s orbitals

Na (upper) / Mg (lower)

	Veillard	Roos	Huzinaga	This work
Veillard	Na / Mg	.0006633	.0035591	.0000258
Roos	.0000214		.0019415	.0006109
Huzinaga	.0066465	.0065223		.0035302
This work	.0000304	.0000248	.0066274	

Al (upper) / Si (lower)

	Veillard	Roos	Huzinaga	This work
Veillard	Al / Si	.0013400	.0061654	.0000358
Roos	.0035036		.0020133	.0013100
Huzinaga	.0062949	.0006951		.0061549
This work	.0030347	.0034899	.0063047	

P (upper) / S (lower)

	Veillard	Roos	Huzinaga	This work
Veillard	P / S	.0000507	.0062906	.0000456
Roos	.0001167		.0061127	.0000385
Huzinaga	.0063753	.0058982		.000306
This work	.0000500	.0000900	.0063963	

Cl

	Veillard	Roos	Huzinaga	This work
Veillard	Cl			
Roos	.0005693			
Huzinaga	.0063677	.0045287		
This work	.0000591	.0005110	.0063990	

TABLE 3. (cont.)

2p orbitals

	Veillard	Roos	Huzinaga	This work
Na	.0007999	.0010358	.0001982	.0012552
Mg	.0004877	.0008792	.0011522	.0010682
Al	.0001273	.0007272	.0007584	.0063254
Si	.0001850	.0005498	.0060464	.0060598
P	.0002171	.0001929	.0003341	.0047765
S	.0002575	.0003426	.0004376	.0050204
Cl	.0001949	.0001709	.0036284	.0045263

TABLE 3. (cont.)

3p orbitals

Na / Mg

	Veillard	Roos	Huzinaga	This work
Veillard	Mg \ Na			
Roos				
Huzinaga				
This work				

P / S

	Veillard	Roos	Huzinaga	This work
Veillard	S \ P	.0042857	.0378756	.001802
Roos	.0034052		.0271050	.0388846
Huzinaga	.0409963	.0324924		
This work	.0014033	.0027438	.0039813	

Al / Si

	Veillard	Roos	Huzinaga	This work
Veillard	Si \ Al	.0091803	.0416993	.0010959
Roos	.0197262		.0095695	.0217828
Huzinaga	.0177840	.0527943		.0013314
This work	.0215377	.0452373	.0435523	

Cl

	Veillard	Roos	Huzinaga	This work
Veillard	Cl			
Roos	.0027914			
Huzinaga	.0014866	.0372887		
This work	.0020286	.0309090	.0404473	.0404114

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, BH_3^-, CH_3, and NH_3^+, to the second row series, AlH_3^-, SiH_3, and 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 HCO.[86] As the radicals AlH_3^-, SiH_3 and PH_3^+, from the e.s.r. data available,[121-128] are thought to have quite large deviations from planarity (18°40', 15°51' and 14°30' for AlH_3^-[126], SiH_3[122] and PH_3^+[128] 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 AlH_3^-, SiH_3 and 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 AlH_2Me^-, SiH_2Me and PH_2Me^+.

Method.

The ab initio UHF method using the l.c.a.o.-m.o. 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[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[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[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_2Me ($X=Al^-$, 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 $X=Al$, Si and P respectively, $r(C-H)$ for the hydrogens of the methyl group was taken as 2·05a.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_3^-.

Catton and Symons[126] on γ- irradiation of
lithium and sodium aluminium hydride at 77K produced
a paramagnetic species which, by analogy with the
γ-irradiation product of KBH_4 (BH_3^-) was expected to be
AlH_3^-. The isotropic coupling constant of aluminium,
$a_{Al}=223G$, 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_3^- are
given in Table 4. The total energy was -243.57247a.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 $a_{Al}=213.8G$ and $a_H=3.48G$. 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_3.

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

TABLE 4.

bond length (a.u.)	hydrogen orbital exponent	bending angle $\theta°$	total energy (a.u.)	coupling constants (G)		$<S^2>$
				a_{Al}	a_H	
3·2	0·9	19·5	-243·56571	225·6	6·14	·750003
3·3	0·9	19·5	-243·56633	242·4	8·03	·750002
3·4	0·9	19·5	-243·56450	260·6	10·36	·750001
3·1	1·0	19·5	-243·56999	190·4	1·10	·750010
3·2	1·0	19·5	-243·57240	203·8	2·45	·750010
3·3	1·0	19·5	-243·57221	217·6	4·02	·750008
3·1	1·1	19·5	-243·56125	170·7	-4·82	·750026
3·2	1·1	19·5	-243·56373	181·6	-3·92	·750028
3·3	1·1	19·5	-243·56315	192·7	-3·00	·750031
3·2	1·0	19·0	-243·57232	200·5	2·10	·750011
3·2	1·0	20·0	-243·57247	207·3	2·83	·750009
3·2	1·0	21·0	-243·57248	213·8	3·48	·750007 *
3·2	1·0	22·0	-243·57232	220·0	4·06	·750006

*marks minimum

Theoretical Results for AlH_3^-
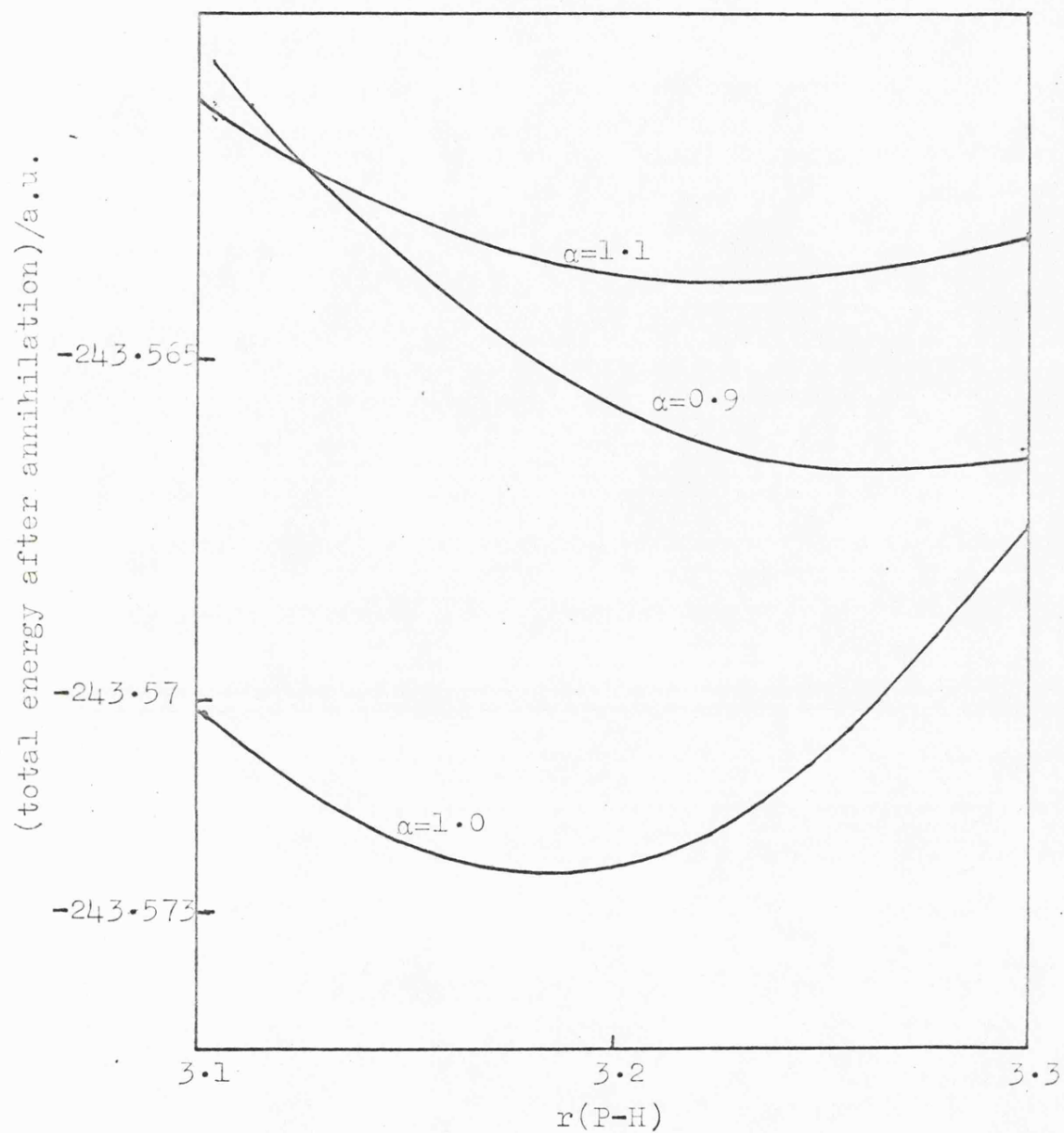
Summary of the calculations of the AlH_3^- radical;
————, variation of the total energy after annihilation
with bond length for those values of the hydrogen orbital
exponent α as indicated.

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[123] have demonstrated that for the radicals SiH_nMe_{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 $a_H=7 \cdot 84G$ and an estimated angle out of plane of 15°51'.

The results of the calculations on SiH_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_3 give isotropic coupling constants of $a_{Si}=-170 \cdot 8G$ and $a_H=-0 \cdot 42G$. 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_3^+.

The species formed when phosphonium sulphate is γ-irradiated at 77K has been assigned to the radical cation PH_3^{+}[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.

bond length (a.u.)	hydrogen orbital exponent	bending angle $\Theta°$	total energy (a.u.)	coupling constants(G)		$<S^2>$
				a_{Si}	a_H	
2·9	1·1	19·5	-290·54541	-207·1	7·12	·750006
3·0	1·1	19·5	-290·54599	-215·5	9·22	·750005
3·1	1·1	19·5	-290·54146	-223·1	11·67	·750004
2·8	1·2	19·5	-290·54207	-184·0	1·54	·750010
2·9	1·2	19·5	-290·54688	-191·4	2·94	·750010
3·0	1·2	19·5	-290·54557	-198·3	4·27	·750011
2·8	1·3	19·5	-290·53512	-169·6	-3·73	·750013
2·9	1·3	19·5	-290·53865	-175·6	-2·26	·750015
3·0	1·3	19·5	-290·53555	-181·0	-1·25	·750018
2·9	1·2	19·0	-290·54702	-187·6	2·33	·750011
2·9	1·2	18·0	-290·54720	-179·4	0·86	·750014
2·9	1·2	17·0	-290·54724	-170·8	-0·42	·750017 *
2·9	1·2	16·0	-290·54718	-162·1	-2·01	·750021

*marks minimum

Theoretical Results for SiH_3

FIGURE 4.
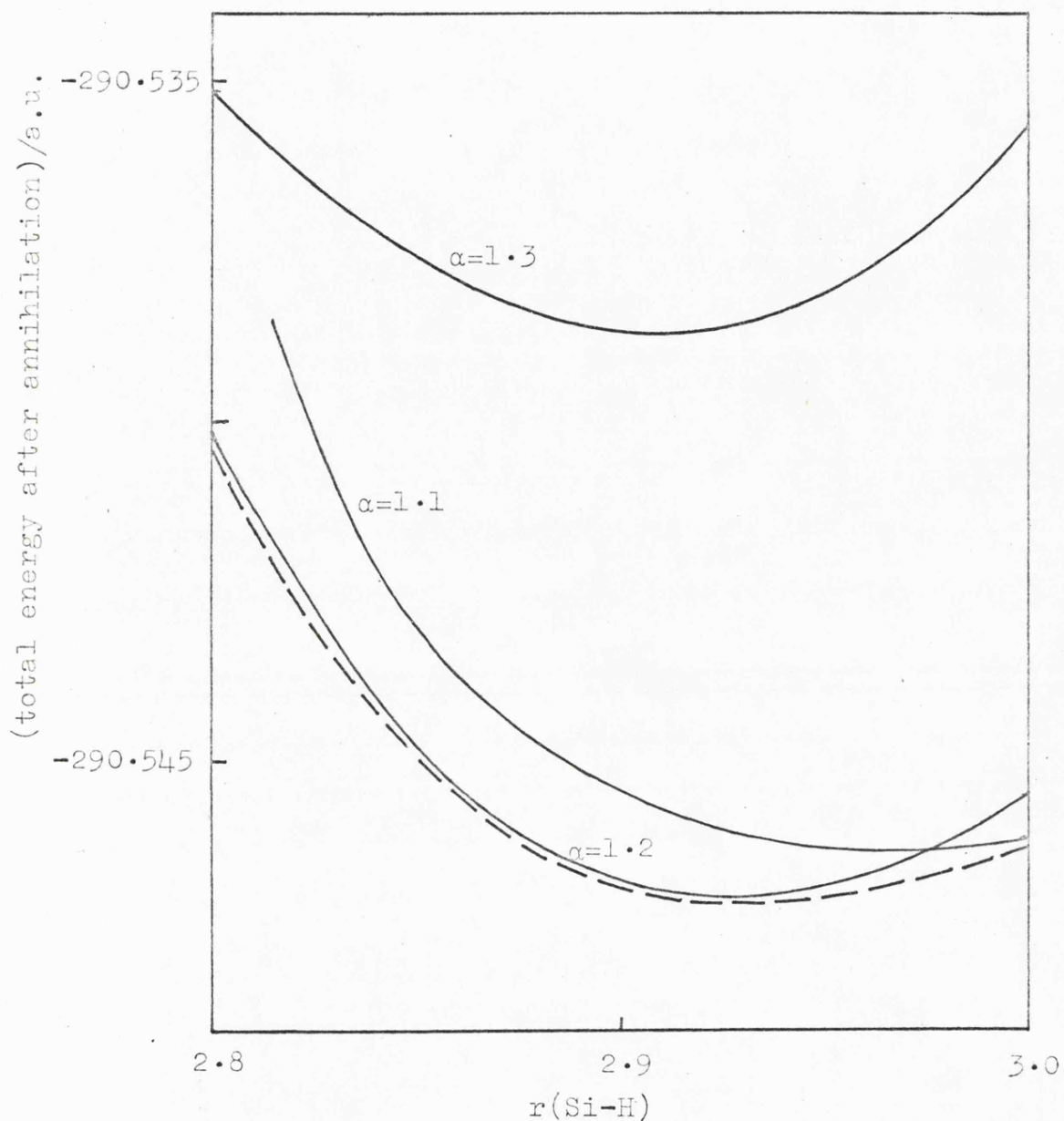
Summary of the calculations on the SiH₃ radical;
——, variation of the total energy after annihilation
with bond length for those values in α indicated.
— — —, estimated minimum total energy after annihilation
as a function of bond length.

estimated, from the e.s.r. data, to be 14°30'.

The theoretical results (Table 6 and figure 5) give hyperfine coupling constants a_P=196·5G, a_H=-15·91G 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_4^+ 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 6.

bond length (a.u.)	hydrogen orbital exponent	bending angle $\theta°$	total energy (a.u.)	coupling constants(G)		$<S^2>$
				a_P	a_H	
2.7	1.2	14.0	-342.03723	330.7	-2.18	.750021
2.8	1.2	14.0	-342.04385	335.0	-1.63	.750026
2.9	1.2	14.0	-342.04258	337.3	-1.26	.750032
2.7	1.3	14.0	-342.04740	310.4	-4.93	.750021
2.8	1.3	14.0	-342.05096	312.6	-4.87	.750028
2.9	1.3	14.0	-342.04639	312.7	-4.94	.750036
2.7	1.4	14.0	-342.04918	286.1	-7.99	.750019
2.8	1.4	14.0	-342.05007	286.4	-8.04	.750025
2.9	1.4	14.0	-342.04258	287.1	-8.46	.750033
2.8	1.3	15.0	-342.05056	333.5	-3.01	.750023
2.8	1.3	13.0	-342.05127	291.8	-6.68	.750033
2.8	1.3	12.0	-342.05150	271.4	-8.55	.750039
2.8	1.3	11.0	-342.05166	251.5	-10.46	.750045
2.8	1.3	10.0	-342.05177	232.2	-12.31	.750047
2.8	1.3	9.0	-342.05183	213.8	-14.15	.750055
2.8	1.3	8.0	-342.05185	196.5	-15.91	.750064 *
2.8	1.3	7.0	-342.05184	180.4	-17.52	.750072

*marks minimum

Theoretical Results for PH_3^+

FIGURE 5.
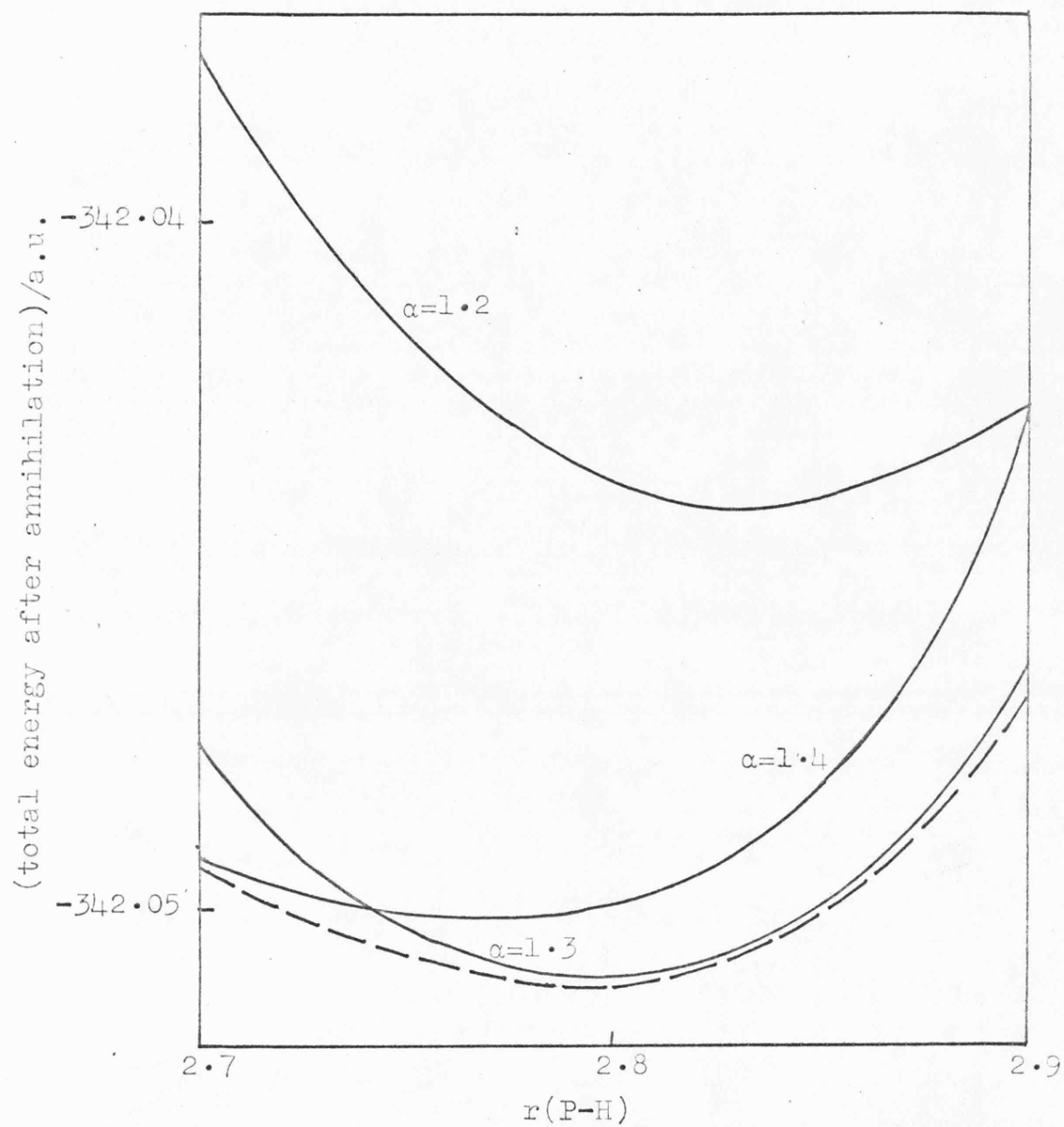
Summary of the calculations on the PH_3^+ radical.
(See also caption to figure 4).

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=337·3G and a_H=-1·26G.

Theoretical trends in the variation of the angle out of plane, for the isoelectronic radicals AlH_3^-, SiH_3 and 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 AlH_3^-, SiH_3, PH_3^+ respectively). Generally the agreement with experiment is satisfactory, if environmental effects are assumed to be important for PH_3^+.

FIGURE 6.

Variation of a_P with α for r(P-H)=2·8a.u. and Θ=14°

FIGURE 7.   121
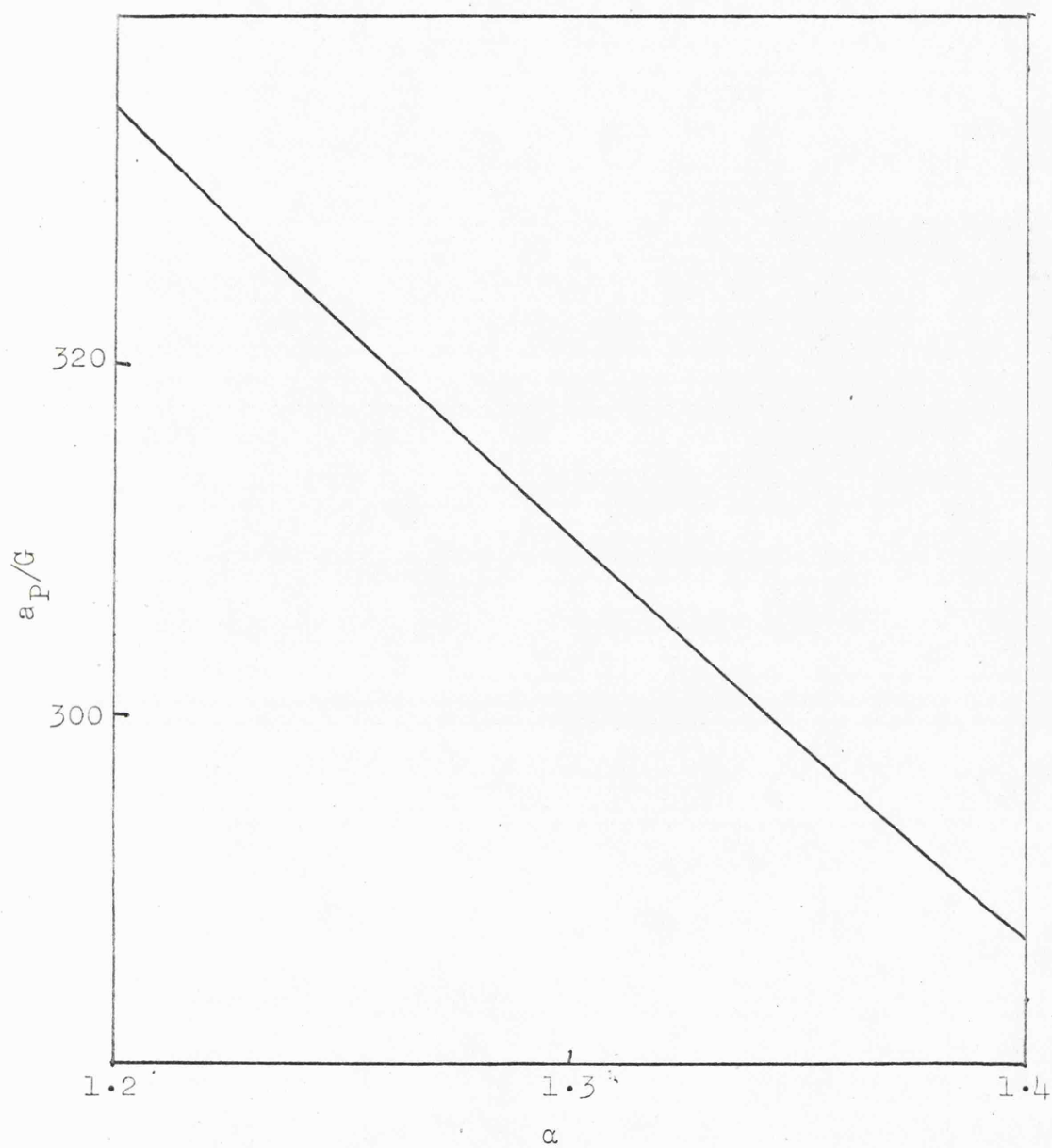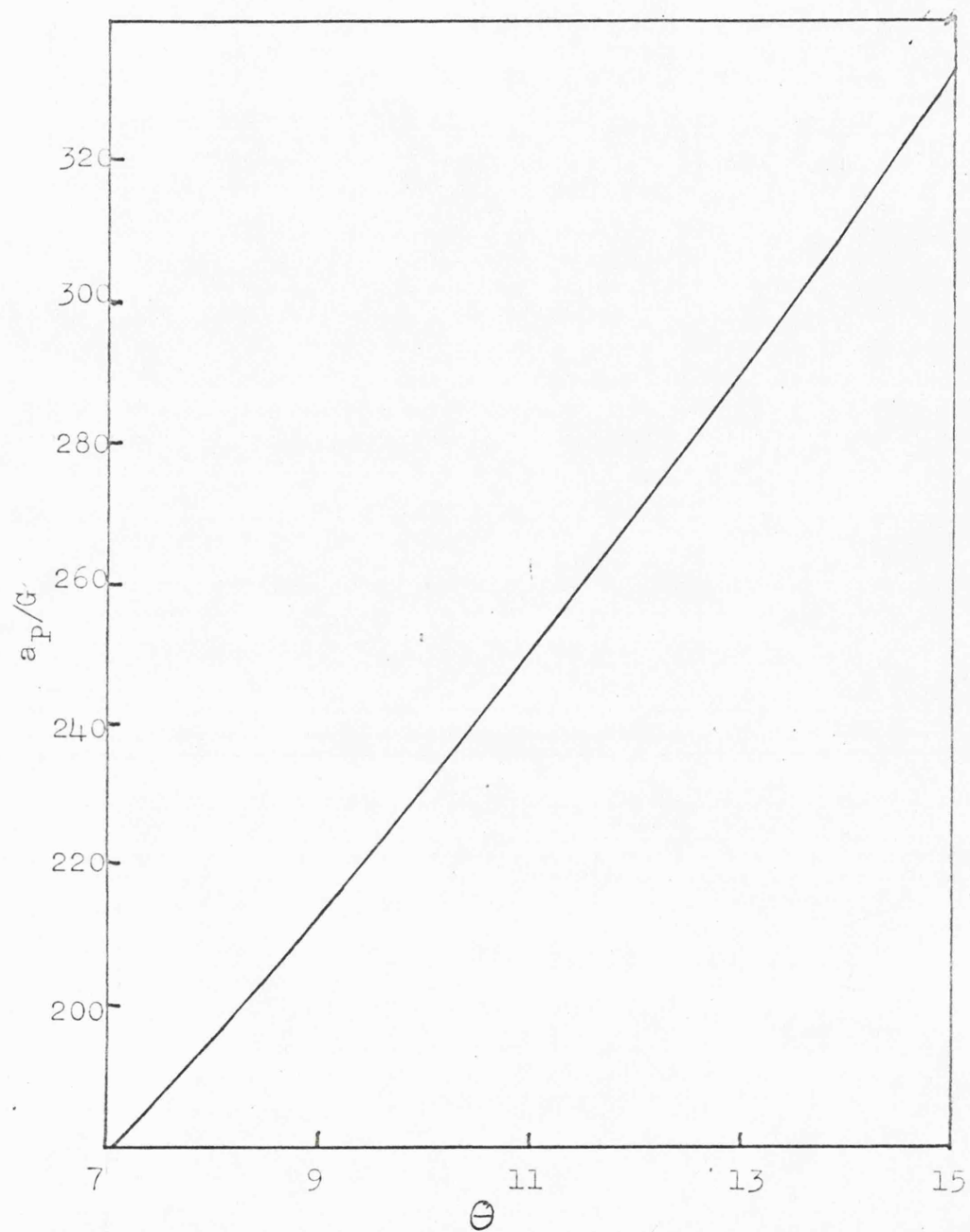
Variation of a_P with Θ for $r(P-H)=2 \cdot 8$a.u. and $\alpha=1 \cdot 3$.

The Radicals AlH_2Me^-, SiH_2Me and PH_2Me^+.

Of the radicals XH_2Me ($X=Al^-$, Si, P^+) only the silicon species has been observed, as the product of γ-irradiation of SiH_3Me[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_2Me 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 [123] for the radicals XR_3 ($X=Al^-$, Si, P^+; R=H or alkyl).

Radical	Hyperfine coupling constant				angle out of plane
	a_M	$a_H(\alpha)$	a_C	$a_H(\beta)$	
AlH_3^-	233				18.67[126]
$AlMe_3^-$	324				21.00[128]
$AlEt_3^-$	325				21.42[128]
$Al(isoBu)_3^-$	322				21.80[128]
$AlH(OCH_2CH_2OCH_3)_2^-$	179				18.05[128]
AlH_3^-	213.8	3.48			21 *
AlH_2Me^-	103.3	-10.88	3.210	49.54	21 *
SiH_3	190	7.84			15.85[122]
SiH_2Me[125]	181	11.8		8.0	
$SiHMe_3$[125]	183	17		7.2	
$SiMe_3$	181			6.3	15.25[125]
SiH_3	-170.8	-0.42			17 *
SiH_2Me	-114.7	-11.56	-5.037	53.56	17 *
PH_3^+	517				14.50[128]
PEt_3^+	384				12.43[128]
$P(n-Bu)_3^+$	360				12.25[128]
PH_3^+	195.5	-15.91			8 *
PH_2Me^+	192.2	-19.98	-5.602	39.48	8 *

*marks calculated values

phosphorus. If the view is taken that the interaction with the environment is important for PH_3^+ then it may be conjectured that the trend is only apparent, as the unrestricted radical, PH_3^+, may have a smaller phosphorus coupling constant, and hence smaller angle of bending, than the alkyl derivatives. The calculated coupling constant of $a_P = 192 \cdot 2G$ for PH_2Me^+ is very similar to the value calculated for 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 PH_2Me^+ than in 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, $a_{Si} = -114 \cdot 7G$, 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_{Si} closer to the experimental value. The experimental β proton coupling constant $(8G)$[125] compares unfavourably with the calculated value $(53 \cdot 56G)$, 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 AlH_2Me^-, $a_{Al} = 103 \cdot 3G$, is surprisingly low. Experimental values for 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_2Me^- 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_2Me^-. 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_2Me 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 $AlH(OCH_2CH_2OCH_3)_2^-$, produced

by gamma irradiation of $NaAlH_2(OCH_2CH_2OCH_3)_2$, has

a reduced value of $a_{Al}=179G$.[129] If the assignment is

correct the result would be compatible with that

calculated for AlH_2Me^-.

Conclusions.

The calculations on the radicals XH_3 and XH_2Me

($X=Al^-$, 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_3^-, CH_3 and NH_3^+ (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_3^-, SiH_3 and PH_3^+ but not for AlH_2Me^-, SiH_2Me and PH_2Me^+, this deficiency in the calculations on the latter series may account for the inconclusive nature of the results obtained.

CHAPTER 5

Introduction.

In the preceeding 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[31,130-132] 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.[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[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[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_3 (Chapter 2).

The function

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

was minimised in the

TABLE 1.

centre	x	z
C(1)	-1·3020464	2·3307193
C(2)	1·3020464	2·3307193
C(3)	-1·3020464	-2·3307193
C(4)	1·3020464	-2·3307193
N(1)	-2·2627005	0·0
N(2)	2·2627005	0·0
H(1)	-2·2941718	4·0491302
H(2)	2·2941718	4·0491302
H(3)	-2·2941718	-4·0491302
H(4)	2·2941718	-4·0491302
H(5)	4·1627005	0·0

The y coordinate is zero.

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, α, 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[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[132], giving as the first electronic transition
the nonbonding to π 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.

type	Clementi[132]	$\alpha=1\cdot2$	$\alpha=1\cdot4$
$A_1(\sigma)$	-15·69544	-15·68278	-15·63389
	-15·69527	-15·67768	-15·62872
	-11·47642	-11·48648	-11·43777
	-11·47541	-11·46762	-11·41879
	-1·37619	-1·45422	-1·41834
	-1·27295	-1·33609	-1·30466
	-·95711	-·88175	-·84282
	-·77967	-·76214	-·71687
	-·72282	-·64203	-·62133
	-·53275	-·49157	-·43807
	-·44125	-·43424	-·38488
$B_2(\sigma)$	-11·47649	-11·47025	-11·42109
	-11·47540	-11·46149	-11·41265
	-1·13257	-1·42624	-1·39938
	-·93097	-·89910	-·85614
	-·75519	-·77060	-·75037
	-·68371	-·69657	-·66113
	-·61071	-·63165	-·59500
$B_1(\pi)$	-·64940	-·87123	-·83834
	-·49355	-·32672	-·29194
$A_2(\pi)$	-·46176	-·29629	-·26158
Total Energy	-261·55432	-262·23830	-262·11569
-V/T		2·0001	1·999

FIGURE 1.

Orbital Energies in Pyrazine.

132

Clementi [132]

α=1·2

σ   π   σ   π

a_1 b_2 b_1 a_2 a_1 b_2 b_1 a_2

orbital energy (a.u.)

0

.5

1.0

1.5

11

13

15

all represent doublet states
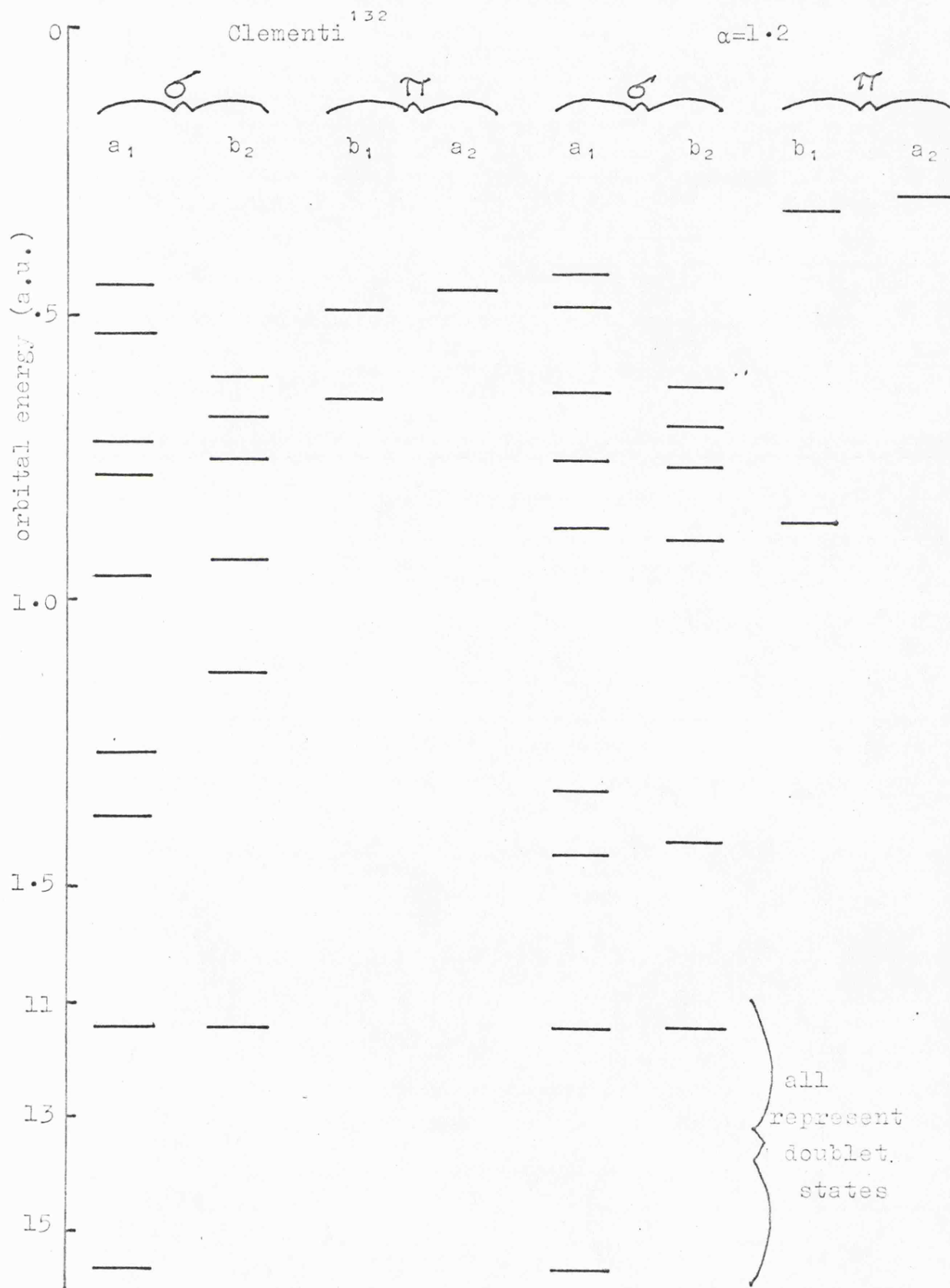
TABLE 3.

Electronic Configuration of Pyrazine.

	separate atoms	In the pyrazine molecule		
		Clementi[132]	$\alpha=1\cdot2$	$\alpha=1\cdot4$
C				
1s	2	1·9992	2·0031	2·0030
2s	2	1·0558	1·0038	1·0366
$2p\sigma_1$	1	1·0954	·9963	1·0292
$2p\sigma_2$	1	1·0190	1·0201	1·0379
$2p\pi$	1	1·0025	·9984	·9955
N				
1s	2	1·9975	1·9998	1·9998
2s	2	1·4927	1·5780	1·5852
$2p\sigma_1$	1	1·0566	1·0432	1·0535
$2p\sigma_2$	1	1·6816	1·6908	1·7013
$2p\pi$	1	·9951	1·0031	1·0090
H				
1s	1	·7739	·8208	·7234

figure 1) show that the highest occupied orbital is
the π 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
$a_N=7 \cdot 22G$, $a_H=2 \cdot 66G$. The theoretical results are
summarised in Table 4, with the π 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.

α	E_{UHFAA}	hyperfine coupling constants		
		a_C	a_N	a_H
.85	-261.9857	-1.28	5.55	-1.97
.90	-261.9901	-2.20	7.05	-1.83
.95	-261.9955.	-3.71	9.19	-1.43
.98	-261.9984	-5.36	11.11	-0.74
1.00	-261.9991	-6.46	12.48	-0.31
Expt.			7.2	±2.7

Unpaired electron in π orbital (A_2)
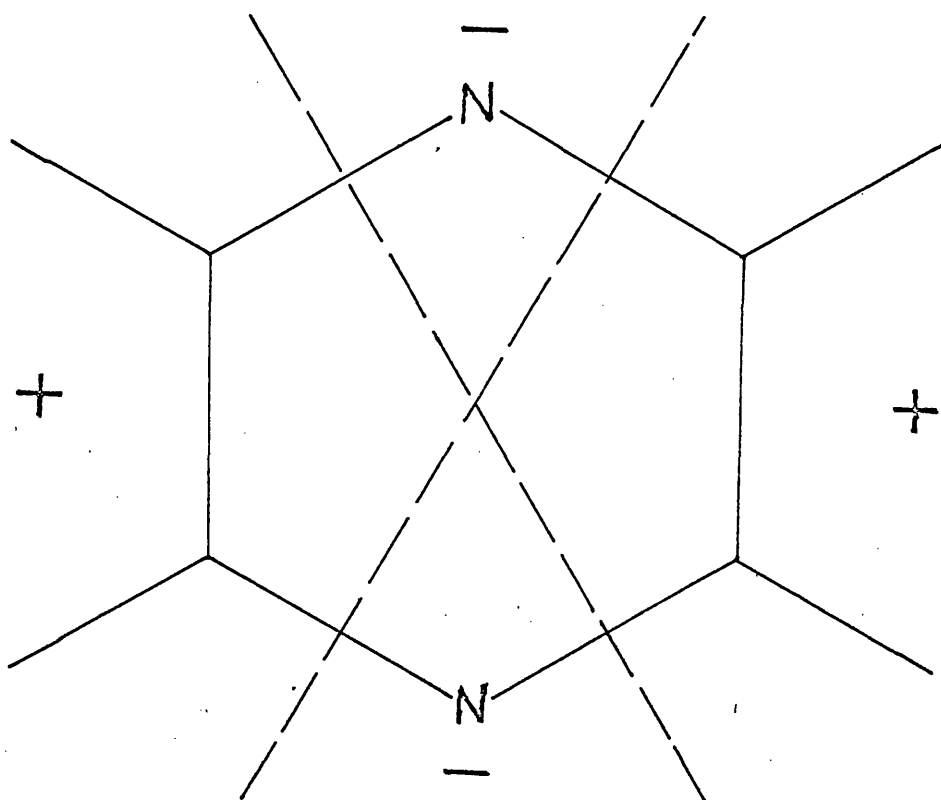
FIGURE 2.

Variation of (i) E_{UHF}, (ii) E_{UHFAA}, (iii) $<S^2>$ and (iv) $<S^2>_{UHFAA}$ with α.
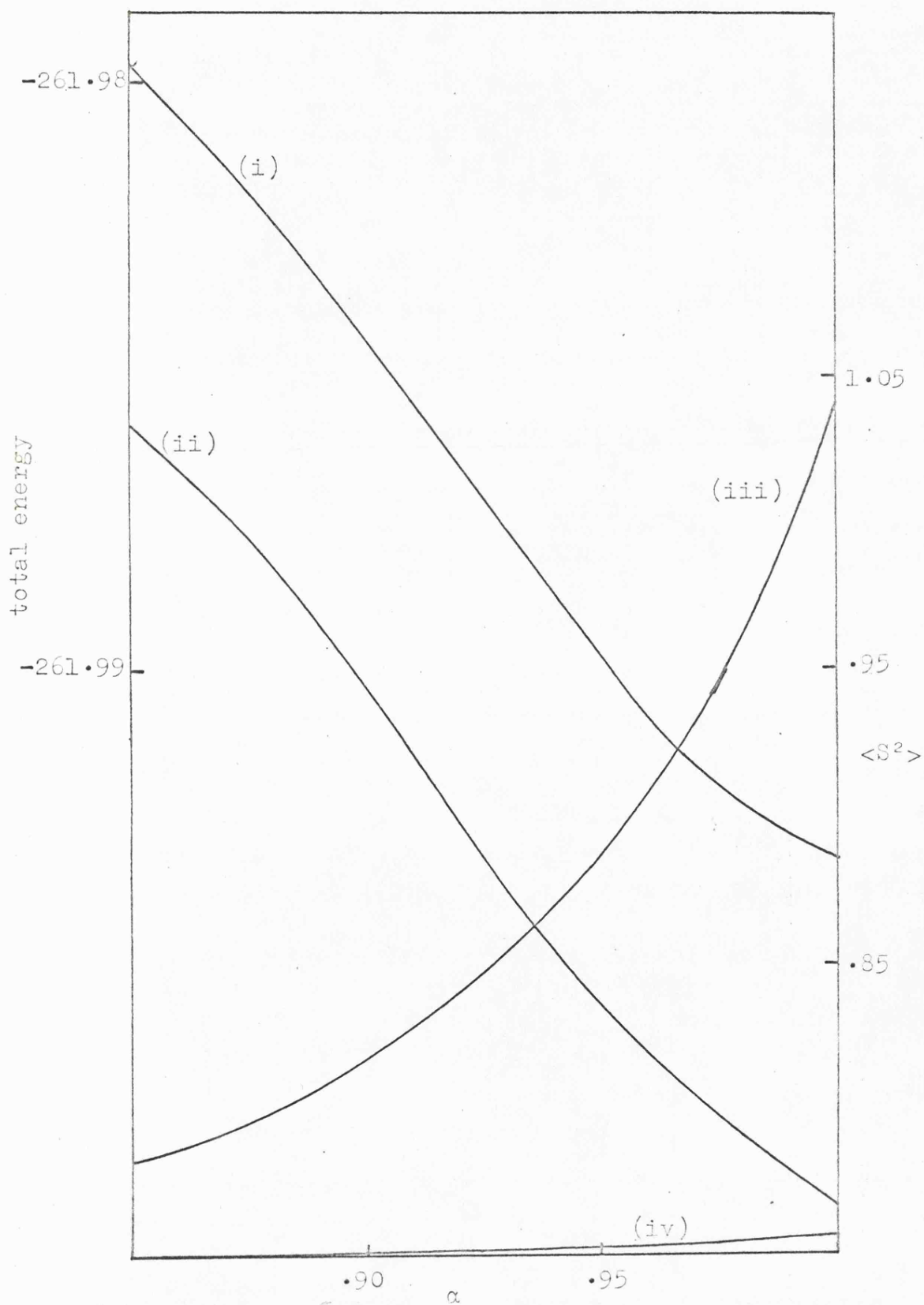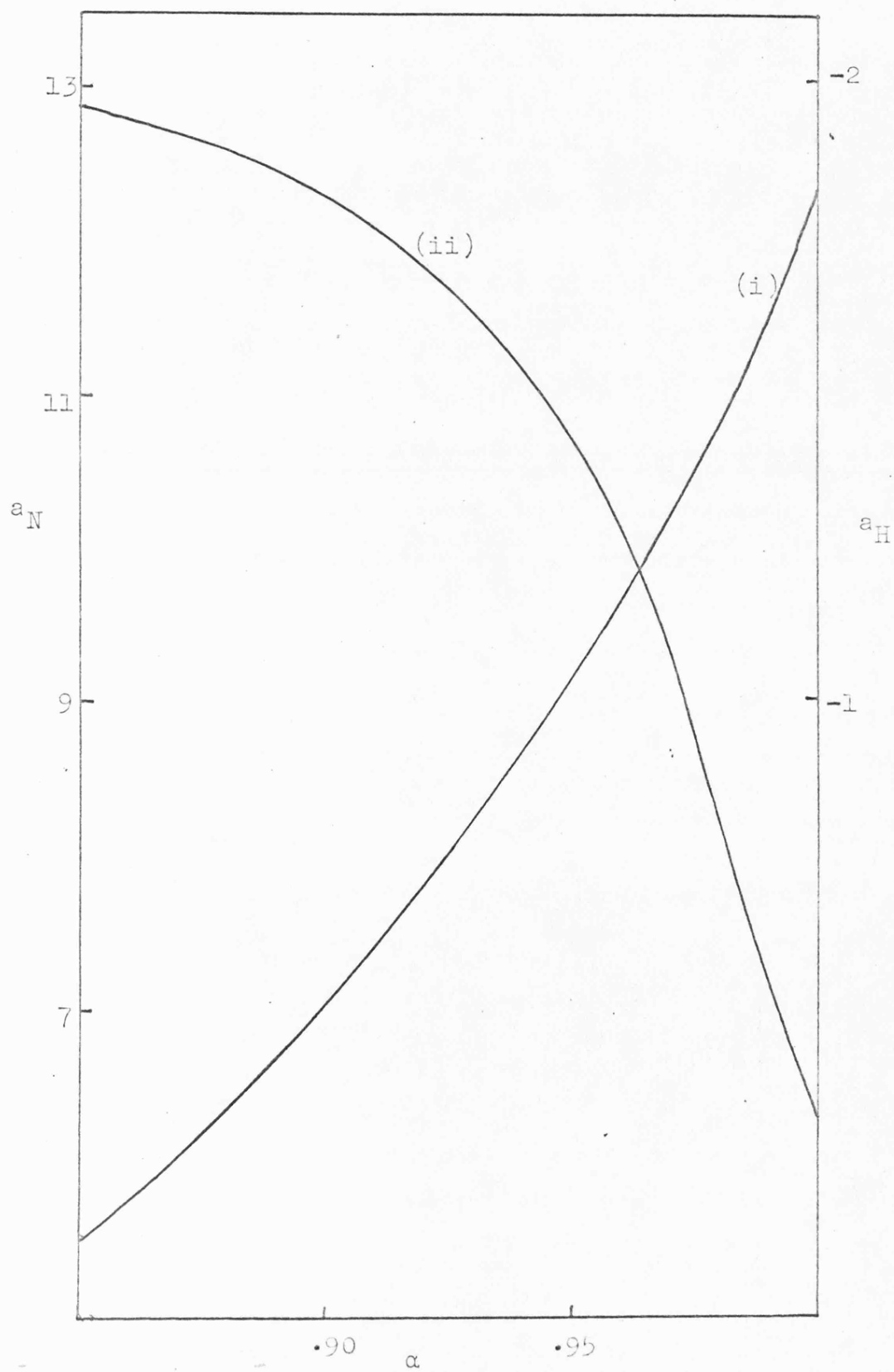
FIGURE 3.

Variation of (i) a_N and (ii) a_H with α.

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

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

was minimised. The variation of the energy, S^2 value, nitrogen and proton hyperfine coupling constants with α 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.
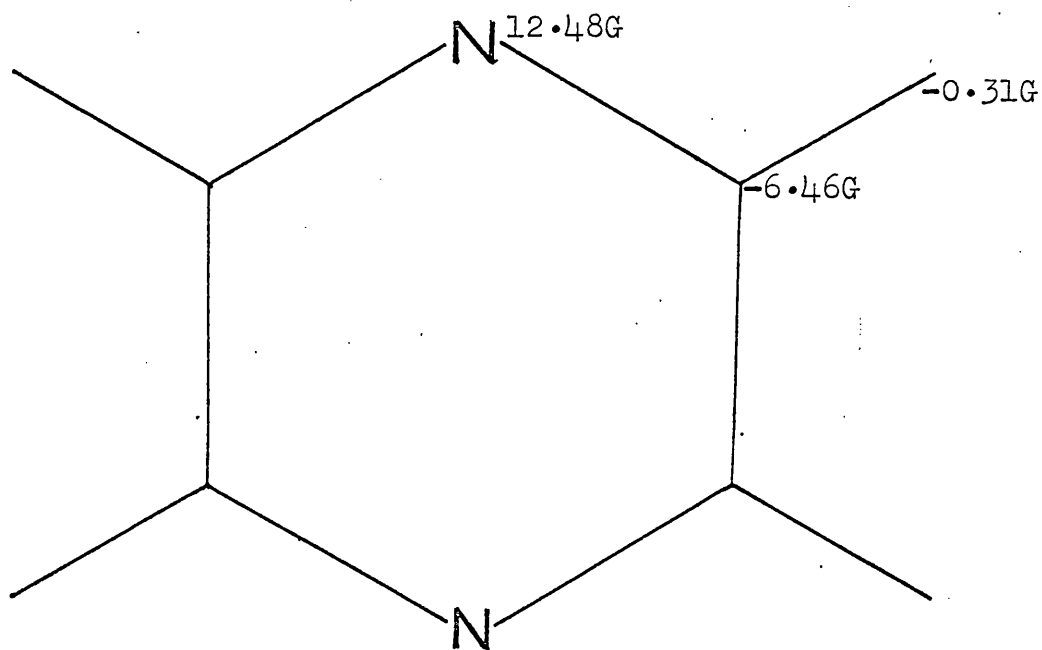
The Monoprotonated Pyrazine Radical.

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.[135,136] 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 Huckel[137] and CNDO/2[138]
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[135,136]
deduced two proton values of 1·98G and 3·33G and two

FIGURE 4.   140
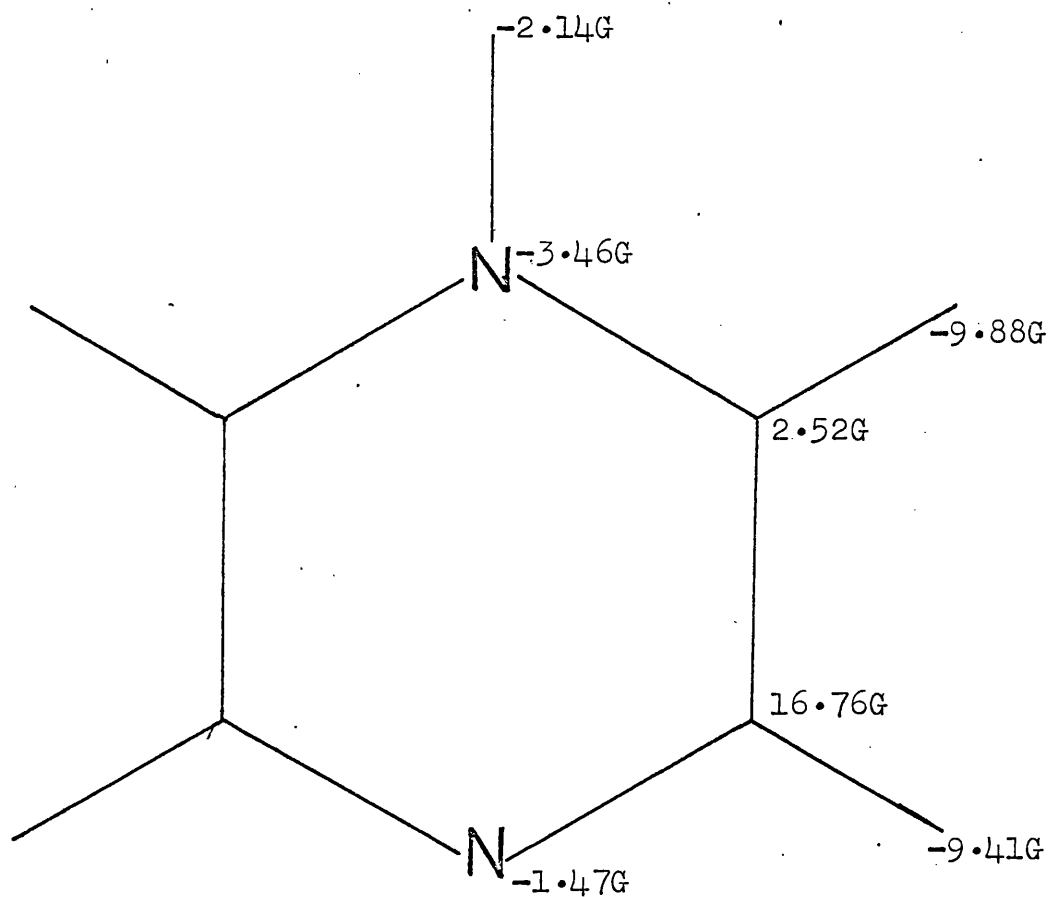
a) Hyperfine coupling constants for the monoprotonated
   Pyrazine.

b) Hyperfine coupling constants for the Pyrazine anion.

TABLE 5.

Electronic configuration of Pyrazine, the Pyrazine anion and monoprotonated Pyrazine. (The hydrogen orbital exponent is 1·4 for all systems.)

	Pyrazine	Pyrazine⁻	Pyrazine–H	
			1,3	2,4
C 1s	2·0030	2·0031	2·0034	2·0024
2s	1·0366	1·0226	1·2661	1·2259
$2p\sigma_1$	1·0292	1·0209	1·1246	1·2240
$2p\sigma_2$	1·0379	1·0423	·8328	1·4766
$2p\pi$	·9955	1·1152	1·1704	1·5198
N 1s	1·9998	1·9999	2·0011	2·0008
2s	1·5852	1·5369	·8530	1·7796
$2p\sigma_1$	1·0535	1·0118	·5968	·9178
$2p\sigma_2$	1·7013	1·6771	·1971	1·0449
$2p\pi$	1·0090	1·2695	·0503	1·5694
H 1s	·7234	·7983	·8212	·8925
H(5) 1s			·8696	

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.

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ABSTRACT.

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.